Errol G. Lewars

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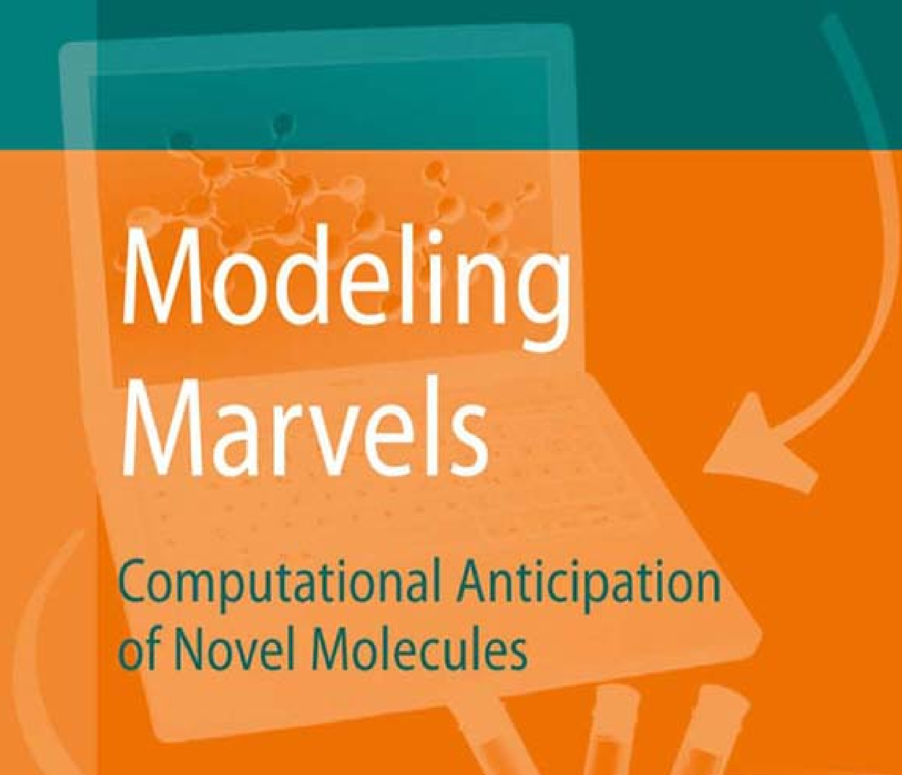

Modeling Marvels

Computational Anticipation of Novel Molecules

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A survey of a variety of novel compounds which have been studied theoretically but have not yet been made. Some of these molecules defy conventional concepts of chemical bonding; all should exhibit novel properties.

To Anne and John

Preface

The aim of this book is to survey a number of chemical compounds that some chemists, theoretical and experimental, find fascinating. Some of these compounds, like planar carbon species or oxirene, offer no obvious practical applications; nitrogen oligomers and polymers, in contrast, have been touted as possible high-energy-density materials. What unites this otherwise eclectic collection is that these substances are unknown and offer a challenge to theory and to synthesis. That such a challenge exists is in some cases almost obvious to most chemists: the instability of nitrogen polymers, for example, might be taken nearly as an axiom, to be quantified but not refuted by computations and to be subjected to an almost superfluous (but rather challenging) validation by synthesis. On the other hand, oxirene, the unsaturated relative of the prosaic oxirane, presents no immediately obvious oddity, yet this molecule has defied all attempts at synthesis and remains a theoretical conundrum, in that it is not certain if it can even exist! I hope that this collection of quirky molecules will appeal to chemists who find the study of chemical oddities interesting and, on occasion, even rewarding.

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Peterborough, Ontario, Canada Errol Lewars
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Contents

Chapter 1
Planar Carbon

Introduction

The tetrahedral geometry of tetracoordinate carbon has been almost axiomatic for more than a century [1, 2]. However, in recent years organic chemists have audaciously explored, theoretically and experimentally, the possibility that the carbon atom may be able to display other stereochemical proclivities. For example, planar tetracoordinate carbon [3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15] and tetracoordinate carbon with all four bonds on the same side of a plane have been considered; the latter arrangement is the basis of the structure of pyramidane (Chapter 2) and the well-known propellanes [16, 17, 18, 19]. (Fig. 1.1). Computational predictions have been experimentally confirmed for organolithium derivatives of cyclopropanes and for carbon in charged clusters and boron-containing species. Calculations and experimental work on such species are reviewed by Merino et al. who also report their work on clusters with planar carbon and provide an analysis of the molecular orbitals in square planar carbon [9, 10]. The subject has also been reviewed by Siebert and Gunale, again with the accent on organometallic species [12], and by Sateesh et al. focusing on neutrals and organoboron molecules [13], and Siebert and Tantillo have studied computationally numerous potentially planar-carbon cations [14]; a recent review includes ions and carbon bonded to boron and metals, and emphasizes fenestranes [15]. Here we will avoid things like organometallic chemistry and charged species, subjects with bonding rules somewhat sui generis, and concentrate on conventional (insofar as that term can be applied to potentially planar carbon species) organic molecules, and in particular on hydrocarbons, which are traditionally the templates from which other compounds are conceptually derived.

We begin examination, within these prescribed limits, of the simplest relevant species: planar methane. The first analysis of this species using modern electronic structure theory was by Hoffmann and coworkers [3], but the methods then available did not permit calculation of reliable relative energies of the planar and tetrahedral configurations. The literature was ably reviewed by Gordon and Schmidt [4] in a paper reporting their reasonably highlevel calculations, MCSCF [20] treatment of electron correlation with a triple-zeta basis set [21] augmented with diffuse and polarization functions, which are informative and somewhat disconcerting. A careful analysis is not simple: one must examine more than one electronic state and

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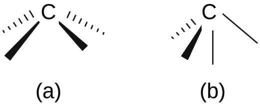


Fig. 1.1 Pyramidane (**a**) and propellane (**b**) bonding

consider the possibility that species other than simple closed-shell are involved. The inversion of methane (Fig. 1.2) was predicted [5] to require (one hesitates to say "occur through") a distorted C_s [22, 23, 24] structure, rather than the square planar (D_{4h}) geometry that might naively be expected. The latter geometry was found to represent a hilltop with two or three imaginary frequencies [25] (electronic states $^1B_{2u}$ electronic state and ^1A_g, respectively [24, 26]). The distorted C_s structure (Fig. 1.3) has, in contrast, but one imaginary vibrational mode and although two of its hydrogens are dangerously close together (0.847Å), suggesting that it is the transition state for elimination of H_2 to form methylene, an intrinsic reaction coordinate analysis [25, 27, 28] confirmed that it connects "enantiomeric" tetrahedral (T_d) methane molecules. The optimization/frequency calculations exploring the potential energy surface (PES) placed the C_s transition state 526 kJ mol^{-1} (125.6 kcal mol^{-1}) above tetrahedral methane, which is of course the global minimum [25]. A higher-level single-point [29] CI [30] calculation lowered this barrier height to 490 kJ mol^{-1} (117 kcal mol^{-1}), which is about 170 kJ mol^{-1} lower than the barrier calculated for a presumed square planar transition state. The authors compared the C_s barrier with the bond dissociation energy of methane: from theory and experiment they estimated this to be ca. 460 kJ mol^{-1} (110 kcal mol^{-1}) (if one takes the 0 K energy difference between CH_3 + H and CH_4 as the appropriate dissociation energy with which to compare the calculated inversion barrier, implying that there is little or no enthalpy barrier to combination of CH_3 and H, then the dissociation

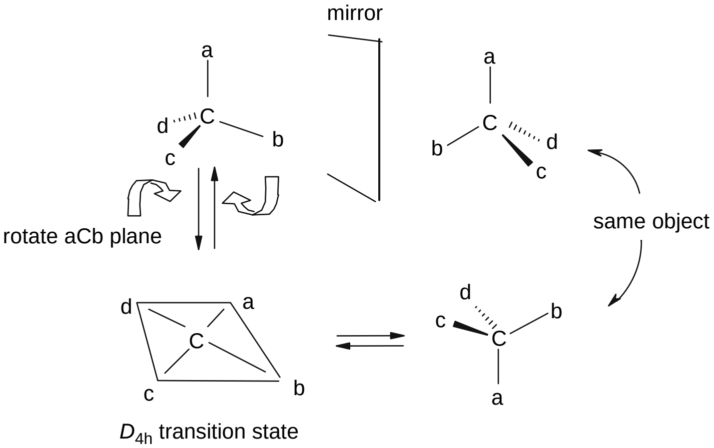
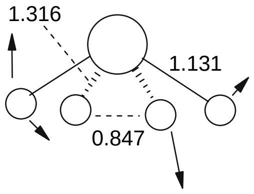


Fig. 1.2 Inversion of methane. The hydrogens are given the (hypothetical) labels a, b, c, d, which would make possible methane enantiomers; the transition state shown here is the naive (and incorrect) square planar one

Fig. 1.3 The transition state calculated for inversion of methane

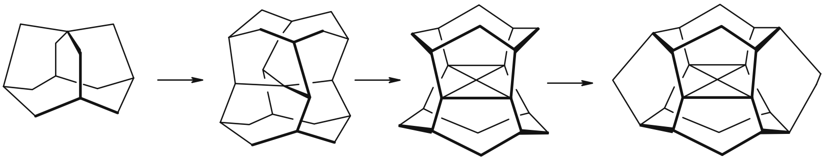


A" 1563i cm^{-1}

value by the highly accurate CBS-APNO method[1] is 434 kJ mol^{-1}). The inversion barrier, then, appears to be about 30–60 kJ mol^{-1} above the energy needed to break a methane CH bond, and so one might suppose that inversion cannot occur, but rather that at the temperature required to appreciably populate the higher-energy tail of a Boltzmann distribution with appropriate energy methane would simply dissociate. If this were true, then perhaps of broader implication for the planar carbon question would be the inference that a hydrocarbon with this entity would be ephemeral and suffer spontaneous CC cleavage (an sp^3–sp^3 CC bond being weaker than the CH bond of methane, bond energy about 330–370 kJ mol^{-1} from standard tables). However, as Gordon and Schmidt point out, “bond dissociation will occur only if most of the available energy is concentrated in one C–H bond” and that this will depend on coupling between the normal mode of the imaginary vibration (Fig. 1.3) and vibrational modes transverse to the intrinsic reaction coordinate which would carry the CH_4 assemblage from the transition state region toward that part of the PES in which the dissociation process resides. The authors suggest that the question of competition between inversion and dissociation could be settled by a molecular dynamics study [31, 32].

Dimethanospiro[2.2]octaplane: A Computational Saga

In designing a hydrocarbon which one hopes will have a planar tetracoordinate carbon atom, we are not allowed the luxury of *electronic* stabilization, by the exotic (to the traditional organic chemist) kinds of bonding present in some organometallic compounds. We must perforce rely on some type of framework to constrain the maverick atom in its unnatural stereochemical configuration. Putative cycloalkanes with planar carbon are discussed by Rasmussen and Radom in a review with the engaging title “The Planar Carbon Story”, which shows the evolution of their potential solutions to this problem [33; this review is summarized and augmented in 34]. The computational odyssey began with examination of the structure of a cycloalkane that had been the subject of study by them and others, namely bowlane (Fig. 1.4) (although bowlane is not in there, for an explanation of the origin of many of the whimsical appellations that have been bestowed on organic molecules, see the book by Nickon and Silversmith [35]). This molecule cannot have a planar central carbon (in this series of molecules, the putative planar carbon will be regarded as the *central* one, the one around which there is a framework designed to constrain its bonds to



1 bowlane

2 octaplane

3 spiro[2.2]octaplane

4 dimethanospiro[2.2]octaplane

Fig. 1.4 The conceptual progression toward a promising planar-carbon cycloalkane

planarity) because it lacks a symmetry plane passing through that atom and the four potentially coplanar bonds. An obvious way to remedy this stereochemical deficiency is to symmetrize the structure by capping it with a cyclooctane moiety identical to that underneath (as drawn in Fig. 1.4) the central carbon; this gives octaplane. Radom and Rasmussen call the family of molecules with a potentially planar carbon and cycloalkane caps top and bottom *alkaplanes* (cycloalkane cap + planar C; octaplane has two cyclooctane caps). The authors' strategy in designing a molecule which would be a strong candidate for harboring a planar tetracoordinate carbon was to examine octaplane and, if need be, increasingly constrained alkaplanes. This examination took the form of a series of MP2/6-31G(d)//HF/6-31G(d) calculations (single-point calculations: a higher-level energy calculation was done at a geometry from a lower-level calculation) with the CCC angle of the central carbon constrained to several values deviating incrementally from 180°. If the candidate molecule really has a planar carbon on the HF/6-31G(d) PES, i.e. if the planar-carbon species is a relative minimum on this surface, then the energy-angle curve (Fig. 1.5) will show one minimum and no maximum, because the 180° CCC angle corresponds to a relative minimum on the PES. If the candidate does not represent a planar-carbon species which is a relative minimum on the HF/6-31G(d) PES, then the curve will show two minima, corresponding to molecules (relative minima on the PES) with a nonplanar central carbon. The maximum connecting these minima likely corresponds to a transition state (a hilltop is also an a priori possibility) for interconversion of the minima, and the height of the barrier is suggestive of how closely the candidate approaches the desired role of possessing a planar carbon. The candidates might, alternatively, have been tested by calculating their normal-mode vibrations and looking for imaginary frequencies; the magnitude of the imaginary frequency/frequencies should be qualitatively suggestive of how far the molecule is from being a genuine planar-carbon species (a relative minimum with a planar carbon). Presumably, however, these workers considered the barrier height (the "inversion potential") to be a clearer indication of qualification for further investigation, and so chose the energy vs. angle route.

To return now to the examination of octaplane and its more-constrained siblings. The optimized HF/6-31G(d) structure of octaplane (the PES minimum) has a CCC angle of 169°, approaching the 180° angle of planar carbon (the tetrahedral angle is of course 109.5°). However, the central carbon of this S_4 structure showed considerable reluctance to flatten to planarity (C_{4h}), as revealed by an

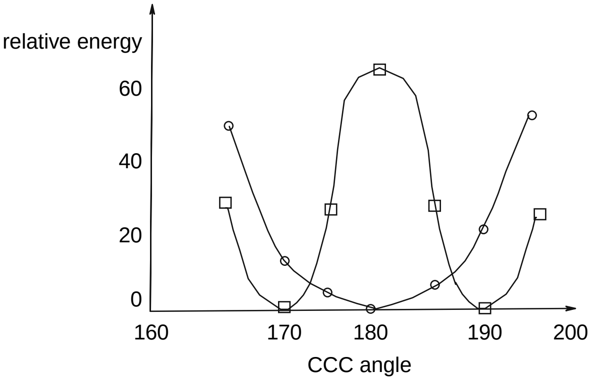


Fig. 1.5 The principle behind the single-point calculations used to probe the likelihood that an alkaplane will have a planar carbon This hypothetical example shows calculations done in five-degree increments below and above a CCC central-carbon (see text) angle of 180°. For a planar carbon the CCC angle must be 180° (imagine a point at the center of a rectangle and the line joining opposite corners), and for a tetrahedral carbon 109.5°. The curve with one minimum (circles) corresponds to a molecule which is a candidate for a possession of a planar carbon, because the 180° CCC angle corresponds to a relative minimum on the PES. The curve with two minima and a maximum (squares) corresponds to a molecule in which the planar carbon species is merely a transition state connecting two minima with CCC angles deviating by 10° from that required for planarity. The height of the barrier is suggestive of how closely the candidate approaches the desired role of possessing a planar carbon

MP2/6-31G(d)//HF/6-31G(d) barrier height (cf. Fig. 1.5) of 70 kJ mol^{-1}. Further calculations indicated that varying the size of the caps, for example replacing the eight-membered rings of octaplane by six- or seven-membered rings, led to little improvement. The strategy was tried of increasing the constraints on the central carbon by linking the two pairs of carbons on opposite sides of the "virtual rectangle" in which it lies in octaplane. This converts octaplane into spiro[2.2]octaplane (note the formally planar spiropentane – two cyclopropane rings sharing a carbon – moiety). The HF/6-31G(d) geometry of spiro[2.2]octaplane (D_2 symmetry) showed a modest increase in the CCC angle to 172° (cf. 169° for octaplane) and, even more encouragingly, a dramatic drop in the barrier height: from 70 to 11 kJ mol^{-1}.

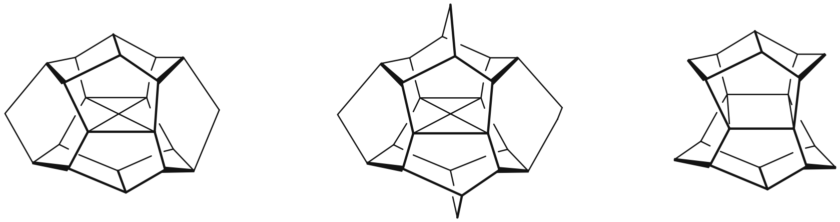
In a final push toward perfect planarity, methano bridges were made to span two pairs of methylene groups of the cyclooctane caps. This hierarchy of constraints (**1**→**2**→**3**→**4**) thus culminated in dimethanospiro[2.2]octaplane (Figs. 1.4 and 1.6): to the question, if these structural adjustments bring us closer to planarity, the authors respond "The answer is a resounding yes!" A HF/6-31G(d) optimization on this candidate showed a CCC angle of 178°, and the MP2/6-31G(d) single points curve exhibited a barrier of only 0.3 kJ mol^{-1}(thus at this level the planar-carbon molecule was almost, but not quite, a relative minimum on the PES). So propitious for the realization of a genuine planar-carbon molecule were these signs that correlated calculations with a reasonably big basis set were embarked upon: ideally, one would have liked to carry out an MP2 (or perhaps

Fig. 1.6 Dimethanospiro[2.2] octaplane, **4**. This is the calculated structure at the MP/6-31G(d) level

DFT; possibly these were considered less reliable because current DFT is somewhat semiempirical [36]; but see below a report on a DFT calculation) geometry optimization/frequency calculation with a bigger basis than the workhorse 6-31G(d). However, dimethanospiro[2.2]octaplane, $C_{23}H_{24}$, was considered to be too big for this: at the time (ca. 1998), and perhaps even today, MP2 frequency calculations, in particular, on molecules with more than twenty heavy atoms (in computational parlance, a heavy atom is any atom other than hydrogen or helium) were not routine. The planar carbon (D_{2h}) structure was therefore subjected to an optimization/frequency calculation with the large 6-311+G(2d) basis (27 basis functions) on the critical carbon, the smaller 6-311+G(d) basis (22 functions for each C) on each of the four α carbons, and a 6-31G(d) basis (14 functions per C if a basis with five d-type functions per heavy atom – rather than the usual six – were was used, and 2 functions per H) on all the other atoms, for a total of $1 \times 27 + 4 \times 22 + 18 \times 14 + 24 \times 2 = 415$ basis functions. This mammoth job took 11 days on 128 nodes of a Cray T3E supercomputer, equivalent to 1365 days on one of its processors. Now, a computational chemist tends to hold her breath on awaiting the results of a frequency calculation, particularly if done at a high level: a single imaginary frequency may dash one's hope of discovering (*in silico*) an extraordinary new molecule. A mere transition state connecting two prosaic molecules is a far cry from a relative minimum on the PES, a genuine new addition to the menagerie of exotic molecules. This calculation showed that "all the frequencies of dimethanospiro[2.2]octaplane are real!" confirming that at this fairly high level of calculation it is a relative minimum, not a mere transition state. The optimism centered on this molecule was surely but slightly tempered by the later finding that B3LYP/6-311+G(3df,2p) calculations predicted a double-well potential (cf. Fig. 1.5) [34]: here the barrier for attaining planarity was only 0.1 kJ mol^{-1}, and DFT, being partly semiempirical in its current implementations, is perhaps less reliable than the ab initio MP2 method for studying unusual molecules.

This study of dimethanospiro[2.2]octaplane must leave little doubt that its central carbon is either perfectly planar, or that the barrier to planarization is very small, in which latter case the relative-minimum species probably has a nearly-planar central carbon (one longs for the day when computer power will permit a CCSD(T) [37, 38] optimization/frequency calculation with a 6-31G(d) or bigger basis on a molecule like this). Radom and Rasmussen followed this discovery of the very promising nearly-planar carbon candidate **4** with a search for similar molecules that may be easier to make in vitro. Closely related to **4** are dimethanospiro[2.2]bioctaplane (**5**) and dimethanospiro[2.2]binonaplane (**6**), in which each cyclooctane capping ring of **4** has been made bicyclic by introducing a zero- or a one-carbon bridge (Fig. 1.7); in these, instead of eight-membered rings, we have possibly more easily-synthesized five- and six-membered rings. Molecule **5** was calculated to have a slightly nonplanar central carbon, with the planar transition state only 4.4 kJ mol^{-1} higher. Although predicted to be marginally short of planar perfection, **5** may merit particular synthetic scrutiny by virtue of its resemblance to the well-known pagodane, **7** [39]. Molecule **6** was calculated, like **4**, to have an exactly planar carbon.

From an intuitive qualitative analysis, the central carbon of dimethanospiro[2.2] octaplane might be expected to have a pure p atomic orbital (AO) perpendicular to the C(C_4) plane and to use its remaining valence orbitals, one 2s and two 2p AOs, to bond to the four surrounding carbons. An NBO (natural bond orbitals) analysis [40] as implemented in the program Gaussian 03,[2] using the STO-3G wavefunction (for simplicity) on the MP2/6-31G* geometry (this author's results), bestowed on the planar carbon a pure p AO with an electron pair ("occupancy" 1.85). This leaves this carbon approximately 2 valence electrons to bond to its four neighbors; if each of them contributes one electron toward the tetracoordination, we have six electrons forming four CC bonds, i.e. 0.75 pairs per bond, giving a bond order of 0.75 in the purely Lewis sense (there is no single, correct definition of bond order).[3] An alternative but electronically equivalent way of looking at the bonding is analogous to that presented by Hoffmann et al. [3] (Fig. 1.8), where the carbon in planar CH_4 was taken to be sp^2 hybridized with two of the carbon valence electrons in the pure p AO; the other two valence electrons were used to bond two hydrogens in normal C–H bonds between carbon sp^2 and hydrogen 1s AOs. Finally, the remaining two hydrogens were bonded to the carbon using only their two electrons and a carbon sp^2 with the hydrogen 1s AOs, in a three-center/two-electron bond. This structure seems to have nonequivalent C–H bonds, but it is not meant to be taken too literally: resonance among three equivalent structures averages the C–H bonds giving four identical bonds with 6/4 = 1.5 electrons, 0.75 pairs, each. The dimethanospirooctaplane version of this picture would substitute for each hydrogen 1s a carbon



5
dimethanospiro[2.2]bioctaplane

6
dimethanospiro[2.2]binonaplane

7
pagodane

Fig. 1.7 Molecules **5** and **6** are closely related to dimethanospiro[2.2]octaplane but perhaps easier to synthesize; **5** resembles closely the well-known pagodane, **7**

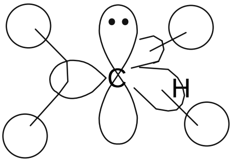


Fig. 1.8 Bonding in planar CH_4, in the model of Hoffmann et al. There are two two-electron C(sp^2)/H(1s) bonds and a three-center/2-electron HCH bond, but resonance among equivalent structure makes all CH bonds the same. The HOMO is a filled p orbital

hybrid AO of some kind. The Wiberg bond order [41] (from the NBO analysis) for the central/neighbor CC bonds was 0.73. The charge on the central carbon was calculated at −0.57, considerably higher than those on the normal carbons of the framework (−0.07 – +0.09), but these charges were quite basis-set-dependent, as is often the case, and in any case atom charges are not uniquely defined, physically measurable quantities [42].

The most striking electronic feature of planar carbon molecules, the presence of a filled carbon pure p AO, gives rise to what is perhaps their most conspicuous (virtually so – none have been made yet) physical property: a remarkably low ionization energy (IE). Radom and coworkers calculate that **4** and related compounds would have an IE of 4–5 eV, comparable to that of lithium (5.4 eV) and sodium (5.1 eV).[4] This is astonishingly low for a hydrocarbon: their typical IEs are ca. 8–10 eV (organosulfur compounds, with their big fluffy sulfur, have IEs of about 7 eV). The octaplane radical cation was calculated to have a planar central carbon planar too [43]. Recognizing this low IE as characteristic of metals, Radom and Rasmussen boldly hinted at practical applications: "Advantage might be taken in this respect of the unique combination of metallike properties . . . and organic properties" [34].

The likelihood that a planar (or near-planar) carbon species can exist is encouraging to chemists fascinated by exotic molecules. However, something beyond a mere "existence theorem" would be satisfying, particularly to the experimentalist yeomen (not a deprecatory term)[5] who help to keep the theoreticians in contact with reality. How stable would dimethanospiro[2.2]octaplane be – could it be handled at room temperature (almost a presupposition for practical applications)? A reasonably reliable answer to this question would require identification of the likely modes of unimolecular reaction and calculation of the barrier height for the most facile mode. Evidently this has not been done, but a qualitative analysis was ventured: opening of the spiropentane moiety could give a molecule with an allene and an ethene moiety.

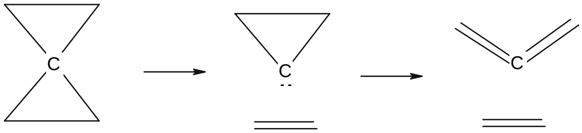


Fig. 1.9 Opening of a spiropentane to give a cyclopropylidene and an ethene moiety; the cyclopropylidene then opens to an allene. Cf. Fig. 1.10

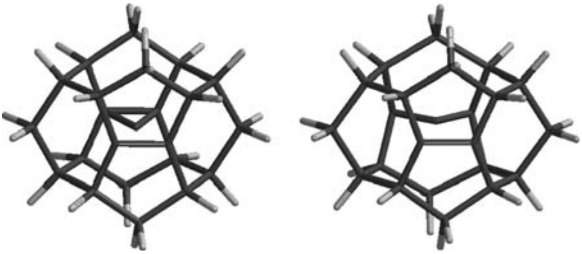
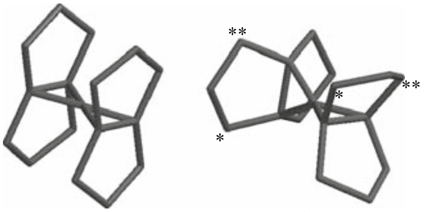


Fig. 1.10 The cyclopropylidene and the allene from opening of the spiropentane moiety of dimethanospiro[2.2]octaplane. These are molecular mechanics structures. The cyclopropylidene structure shown here actually has the carbons of the three-membered ring and the two carbons of the double bond in the same positions as the corresponding carbons of the spiropentane moiety of dimethanospiro[2.2]octaplane, and so its function here is only heuristic (cf. Fig. 1.9)

I show this in Figs. 1.9 and 1.10. Taking this, if only heuristically, as a two-step process, the first step is the reverse of the well-known addition of a carbene to a CC double bond to give a cyclopropane [44] and the second step is the opening, also well-known [45, 46], of a cyclopropylidene to an allene. It was optimistically suggested that these reactions were unlikely within the constraints imposed on the spiropentane moiety by the surrounding framework. However, although this retro-carbene addition reaction is apparently unknown for spiropentanes, the unique properties of the planar carbon in **8** may surprise us.

Synthesis

The most likely abode that has been devised for a planar carbon atom, dimethanospiro[2.2]octaplane (**4**), poses a formidable synthetic challenge by virtue (?) of its



8 **9**

Fig. 1.11 Illustration of the idea behind a suggested synthesis of dimethanospiro[2.2]octaplane: **8** depicts the spiropentane moiety of the target molecule, with a planar carbon and cyclopentane rings; **9** shows a normal spiropentane with tetrahedral carbon and cyclopentane rings. Connecting C* and C*, and C** and C** by a sufficiently long chain should make possible the synthesis of an intermediate with a normal, tetrahedral central carbon; contracting the chain by reactions going through a high-energy intermediate might snap the molecule into the high-energy twisted geometry of **8**, in which the marked carbons are connected by one-carbon “chains”. This is elaborated on in Fig.1.12

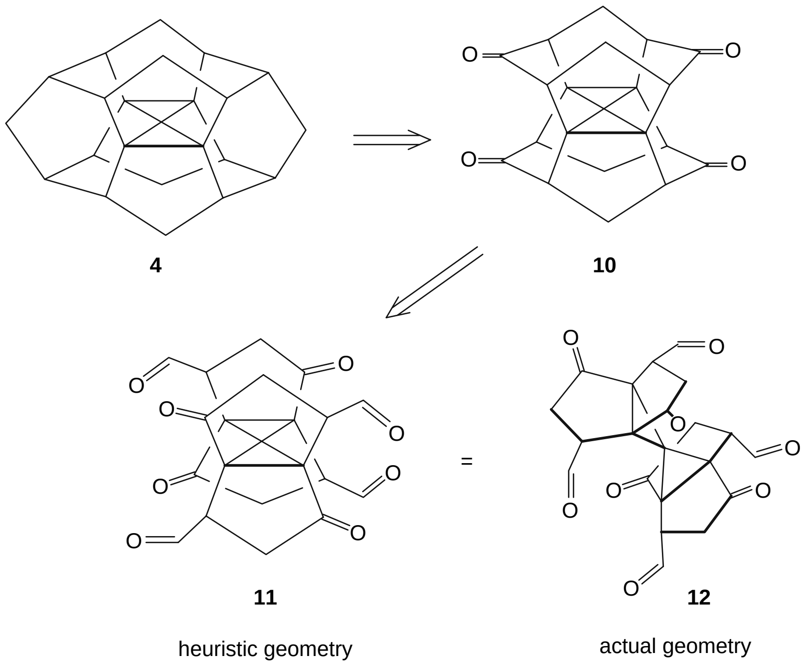


Fig. 1.12 An elaboration on the concept shown in Fig. 1.11. Retrosynthetic analysis of dimethanospiro[2.2]octaplane (**4**) leads here to **10**, and then to **11**, which is depicted more realistically as **12**, with a tetrahedral, rather than a planar, central carbon. The carbonyl groups shown are only suggestive of the synthetic "handles" that might be used to manipulate carbon–carbon bond-making

complexity. One suggestion might be to construct a much less strained precursor which could then be twisted into shape by contracting longer, permissive chains to one-carbon "chains" through a high-energy intermediate [47, 48] (Figs. 1.11 and 1.12). However, the molecule is so concatenated that it might profit well from a thorough retrosynthetic analysis [49] by an artificial intelligence retrosynthesis computer program[6] (cf. Fig.1.12).

Conclusions

A series of computer "experiments" by Radom and Rasmussen identified promising candidates for perfectly-planar-carbon molecules, the most promising of which were dimethanospiro[2.2]octaplane and dimethanospiro[2.2]binonaplane. Because of their size, complexity, and the strain incurred by planar carbon, these compounds represent formidable synthetic challenges; nevertheless, it is conceivable that they could yield to a thorough retrosynthetic analysis followed by skillful implementation of one of the thus-revealed putative routes.

Notes

1. E. Lewars, "Computational Chemist", Kluwer, Boston, 2003; p. 275.
2. Gaussian 03, Revision B.05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 2003.
3. (a) C. J. Cremer, "Essentials of Computational Chemistry", Wiley, New York, 2002; Chapter 9. (b) E. Lewars, "Computational Chemistry", Kluwer, Boston, 2003; pp. 300–307. (c) Mayer B.O.: I Mayer, M. Revesz, Inorganica Chim. Acta, 1983, *77*, L205; A. J. Bridgeman, G. Cavigliasso, L. R. Ireland, J. Rothay, J. Chem. Soc., Dalton Trans., 2001, *14*, 2095. (d) M. A. Natiello, J. A. Medrano, Chem. Phys., 1984, *105*, 180; M. A. Natiello, J. A. Medrano, Chem. Phys., 1984, *110*, 445. (e) AIM B.O.: R. F. W. Bader, J. Phys. Chem. A, 1998, *102*, 7314. (f) ELF B.O.: H. Grützmacher, T. F. Fässler, Chem. Eur. J., 2000, *6*, 2317. (g) an experimental expression: L. Jules, J. R. Lombardi, J. Mol. Struct. (Theochem), 2003, *664–665*, 255. (h) various B.O. Concepts: A. Torre, L. Lain, R. Bochicchio, J. Phys. Chem. A, 2003, *107*, 127.
4. NIST website, http://webbook.nist.gov/chemistry/.
5. "The yeoman work in any science. . .is done by the experimentalist, who must keep the theoreticians honest": Michio Kaku, "Hyperspace", Oxford University Press, 1995; p. 263.
6. Currently the most powerful program for computer-assisted synthesis is probably LHASA (Logic and Heuristics Applied to Chemical Synthesis), which has evolved from work begun at Harvard university in the late 1960s by Corey and Wipke; for more information, contact the LHASA Group at Harvard.

References

1. J. H. van't Hoff, Bull. Soc. Chim. Fr. II, 1875, *23*, 295.
2. J. A. Le Bel, Bull. Soc. Chim. Fr. II, 1874, *22*, 337.
3. R. Hoffmann, R. W. Alder, C. F. Wilcox, Jr., J. Am. Chem. Soc., 1970, *92*, 4992.
4. M. S. Gordon, M. W. Schmidt, J. Am. Chem. Soc., 1993, *115*, 7486.
5. M. P. McGrath, L. Radom, H. F. Schaefer, J. Org. Chem., 1992, *57*, 4847.
6. M. P. McGrath, L. Radom, J. Am. Chem. Soc., 1993, *115*, 3320.
7. J. E. Lyons, D. R. Rasmussen, M. P. McGrath, R. H. Nobes, L. Radom, Angew. Chem. Int. Ed. Engl., 1994, *33*, 1667.
8. H. Dodziuk, K. S. Leszcynski, J. Org. Chem., 1995, *60*, 6860.
9. G. Merino, M. A. Mendez-Rojas, H. I. Beltran, C. Corminboeuf, T. Heine, A. Vela, J. Am. Chem, Soc., 2004, *126*, 16160.
10. P. D. Pancharatna, M. A. Mendez-Rojas, G. Merino, A. Vela, R. Hoffmann, J. Am. Chem, Soc., 2004, *126*, 15309.
11. G. Merino, M. A. Mendez-Rojas, A. Vela, T. Heine, J. Comp. Chem., 2007, *28*, 362.
12. W. Siebert, A. Gunale, Chem. Soc. Rev., 1999, *28*, 367.
13. B. Sateesh, S. Reddy, G. N. Sastry, J. Comp. Chem., 2007, *28*, 335.

14. M. R. Siebert, D. J. Tantillo, J. Org. Chem., 2006, *71*, 645.
15. R. Keese, Chem. Rev., 2006, *106*, 4787.
16. K. B. Wiberg, Acc. Chem. Res., 1985, *17*, 379.
17. K. B. Wiberg, Chem. Rev., 1989, *89*, 975.
18. D. Ginsburg, “The Chemistry of the Cyclopropyl Group”, H. Rappaport, ed., Part 2, Wiley, New York, 1987; pp. 1193–1221.
19. D. Ginsburg, Top. Curr. Chem., 1987, *137*, 1.
20. I. N. Levine, “Quantum Chemistry”, Fifth Edn., Prentice Hall, Engelwood Cliffs, NJ, 2000; pp. 447–451.
21. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 210–231.
22. I. N. Levine, “Quantum Chemistry”, Fourth Edn., Prentice Hall, Engelwood Cliffs, NJ, 2000; Chapter 12.
23. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 33–38.
24. J. P. Lowe, “Quantum Chemistry”, Second Edn., Academic Press, New York, 1993; Chapter 13.
25. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 2.
26. C. J. Cremer, “Essentials of Computational Chemistry”, Wiley, New York, 2002; pp. 256, 445–447.
27. J. B. Foresman, A. Frisch, “Exploring Chemistry with Electronic Structure Methods”, Second Edn., Gaussian Inc., Pittsburgh, 1996; pp. 173–181.
28. C. J. Cremer, “Essentials of Computational Chemistry”, Wiley, New York, 2002; pp. 474–476.
29. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 241–242.
30. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 231–253.
31. R. D. Levine, R. B. Bernstein, “Molecular Reaction Dynamics and Chemical Reactivity”, Oxford, New York, 1987.
32. C. J. Cremer, “Essentials of Computational Chemistry”, Wiley, New York, 2002; pp. 66–92.
33. L. Radom, D. R. Rasmussen, Pure Appl. Chem., 1998, *70*, 1977.
34. D. R. Rasmussen, L, Radom, Angew. Chem. Int. Ed. Engl., 1999, *38*, 2876.
35. A. Nickon, E. F. Silversmith, “Organic Chemistry: The Name Game”, Pergamon, New York, 1987.
36. C. J. Cremer, “Essentials of Computational Chemistry”, Wiley, New York, 2002; Chapter 8.
37. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; p. 248.
38. J. Hrusak, S. Ten-no, S. Iwara, J. Chem. Phys., 1997, *106*, 7185.
39. H. Prinzbach, K. Weber, Angew. Chem. Int. Ed. Engl., 1994, *33*, 2239.
40. A. E. Reed, L. A. Curtis, F. Weinhold, Chem. Rev., 1988, *88*, 899.
41. K. B. Wiberg, Tetrahedron, 1968, *24*, 1083 (Wiberg B.O.).
42. S. M. Bachrach, “Reviews in Computational Chemistry”, K. Lipkowitz, D. B. Boyd, eds., VCH, New York, 1994; vol. 5, Chapter 3.
43. J. E. Lyons, D. R. Rasmussen, M. P. McGrath, R. H. Nobes, L. Radom, Angew. Chem. Int. Ed. Engl., 1994, *33*, 1667.
44. F. R. Carey, R. J. Sundberg, “Advanced Organic Chemistry”, Part B, Kluwer, New York, 2000; pp. 625–634.
45. H. F. Bettinger, P. R. Schreiner, P. v. R. Schleyer, H. F. Schafer, J. Phys. Chem., 1996, *100*, 16147.
46. H. F. Bettinger, P. v. R. Schleyer, P. R. Schreiner, H. F. Schafer, J. Org. Chem., 1997, *62*, 9267.
47. P. E. Eaton, P. G. Jobe, I. D. Reingold, J. Am. Chem. Soc., 1984, *106*, 6437.
48. K. B. Lipkowitz, M. A. Peterson, Chem. Rev., 1993, *93*, 2463.
49. E. J. Corey, X.-M. Cheng, “The Logic of Chemical Synthesis”, Wiley, New York, 1979.

Chapter 2
Pyramidal Carbon

Introduction

We saw in Chapter 1 the theoretical study of one species of distorted, nonclassical tetracoordinate carbon, namely planar carbon. The disposition of bonds in the two cases is shown in Fig. 2.1 (as well as the well-known propellane type of carbon). We begin with pyramidal CH_4. Planar methane, which inaugurated Chapter 1, was initially conceived of as a square planar transition state for inversion of normal, tetrahedral methane; further study showed the required transition state to be nonplanar. Choosing pyramidal methane as the starting point for our foray into the study of this stereochemical variant of carbon, we immediately encounter a structural ambiguity that was not present in the planar case, even when we insist on a fourfold symmetry axis: the HCH angle has no obviously favored value; square planar carbon in contrast must have HCH = 90°. This dilemma can be addressed by a series of calculations on pyramidal CH_4 in which the HCH angle is varied; the result of this is shown in Fig. 2.2. The calculational level, MP2/6-31G*,[1] is not as high as those used in the study of planar methane by Gordon and Schmidt [1] (Chapter 1), but this modest level should be at least semiquantitatively correct: planar methane here lies 669 kJ mol^{-} above the tetrahedral, while the highest level used by Gordon and Schmidt places it 490 kJ mol^{-1} higher. The optimal pyramidal angle is predicted (Fig. 2.2) to be ca. 115°. Of course, as with planar methane, this optimal structure does not correspond to a potential energy surface (PES) minimum, and is in fact not even a stationary point[2] on the PES.

Molecules of this sort appear to have been first considered (surprisingly, as he is usually cited with van't Hoff as a promoter of the tetrahedral carbon atom) by Le Bel in 1882. He was misled by supposed correlations between crystal structure and molecular geometry into thinking that in carbon tetrabromide and tetraiodide the carbon was at the apex of a square pyramid. This led him to the task, strange-seeming to us, of trying to resolve stereoisomers of (*Z*)-methylbutenedioic acid (methylmaleic acid, citraconic acid) and (*E*)-methylbutenedioic acid (methylfumaric acid, mesaconic acid) [2]. Astonishingly, as late as 1926 Weissenberg tried to explain the crystal structure of some pentaerythritol derivatives by invoking

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_2,

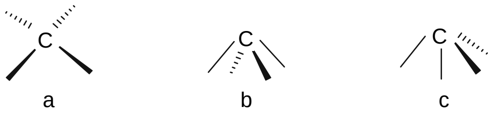
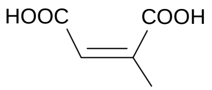
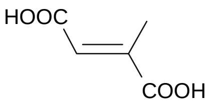


Fig. 2.1 Planar- (**a**), pyramidal- (**b**) and propellane-type (**c**) carbon atoms

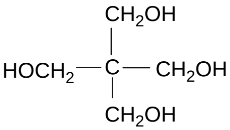
pyramidal carbon [3] (these historical curiosities are recalled in a discussion of the history of the concept of directed valence by Russell [4]).



(*Z*)-methylbutenedioic acid



(*E*)-methylbutenedioic acid

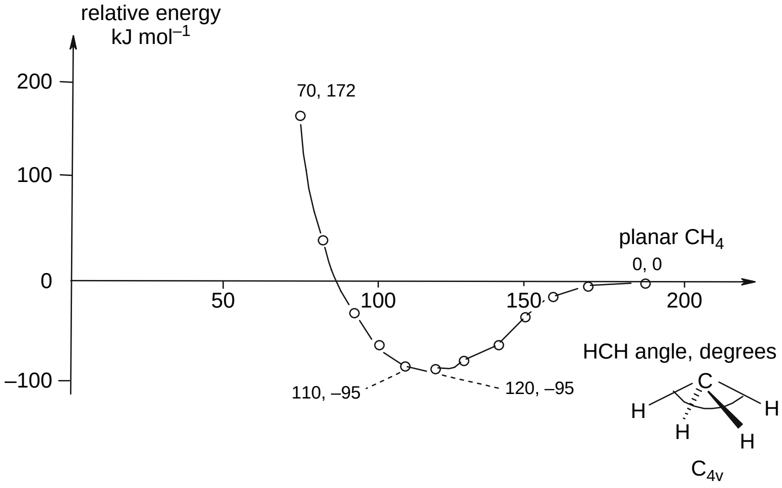


$$HOCH_2-\overset{\displaystyle CH_2OH}{\underset{\displaystyle CH_2OH}{C}}-CH_2OH$$

pentaerythritol

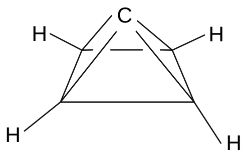
Pyramidane

The modern chemist could not reasonably have expected either planar or pyramidal CH_4 to be potentially isolable molecules, i.e. to be potential energy surface minima, and indeed as we have seen calculation indicates that they are not (and the inversion transition state for tetrahedral methane is not planar: Chapter 1). Consider however the simple artifice of anchoring the basal bonds of pyramidal methane to a



tetrahedral CH_4 lies at –669 kJ mol^{-1}

Fig. 2.2 Variation of the energy of pyramidal CH_4 with HCH angle (H–C–opposite H), calculated at the MP2/6-31G* level. The planar carbon structure, with HCH angle 180°, is taken as the energy zero cyclobutane ring; this minimal restraint delivers (on paper!) a structure worthy of serious investigation:



1

Unlike the case of planar methane, where a serious candidate molecule for the housing of a planar carbon was discovered only after much computational experimentation, a moment thought leads us straight to the prototypical pyramidal-carbon candidate, pyramidane.* This molecule seems to have first appeared in the literature in 1978, in a study by Minkin and coworkers using MINDO/3[3] and other semiempirical[4] methods, and small-basis-set ab initio[5] calculations, work that was soon followed by other similar studies [5, 6, 7]. These investigations suggested that pyramidane is a relative minimum on the PES and thus worthy of attempted experimental realization, and possible paths to this end were computationally examined [8, 9]. This pioneering work was conducted with the semiempirical MINDO/3 technique and with Hartree-Fock ab initio calculations using the small STO-3 G basis set. Such calculations, although suggestive, are at best semiquantitative, and in particular, cannot be trusted to provide reliable information on exotic species like pyramidane. Much higher-level calculations, at post-Hartree-Fock levels with bigger basis sets, strongly indicated that pyramidane should be a surprisingly stable molecule [10, 11]. For the decomposition pathways considered, the lowest hurdle was that for conversion to the carbene **2**, with a calculated barrier of 96 kJ mol^{-1} at the QCISD(T)/6-31 G*//MP2(fc)/6-31G* level (Fig. 2.3).[6] Pyramidane is predicted to be stabler than the strained carbenes **2** and **3**, and even the highly reactive spiropentadiene, **4** [12]. The computational aspect of the pyramidane saga was essentially closed with the calculation of a CCSD(T)/TZ2P[7] PES by the Schaefer group [13], which confirmed the substantial barrier to isomerization found by Lewars [10, 11] (100 kJ mol^{-1}, cf. 96 kJ mol^{-1}). The CCSD(T) method is the highest-level one currently used fairly frequently (but not routinely) for calculating geometries and relative energies. Experience shows that the threshold for a compound's being isolable at room temperature is about 100 kJ mol^{-1},[8] and a simple calculation gives pyramidane a room temperature halflife of a few hours (in reality it might actually last for anywhere from minutes to days) [11].

A brief discussion of the calculated structure of pyramidane is in order.

The most striking electronic feature is the presence of a lone pair on the apical carbon [11], as revealed by NBO (natural bond orbital) analysis[9] and, strikingly, by visualizing the electrostatic potential around the molecule (Fig. 2.5 shows

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*Pyramidane was erroneously called tetrahedrane (which is $(CH)_4$) in a recent publication: Y. Feng, L. Liu, J.-T. Wang, S.-W. Zhao, Q.-X. Guo, J. Org. Chem., 2004, *69*, pp. 3129, 3133.

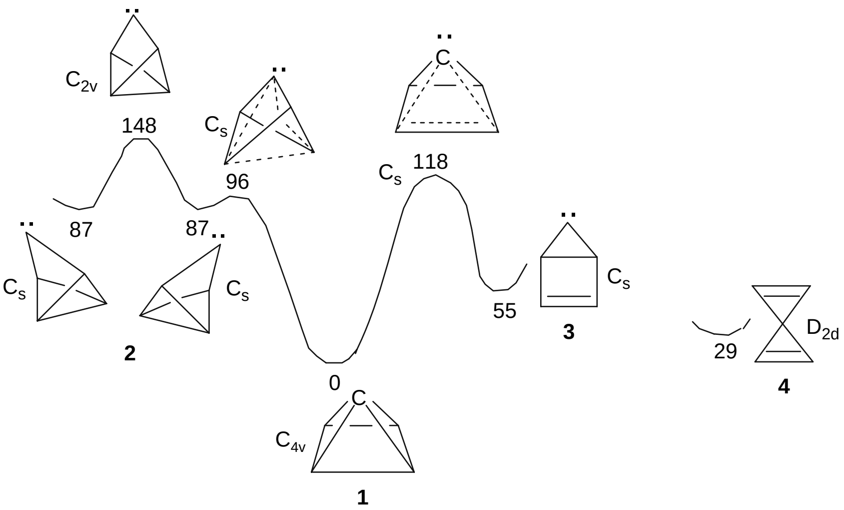


Fig. 2.3 The pyramidane potential energy surface at the QCISD(T)/6-31 G*//MP2(fc)/6-31G* level [10, 11]. Relative energies are in kJ mol^{-1}

calculations on pyramidane and CH_2, using the Spartan program).[10] This feature led naturally to an orbital analysis in which the molecule is idealized as an unhybridized C^{2-} bonded to a cyclobutadiene dication [11] (Fig. 2.6). Here three p orbitals of the apical carbon dianion overlap with the π system of the cyclobutadiene dication. The C^{2-} has two of its six valence electrons in a nonbonding 2s atomic orbital; the other four, plus the two π electrons of the cyclobutadiene dication are used to form four bonds joining the apical carbon to the base. Thus each of these four bonds has 6/4 = 1.5 electrons; defining bond order as the number of electron pairs in the bond, we have here a bond order of 1.5/2 = 0.75, essentially the same as the calculated Löwdin bond order[11] of 0.79 [11].

Apart from the iconic pyramidal carbon, the structure shows only one clearly somewhat unusual geometric feature, namely exceptionally long base-to-apex CC bond lengths of 1.672 Å (Fig. 2.4). CC single bonds are typically about 1.54 Å and a CC bond over 1.60 Å is exceptionally long [14, 15]. The record seems to be 1.72 Å for the sp^3–sp^3 bond of a tetraphencyclobutene fused to a phenanthrene ring [16],

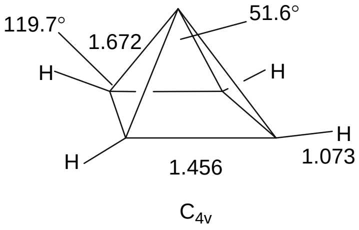


Fig. 2.4 The structure calculated for pyramidane at the SSCD(T)/TZ2P level [13]. The apical CCC angle is 76.0°

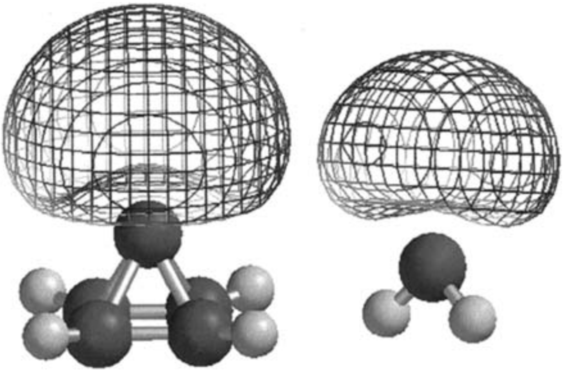


Fig. 2.5 Visualizing the electrostatic potential around pyramidane reveals the presence of a lone pair on the apical carbon (calculations with the Spartan program).[10] For comparison, methylene, CH_2, is shown

but a theoretical study suggests that CC bond lengths up to 2.00 Å are possible [17]. These CC bonds calculated here are therefore entirely reasonable.

The possibility that pyramidane might be more than an evanescent molecule (see above) makes the calculation of its chemical properties more than a frivolous exercise [10]. Addressing first basicity: the lone electron pair on the apical carbon endows the molecule, almost by definition, with this property. With remarkable basicity, in fact: pyramidane is evidently more basic (proton affinity 976 kJ mol^{-1}) than common nitrogen bases like pyridine or ammonia (922, 855 kJ mol^{-1}); the high-accuracy CBS-4 method[12] was used for all these calculations on the thermochemistry of pyramidane. Calculations by Rasmussen and Radom on this and other pyramidal-carbon molecules gave essentially the same result (965 kJ mol^{-1} for pyramidane; these workers also give a general review of pyramidal-carbon molecules) [18]. Figure 2.7 places in perspective the basicities of some common molecules, ranging from the scarcely basic methane to its extremely basic conjugate base [cf. 11]. Pyramidane is an alkane (a cycloalkane), and ordinary alkanes owe such feeble basicity as they possess to the fact that super acids [19] can protonate the electron pairs of CC and CH bonds. Thus the anomaly of an alkane with a lone pair is mirrored in the its extraordinary – for this class of compounds – basicity. Although pyramidane itself is unknown and there is a dearth of reported studies on it, there

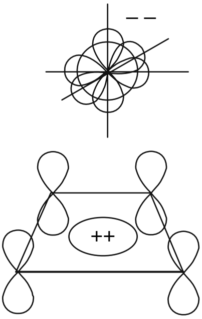
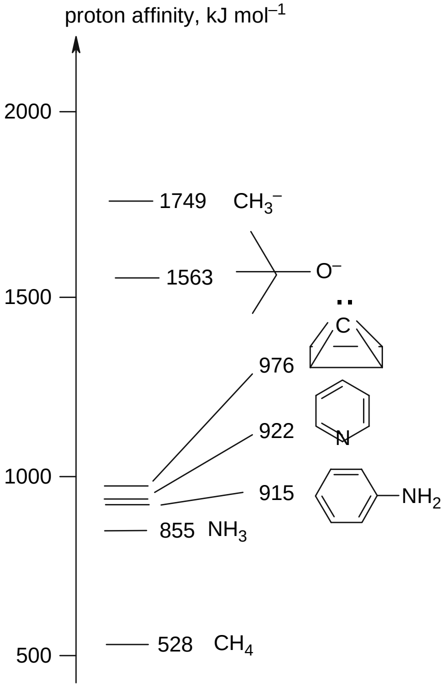
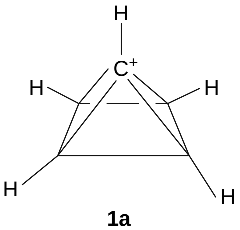


Fig. 2.6 Representation of pyramidane as an unhybridized C^{2-} bonded to a cyclobutadiene dication [11]

Fig. 2.7 Basicities of some molecules, calculated by the CBS-4 method. The proton affinities refer to the acidity of the conjugate acids. Methane is extremely weak as a base and the methyl anion is extremely strong



have been several theoretical studies of the cation resulting from its protonation [20, 21], and there is some experimental evidence for derivatives of it [22, 23, 24]:



1a

There is no special reason to expect the acidity of pyramidane to deviate significantly from that of other fused-ring cyclopropanes, and indeed the calculated value is similar to that of tetrahedrane (the basicity of the conjugate bases were used as a measure of acidity); Fig. 2.8 places in perspective the acidities of some hydrocarbons (calculated by the CSB-4 method), ranging from the extremely weakly acidic methane to the fairly strongly acidic (for a hydrocarbon) cyclopentadiene and, interestingly, the slightly more acidic methylpyramidane; this is commented on below. The acidity of pyramidane (1613 kJ mol^{-1}) is calculated to be about the same as that of tetrahedrane (1610 kJ mol^{-1}), indicating that a lone pair on the pyramidyl framework is not subject to any special effects beyond those due to

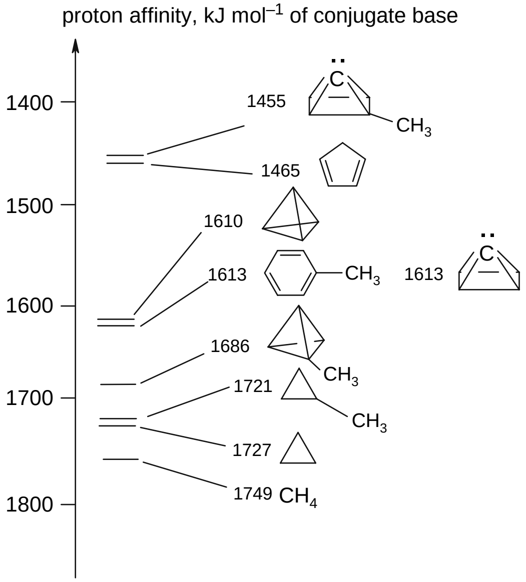
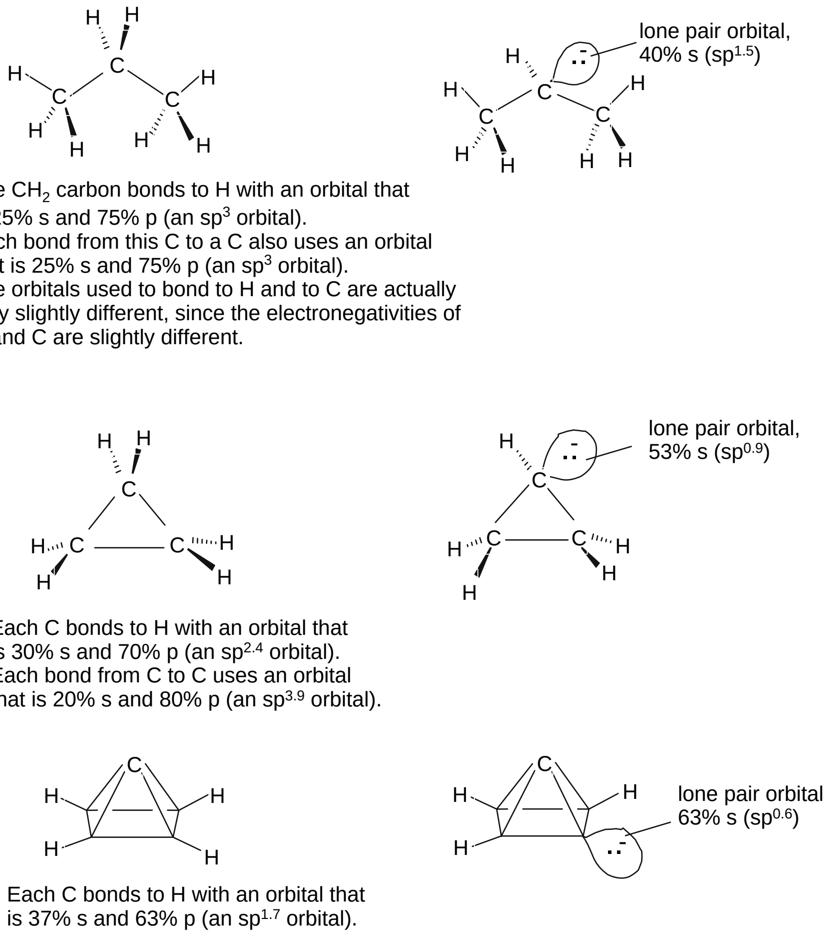


Fig. 2.8 Acidities of some hydrocarbons, calculated by the CBS-4 method. For the methyl-substituted molecules the proton being removed is one on the methyl group. Methane is extremely weak as an acid and methylpyramidane is relatively strong

ordinary fused cyclopropane rings, as in tetrahedrane. Tetrahedrane (1610 kJ mol^{-1}) and pyramidane (1613 kJ mol^{-1}) are considerably more acidic than cyclopropane (1727 kJ mol^{-1}), probably because fusing cyclopropane rings together increases strain and thus the s character of lone-pair orbitals. This is in accord with the well-known fact that the carbons of small-ring, strained cycloalkanes must dedicate exceptionally large p character to the ring bonds, leaving the bonds to hydrogen with unusually (compared to unstrained alkanes) large s character [25]. This large s character makes the CH bond exceptionally acidic [26], presumably because a lone pair in an s orbital is of lower energy than one in a p orbital (since 2s electrons are, on the average, closer to the nucleus than are 2p electrons). This is exemplified in Fig. 2.9. Note the smooth increase in the s character of the relevant orbitals as strain increases from propane through cyclopropane to pyramidane.

The properties of a hydrocarbon group are of particular interest to organic chemists. Alkyl, phenyl, benzyl, cyclopropyl groups – all these have their characteristic properties. The modern chemist interprets these properties using electronic theory; in particular, one examines the electronic proclivity of a group: whether, and to what extent, it withdraws or releases electrons. For the very novel pyramidyl group, C_5H_3 (designated Py here), this question was investigated computationally [10]. The obvious way to explore the ability of a group R to withdraw or donate electrons is to compare with other groups its ability to stabilize $R{-}CH_2^-$ or RCH_2^+; one way to do this is to calculate the energies for loss of H^+ and of H^- from $R{-}CH_3$. The loss of H^+ from the CH_3 group of methylpyramidane was calculated to be relatively favorable, making this molecule very acidic for a hydrocarbon: comparing the proton affinities of conjugate bases, Py–CH_3 is slightly more acidic than cyclopentadiene (1455 cf. 1465 kJ mol^{-1}) and much more acidic than toluene (1613 kJ mol^{-1});



lone pair orbital, 40% s (sp$^{1.5}$)

The CH_2 carbon bonds to H with an orbital that is 25% s and 75% p (an sp^3 orbital). Each bond from this C to a C also uses an orbital that is 25% s and 75% p (an sp^3 orbital). The orbitals used to bond to H and to C are actually very slightly different, since the electronegativities of H and C are slightly different.

lone pair orbital, 53% s (sp$^{0.9}$)

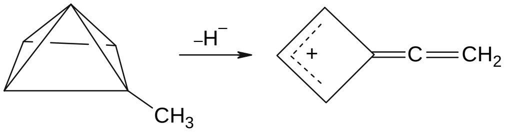
Each C bonds to H with an orbital that is 30% s and 70% p (an sp$^{2.4}$ orbital). Each bond from C to C uses an orbital that is 20% s and 80% p (an sp$^{3.9}$ orbital).

lone pair orbital 63% s (sp$^{0.6}$)

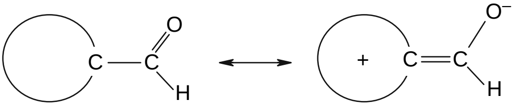
Each C bonds to H with an orbital that is 37% s and 63% p (an sp$^{1.7}$ orbital).

Fig. 2.9 The relevance of the s character of a CH bond to its acidity. Cyclopropane rings put more p character in their ring bonds than do unstrained analogues, because p orbitals, at mutual 90° angles, can accommodate better the geometric CCC angle of 60°. The “excess” s character of C orbitals used to bond H is survives in the lone-pair orbitals resulting from deprotonation

these are CBS-4 calculations, as usual (Fig. 2.8). The pyramidyl group strongly stabilizes an anionic carbon, and is thus strongly electron-withdrawing. An analogous methodology for probing the effect of this group on a cationic carbon as thwarted by the inability to compare the energies of Py–CH3 and Py–CH_2^+: the cation was not a stationary point, but instead rearranged (*in silico*):



To investigate the effect of the Py group on a positive carbon, the subterfuge was adopted of comparing pyramidanecarbaldehyde (Py–CHO), benzaldehyde (Ph–CHO), cyclopropanecarbaldehyde (Cy–CHO), and acetaldehyde (CH_3CHO) with regard to their rotational barriers and infrared carbonyl stretching values. A trend of increasing barrier height and decreasing wavenumber ("frequency") should correspond to increasing donation of electrons into the carbonyl group; in resonance terms:



The results of the barrier and IR calculations are summarized in Fig. 2.10. The results are consistent with PyCHO and PhCHO being about equal in ability to conjugate with carbonyl and CyCHO being somewhat better. In this respect the pyramidyl group resembles Ph and Cy, rather than the nonconjugating CH_3.

We saw in connection with the acidity calculations (cf. Figs. 2.8 and 2.9) that the pyramidyl group is quite strongly electron withdrawing when attached to an anionic carbon. The results for the barriers and IR stretch of the various aldehydes indicates that the pyramidyl group can donate electrons toward the somewhat cationic carbon of a carbonyl group (Wiberg goes so far as to say that the carbonyl group is essentially C^+–O^- [27]). The novel hydrocarbon group thus seems to be able to adjust its electronic nature according to whether the center to which it is conjugated is electron-rich or electron-poor. In this respect it is like the phenyl or vinyl groups.

In Chapter 1 we saw that the lone pair on the putative planar carbon of octaplane conferred on that alkane a rather low ionization energy (IE): ca. 4–5 eV, comparable to that of lithium (5.4 eV) and sodium (5.1 eV), and it might have been suspected that the lone pair on the pyramidal carbon of **1** would likewise give that molecule an anomalously low IE. However, from the energy of the HOMO (using Koopmans' theorem) and from the energy difference of the neutral and the radical cation, the IE of **1** was calculated [10] to be ca. 9.0 eV, a reasonable value for a strained cycloalkane (cyclohexane, 9.9 eV; the strained cubane, 8.6 eV [28]) with no special lone-pair effect. This is not so surprising if one notes that the lone pair in planar-carbon species is in a p orbital, while that in pyramidal-carbon molecules is in a largely s-character orbital. As pointed out above in the discussion of the acidity of pyramidane, 2s electrons are more tightly bound than 2p electrons.

We close our examination of **1** with a look at its heat of formation and strain energy. The heat of formation (enthalpy of formation) of a compound (the heat or enthalpy needed to make a mole of the compound from its elements in their standard states) is a useful quantity because from a table with the relevant heats of formation one can calculate simply by appropriate subtraction heats of reaction (enthalpy changes). Here we shall focus on the use of the heat of formation of **1** to calculate its strain energy; this provides some indication of the stability of the molecule, although, as has been pointed out [18], it does not necessarily indicate kinetic

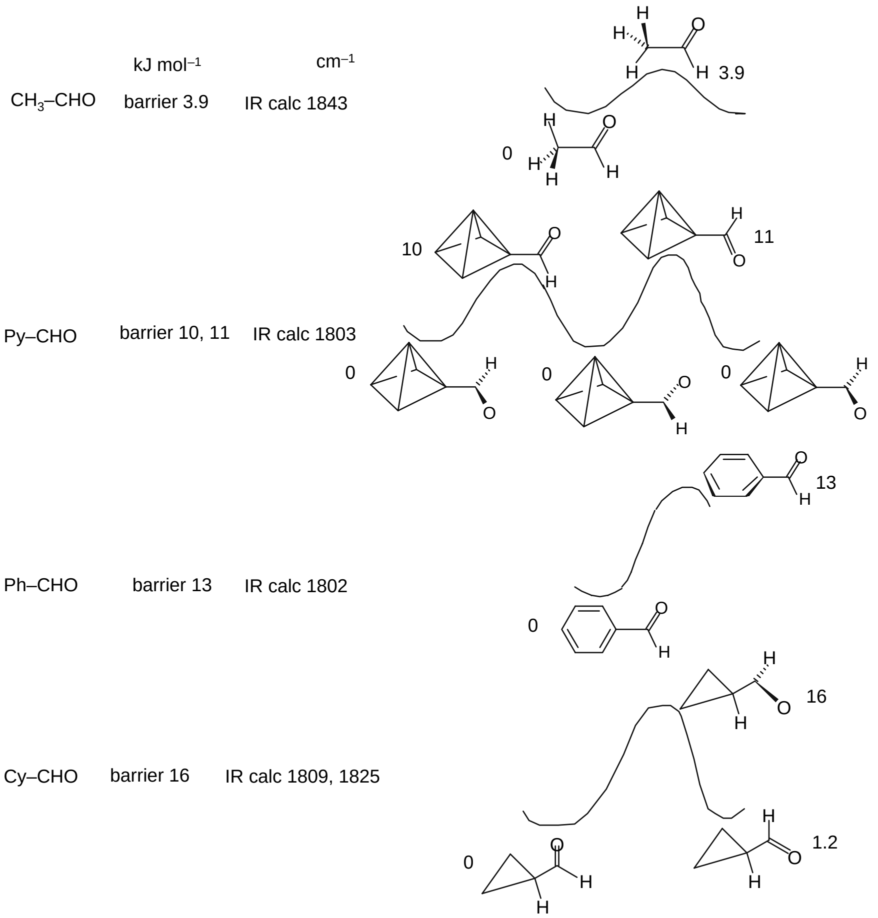


Fig. 2.10 Rotation barriers (kJ mol^{-1}) and IR CO stretching values (cm^{-1}) for pyramidyl-CHO (PyCHO) compared to CH_3CHO, PhCHO, and cyclopropyl-CHO (CyCHO). The results are consistent with PyCHO and PhCHO being about equal in ability to conjugate with carbonyl and CyCHO being somewhat better. In this respect the pyramidyl group resembles Ph and Cy, rather than the nonconjugating CH_3. B3LYP/6-31G* calculations

stability (cubane is very strained, but perfectly stable kinetically at room temperature). The easiest way to calculate a heat of formation for a compound is to use a semiempirical method which has been parmeterized to give molecular energies as heats of formation. Currently the most popular such methods are AM1 and PM3.[13] The heat of formation of pyramidane from AM1 and PM3 are 1047 and 916 kJ mol^{-1}, respectively. Unfortunately, semiempirical heats of formation, although trivial to calculate, thus rendering such calculations useful for some purposes, are subject to considerable errors, often tens or occasionally even hundreds of kJ mol^{-1}.

Chemists nowadays often expect their computations to deliver quantities like heats of formation with errors of no more than a few tens of kJ mol^{-1} and, if possible, ca. 10 kJ mol^{-1}. The calculation of molecular thermochemical data to within “a prescribed accuracy of about ±2 kcal mol^{-1}” [29], which we may take as about ±10 kJ mol^{-1}, became known as “chemical accuracy”; in recent years the term seems to have tended to become subject to the narrower stricture of about ±5 kJ mol^{-1}.** Ab initio and DFT calculations can reliably provide heats of formation accurate to within about 10 kJ mol^{-1}, but unlike semiempirical methods like the widely-used AM1 and PM3, they do not give these quantities directly. Rather, the ab initio or DFT energies (which are energies for the complete dissociation of molecules into their nuclei and electrons), must be inserted into a thermodynamic cycle, from which the heat of formation can be extracted [30]. From the heat of formation the strain energy of **1** can be calculated by comparison with tabulated group values [31] (it can alternatively be calculated from isodesmic ring-opening reactions) [32]:

Heat of formation at 298 K, kJ mol^{-1}

601	atomization method with CBS-Q [10]
602	atomization method with G2(MP2) [10]
585	isodesmic reaction with G2(MP2) [10]
602	isodesmic reaction with HF/6-31G* [32]
611	isodesmic reaction with MP2/6-311+G(2d,p)//MP2/6-31G* [18]

Strain energy, kJ mol^{-1}

622	from ΔH_f group values, CBS-Q [10]
639	from a group equivalent method, HF/6-31G* [31]
664	from isodesmic ring opening, MP2/6-311+G(2df,p) [32]
645	from isodesmic ring opening, MP2/6-311+G(2d,p)//MP2/6-31G* [18]

Values calculated for pyramidane are thus about 600 kJ mol^{-1} (a value much less than the AM1 or PM3 values of 1047 and 916 kJ mol^{-1}) for the heat of formation, and about 640 kJ mol^{-1} for the strain energy. By comparison, the calculated heat of formation and strain energy of the known [12], highly reactive pyramidane isomer spiropentadiene are 658 and 500 kJ mol^{-1} (298 K, atomization method with CBS-Q [10]). The heat of formation calculation thus concurs with the PES calculations in predicting that pyramidane (**1**, Fig. 2.3) is thermodynamically stabler than spiropentadiene (**4**, Fig. 2.3). Pyramidane might seem to be significantly more strained than spiropentadiene ca. (640 vs. 500 kJ mol^{-1}), but the strain *per CC bond* is probably more chemically meaningful than the total strain; some values of this are (the experimental heat of formation of cubane is 605 kJ mol^{-1}, which yields a calculated strain energy of 695 kJ mol^{-1} [33]):

**The term apparently originated with John Pople, who won the 1998 Nobel prize for making ab initio calculations practical tools for chemists; the prize was shared with Walter Kohn, who did the analogous thing for density functional theory calculations.

Strain energy per CC bond, kJ mol^{-1}, from the above values

pyramidane	81	unknown
spiropentadiene	83	kinetically highly reactive
cubane	58	kinetically stable

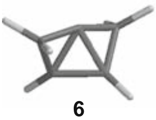
This admittedly small sample does not suggest any particular connection between strain energy and kinetic stability.

Other Molecules with Possibly Pyramidal Carbon

Besides pyramidane, many other molecules with pyramidalized carbon have been examined computationally. Much of the earlier computational work on carbon with unusual configurations was carried out by the groups of Dodziuk and of Radom. The former group explored various unusual configurations at carbon (planar pyramidal, and carbon tetracoordinate with a CCC angle close to linear), while the latter focused on planar carbon, as discussed in Chapter 1, and on pyramidal carbon.

Among the molecules examined by the Dodziuk group were **5** (bowlane) which we met in Chapter 1, and **6**, **7**, and **8**, in which two cyclopropane rings have been fused *anti* to a three-, four-, and five-membered ring [34] (these are AM1-computed structures):

5



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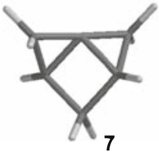
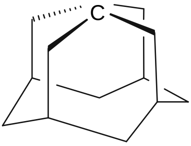


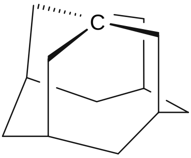
7

8

Bowlane was (Chapter 1) the starting point in the search for a molecule with truly planar carbon. Drawn conventionally (**9**), it appears to possess a pyramidal carbon, but ab initio calculations indicate that the carbon in question actually disposes two of its bonds nearly linearly, with the other two pointing downward:

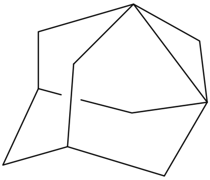


C_{4v}



C_{2v}

The C_{4v} structure is a transition state leading to the relative-minimum C_{2v} species [32]. Structures **6**, **7** and **8**, rather than housing a pyramidal carbon, also turn out to be of relevance to the question of how nearly two bonds at a tetracoordinate carbon can approach linearity (the relevant CCC angle of **7** is calculated to be 178°). Another molecule that, drawn intuitively, looks like it may have a pyramidal carbon, but on subjection to computation turns out to be otherwise, is 1,3-dehydroadamantane: geometry optimization by molecular mechanics,^{14} semiempirical, or ab initio methods show the deceptive atom to be tetrahedral, albeit strongly distorted:



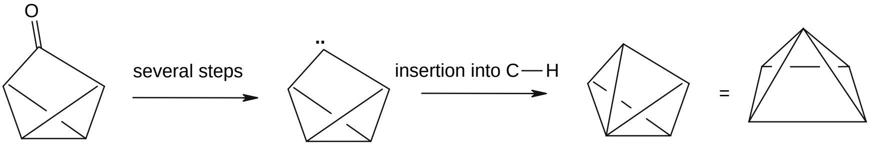
intuitive

computed

In a review of pyramidal carbon species [18], Rasmussen and Radom approach these from the viewpoint of their potentially planar carbon molecules [35, 36] from which one “cap” has been removed (Fig. 2.11). The resulting molecules are called hemialkaplanes and hemispiroalkaplanes. The former have a neopentane moiety capped by a cycloalkane, the latter a spiropentane moiety capped by a cycloalkane. Molecules representing decapped alkaplanes do not have truly pyramidal carbon, as pointed out above for bowlane. However, decapping spiroalkaplanes can lead to genuine pyramidal-carbon structures; in particular, the iconic pyramidane.

Synthesis

Consonant with the predictions of calculated potential energy surfaces, e.g. Fig. 2.3, it has been suggested that the carbene **2** (tricyclo[2.1.0.0^{2,5}]pentylidene, which evidently lies about 90 kJ mol^{-1} above pyramidane, might serve as a precursor to the fascinating hydrocarbon [8, 9, 31]. A promising precursor of this carbene would seem to be the ketone tricyclo[2.1.0.0^{2,5}]pentanone (**9**), a known compound [37]:



9 **2**

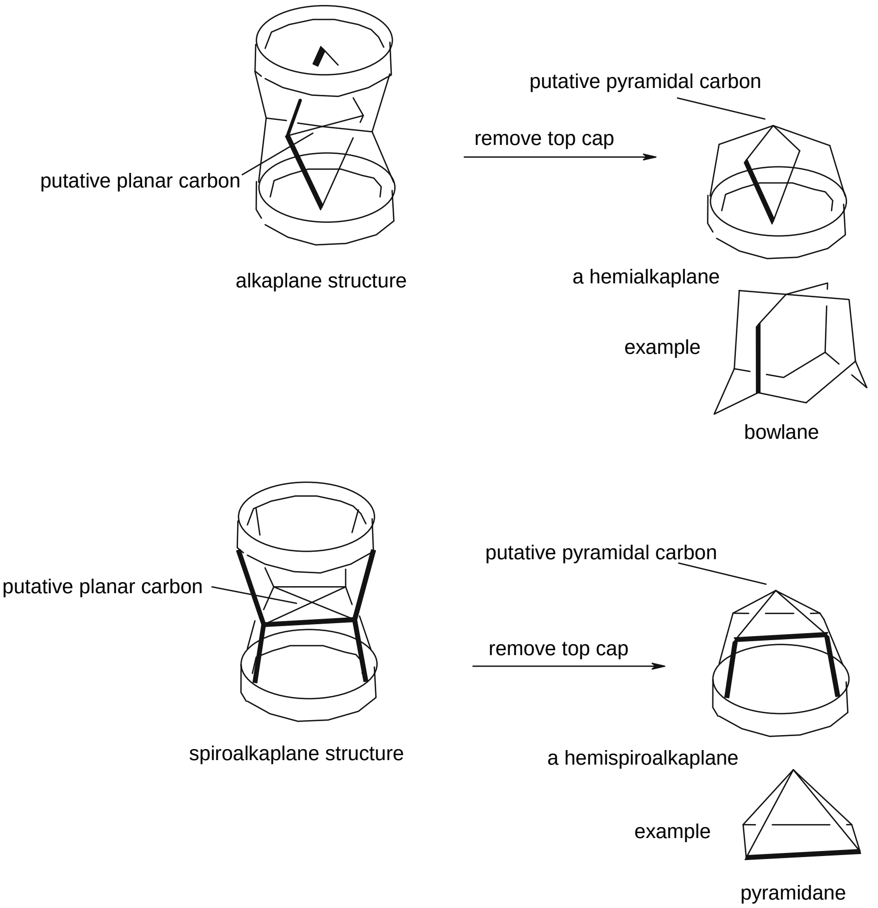
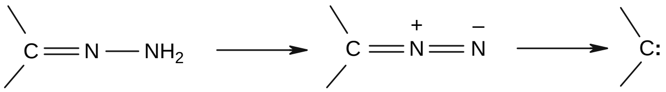


Fig. 2.11 Potentially pyramidal-carbon molecules, viewed as potentially planar-carbon molecules with a cap removed [18]

Substituted tricyclopentanols (alcohols related to **9**) have served as precursors of pyramidal cations by protonation and dehydration [37], but the sequence proposed above requires conversion of the ketone to a carbene and the insertion of the carbene center into a CH bond (a distal CH; insertion into a proximal CH would form a highly strained bridgehead alkene), a known process [38]. A possible sequence for the conversion of **9** to the carbene is preparation of the hydrazone and oxidation of this to the diazo compound [39], followed by catalytic or photochemical expulsion of nitrogen [40]:



Conclusions

The simplest compound with an unequivocally pyramidal carbon, pyramidane, is almost certainly a minimum on the $C(CH)_4$ potential energy surface, in other words, capable of existing. Furthermore, there is good computational evidence that it is separated from its most likely proximate decomposition products by a substantial barrier, and may even be isolable at room temperature. The simplicity of the molecule and the availability of promising putative synthetic precursors make pyramidane a very realistic synthetic goal.

Notes

1. In calculations on molecules a "higher" level often means a level that treats interelectronic repulsion more accurately than a "lower" level. The most widely used method explicitly designed to address the repulsion problem is MP2 (Møller-Plesset). 6-31 G* refers to the basis set used. See Note 4.
2. A potential energy surface is a diagram (or the corresponding mathematical function) describing how the energy of a molecule or a collection of molecules varies with their geometry. The pictorial aspect is a very useful aid in thinking about the stability of molecules; a stable molecule sits in a deep well, needing significant energy to climb up the walls of the well and reach some other well(s) (be transformed into another/other molecules). The bottom of such a well is called a *minimum*, and is one kind of *stationary point*. The other important kind of stationary point is the middle of the saddle-shaped region connecting two minima; this point is the *transition state* (transition *structure* might be preferable) for the reaction. A transition state is a first-order saddle point; higher-order saddle points are usually not chemically significant. See E. Lewars, "Computational Chemistry", Kluwer, Boston, 2003; Chapter 2.
3. MINDO/3 was the first widely-used (1975) semiempirical method for obtaining chemically useful properties, in particular geometries and relative energies.
4. See Note 3.
5. Ab initio calculations are, in contrast to semiempirical [30] not *parameterized*, that is they do not rely on empirical (experimental) quantities in the algorithms used to calculated geometry, energy, etc. The simplest kind of ab initio procedure is the HF (Hartree-Fock), in which interelectronic repulsion is treated very approximately: *electron correlation*, the fact that each electron sees each other one as a moving particle rather than seeing the others as a smeared-out cloud, is not treated effectively. Post-HF calculations, e.g. MP2, try to handle this correlation phenomenon better (cf. Note 1). Like all current quantum mechanical methods, ab initio calculations use a *wavefunction*, a mathematical function from which various properties can be calculated. The wavefunction is built up from a set of *basis functions* (smaller mathematical functions) called a basis set, and, generally, the bigger the basis set the better. Nowadays the smallest respectable (though but little seen in the research literature) basis set is the STO-3 G basis, but in the 1970s a large "STO-3 G chemistry" grew up. The 6-31 G* basis, considerably bigger than the STO-3 G, is probably the most popular basis set used nowadays. An introduction to ab initio calculations: E. Lewars, "Computational Chemistry", Kluwer, Boston, 2003; Chapter 5.
6. This is a fairly high ab initio (see Note 4) level. The notation QCISD(T)/6-31 G*//MP2(fc)/6-31G* means that the energy of the molecule was calculated by the QCISD(T)/6-31G* method, at the geometry obtained from a MP2(fc)/6-31G* (fc means frozen core: the core electrons – the non-valence electrons – are ignored in the MP2 procedure; the alternative is MP2(full)) optimization. QCISD(T) (quadratic configuration interaction, singles, doubles, perturbative triples) is a higher-level correlation method than MP2 (see Note 5). A calculation

of energy at a geometry obtained at a lower level is called a single-point calculation; it saves time at the cost of a possible loss of accuracy. See E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 5.

7. CCSD(T)/TZ2P is a high-level electron correlation method somewhat like QCISD(T), but more accurate.
8. Some barriers/room temperature halflives for unimolecular reactions: (a) Decomposition of pentazole and its conjugate base: 75 kJ mol^{-1}/10 minutes and 106 kJ mol^{-1}/2 days, respectively. V. Benin, P. Kaszynski, J. G. Radziszki, J. Org. Chem., 2002, *67*, 1354. (b) Decomposition of $(CF_3CO)OOO(COCF_3)$: 86.5 kJ mol^{-1}/1 minute. S. v. Ahsen, P. Garciá, H. Willner, M. B. Paci, G. Argüello, Chem. Eur. J., 2003, *9*, 5135.
9. Natural bond orbital analysis employs set of algorithms which dissect the electron distribution in a molecule into entities familiar to chemists, like the percentage of s and p character in orbitals and the hybridization state of atoms. The NBO suite of methods and algorithms is largely associated with the Weinhold group. See F. Weinhold, C. R. Landis, “Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective”, Cambridge University Press, Cambridge, 2003; A. E. Reed, A. Curtis, F. Weinhold, Chem. Rev., 1988, *88*, 899.
10. Spartan ‘04, Wavefunction Inc., 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612.
11. The bond order concept finds its simplest expression in conventional chemical structures: as single, double, and triple bonds, where it can be considered to represent the number of pairs of electrons being shared between two atoms. However, since electrons presumably do not always reside accommodatingly in pairs between (or on) atoms, it is useful to have some way of calculating a number that corresponds, at least approximately, to the simple picture. There are several methods of calculating some kind of bond order, and none of them is the “right” one. The oldest general method is due to Mulliken; more popular nowadays are methods due to Weinhold, Wiberg, and Löwdin: R. S. Mulliken, J. Chem. Phys., 1955, *23*, 1833; R. S. Mulliken, J. Chem. Phys., 1962, *36*, 3428; F. Weinhold, C. R. Landis, “Valency and Bonding: A Natural Bond Orbital Donor-Acceptor Perspective”, Cambridge University Press, Cambridge, 2003; A. E. Reed, A. Curtis, F. Weinhold, Chem. Rev., 1988, *88*, 899; K. B. Wiberg, Tetrahedron, 1968, *24*, 1083; P.-O. Löwdin, Adv. Quantum Chem., 1970, *5*, 185.
12. Complete basis set (CBS) methods are a family of *high-accuracy multistep* methods; the other family of such high-accuracy methods is constituted by the *Gaussian methods*, named after their association with Gaussian Inc., which produces the Gaussian series of programs. Both families are designed to yield “chemical accuracy” [31], ± ca. 10 kJ mol^{-1}, for thermochemical reactions. The CBS methods obtain high accuracy with the aid of an approach to extrapolation to an infinitely large basis set (see Note 5): G. A. Petersson, “Computational Thermochemistry”, K. K. Irikura, D. J. Frirup, eds., American Chemical Society, Washington, DC, 1998. The Gaussian family rely on a series calculations with increasingly higher correlation methods and basis sets (see Note 4): L. A. Curtiss, K. Raghavachari, “Computational Thermochemistry”, K. K. Irikura, D. J. Frirup, eds., American Chemical Society, Washington, DC, 1998. Both methods make use of one or more empirical parameters and so are not fully ab initio.
13. These semiempirical methods are in essence based on parameterized and simplified versions of the ab initio (see Note 5) approach. They are far faster and usually give good geometries but less reliable relative energies. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 6.
14. Molecular mechanics is, in contrast to ab initio (see Note 4) and semiempirical methods (see Note 12), not based on electronic theory (more specifically, not based on the Schrödinger equation). Instead it relies on a *mechanical* picture of a molecule as a collection of balls held together by springs. Knowing the resistance of the springs to stretching (their force constants), and other sources of resistance to geometric deformation, an optimized geometry (a potential energy surface minimum (see Note 2)) can be calculated.

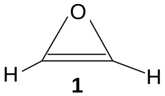
References

1. M. S. Gordon, M. W. Schmidt, J. Am. Chem. Soc., 1993, *115*, 7486.
2. J. A. Le Bel, Bull. Soc. Chim. France, 1893, *3*, 11.
3. K. Weissenberg, Berichte, 1926, *59*, 1526.
4. C. A. Russell, “The History of Valency”, Leicester University Press, Leicester, 1971; pp. 166, 167.
5. V. I. Minkin, R. M. Minyaev, I. I. Zakharov, V. I. Avdeev, Zh. Org. Khim., 1978, *14*, 3.
6. V. I. Minkin, R. M. Minyaev, Zh. Org. Khim., 1979, *15*, 225.
7. V. I. Minkin, R. M. Minyaev, G. A. Orlova, J. Mol. Struct. (Theochem), 1984, *110*, 241.
8. R. M. Minyaev, V. I. Minkin, N. S. Zefirov, Yu. A. Zhdanov, Zh. Org. Khim., 1979, *15*, 2009.
9. R. M. Minyaev, V. I. Minkin, N. S. Zefirov, V. I. Natanzon, S. V. Kurbatov, Zh. Org. Khim., 1982, *18*, 3.
10. E. Lewars, J. Mol. Struct. (Theochem), 2000, *507*, 165.
11. E. Lewars, J. Mol. Struct. (Theochem), 1998, *423*, 173.
12. W. E. Billups, M. M. Haley, J. Am. Chem. Soc., 1991, *113*, 5084.
13. J. P. Kenny, K. M. Krueger, J. C. Rienstra-Kiracofe, H. F. Schaefer, J. Phys. Chem. A, 2001, *105*, 7745.
14. G. Kaup, J. Boy, Ang. Chem. Int. Ed., 1997, *36*, 48.
15. S. Kammermeier, P. Jones, R. Herges, Ang. Chem. Int. Ed., 1997, *36*, 1757.
16. K. K. Baldridge, Y. Kasahara, K. Ogawa, J. S. Siegel, K. Tanaka, F. Toda, J. Am. Chem. Soc., 1998, *120*, 6167.
17. I. Isea, J. Mol. Struct. (Theochem), 2001, *540*, 131.
18. D. R. Rasmussen, L. Radom, Chem. Eur. J., 2000, *6*, 2470.
19. G. A. Olah, G. K. S. Prakash, J. Sommer, “Super Acids”, Wiley, New York, 1985.
20. M. N. Glukhovtsev, R. D. Bach, S. Laiter, J. Phys. Chem., 1996, *100*, 10952.
21. E. D. Jemmis, P. v. R. Schleyer, J. Am. Chem. Soc., 1982, *104*, 4781.
22. S. Masamune, M. Saki, H. Oma, J. Am. Chem. Soc., 1972, *94*, 8955.
23. S. Masamune, M. Saki, H. Oma, A. Jones, J. Am. Chem. Soc., 1972, *94*, 8956.
24. H. Hart, M. Kuzya, J. Am. Chem. Soc., 1972, *94*, 8958.
25. F. A. Carey, R. J. Sundberg, “Advanced Organic Chemistry”, Fourth Edn., Kluwer, New York, 2000; pp. 4–8.
26. F. A. Carey, R. J. Sundberg, “Advanced Organic Chemistry”, Fourth Edn., Kluwer, New York, 2000; pp. 405–416.
27. K. B. Wiberg, Acc. Chem. Res., 1999, *32*, 922.
28. NIST website: http://webbook.nist.gov/chemistry/
29. L. A. Curtis, K. Raghavachari, G. W. Trucks, J. A. Pople, J. Chem. Phys., 1991, *94*, 7221.
30. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; section 5.5.2.3.
31. V. Balaji, J. Michl, Pure Appl. Chem., 1988, *60*, 189.
32. M. P. McGrath, L. Radom, H. F. Schaefer, J. Org. Chem., 1992, *57*, 4847.
33. G. W. Griffin, A. P. Marchand, Chem. Rev., 1989, *89*, 997.
34. H. Dodziuk, J. Leszczyński, K. S. Nowiński, J. Org. Chem., 1995, *60*, 6860, and refs. therein.
35. L. Radom, D. R. Rasmussen, Pure and Appl. Chem., 1998, *70*, 1977.
36. D. R. Rasmussen, L. Radom, Angew. Chem. Int. Ed. Engl., 1999, *38*, 2875.
37. P. Dowd, H. Irngartinger, Chem. Rev., 1989, *89*, 885.
38. M. B. Smith, K. March, “March’s Advanced Organic Chemistry”, Wiley, New York, 2001; p. 789.
39. M. B. Smith, K. March, “March’s Advanced Organic Chemistry”, Wiley, New York, 2001; p. 1519.
40. W. Kirmse, “Carbene Chemistry”, Academic Press, New York, 1971.

Chapter 3
Oxirene

Introduction

The molecules of Chapters 1 and 2 were species that defy one of the basic principles of the structural theory of organic chemistry (or at least the theory in its simplest form, based on experience, without invoking electronic theory): the valences of tetracoordinate carbon are directed toward the corners of a tetrahedron. They are molecules that, within the confines of the theory, "should" not exist. The subject of this chapter, in contrast, appears to defy no rules of the structural theory: oxirene (this is the usual name; it is based on the clumsy Hantzsch-Widman system, in which heterocyclic rings of 3, 4, etc. atoms are given special names like oxirane, oxirene, oxetane, etc. An alternative system utilizes the currently neglected logical and convenient method of replacement nomenclature: oxacyclopropane, oxacyclopropene, oxacyclobutane, etc.[1]), **1**, looks at first glance like a normal molecule. No unusual stereochemical constraints are imposed on the molecule, all atoms have their normal valence numbers, and (unlike the case of the subject of the next chapter, NF_5) no octet limitations are transgressed. Why should this simple, reasonable-looking molecule be so elusive, can it exist, and what are its properties?



1

On reflection two moderately disturbing features emerge: having a three-membered ring oxirene is strained [1, 2, 3, 4, 5], and (Fig. 3.1) one electron pair on the oxygen is at least potentially able to enlist the assistance of the two π electrons of the double bond to confer antiaromaticity [6, 7] on the ring and thus to electronically destabilize it. Let us consider these features in turn.

Strain is a ubiquitous and enormously important concept in chemistry, although there is no uniquely correct quantitative definition of it. A qualitative – and useful – feel for the idea is readily acquired by attempting to construct strained molecules like oxirene or cyclopropane with ball- and stick molecular models; if the sticks are

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_3,

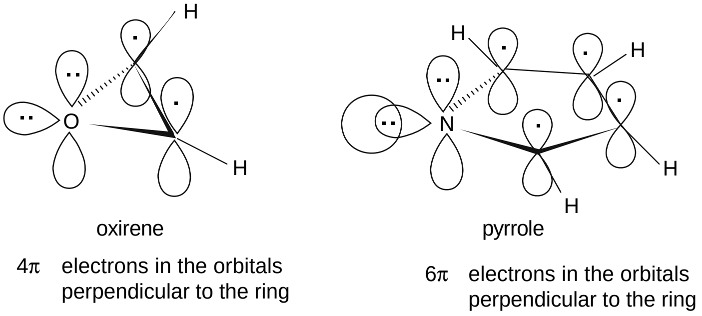


Fig. 3.1 Oxirene has 4π electrons in the atomic orbitals perpendicular to the ring plane, and is thus expected to be antiaromatic; pyrrole, in contrast, with 6 such π electrons, is considered to be aromatic

of rigid plastic, broken models will reinforce one's intuitive grasp of the concept. Strain should by no means be an absolute, or even a very formidable, barrier to the preparation of oxirene: its carbocyclic analogue, cyclopropene [8, 9, 10, 11, 12], has been known for over 80 years and, although it polymerizes at room temperature, is tolerably stable by comparison with many exotic but well-characterized compounds which have been studied by low-temperature (e.g. matrix isolation) techniques [13]. Strain in small rings arises largely from the fact that the geometric angle deviates from the interorbital angle, resulting in poorer overlap, and thus weaker bonds, than would result from end-on overlap, as shown for cyclopropane in Fig. 3.2 [14]. Although it makes the deviation even greater, mixing in some s character gives stronger bonds than would result from using pure p orbitals: an NBO [15, 16, 17, 18] calculation indicates that each carbon of cyclopropane utilizes about 20% s character in each of the two hybrids used to bond to the other ring carbons; this may be compared with a normal tetracoordinate carbon, ideally sp^3 and using orbitals

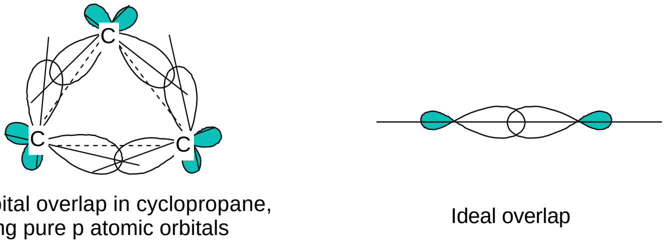
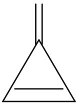


Fig. 3.2 In cyclopropane the ring orbitals cannot overlap end-on, even if pure p atomic orbitals were used, as shown here: the interorbital angle in that best-case scenario would be 90°, while the geometric angle is 60°, a deviation of 30°. In fact, by mixing in some s character stronger bonds are obtained although the deviation from the geometric angle is then even greater; in the limit of sp^3 hybridization, the usual case for tetracoordinate carbon, the interorbital/geometric deviation would be 109° – 60° = 49°

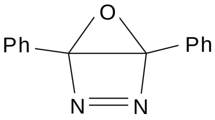
with 25% s character. Cyclopropene is more strained than cyclopropane and thus more reactive, because the two carbons of the double bond ideally splay their hybrid orbitals 120° apart, but in the cycloalkene the geometric angle is 60°, leading to an interorbital/geometric deviation of 120° – 60° = 60°, compared to only 109° – 60° = 49° for cyclopropane (Fig. 3.2). Methylenecyclopropene, with three sp^2 carbons in a three-membered ring, is well-known [19, 20, 21], although there is evidently no clear consensus on its electronic properties [22].



The Oxirene Problem: History

Oxirenes to 1981; Summary

The oxirene literature from earliest times through 1981 has been reviewed in detail [23], so this period will be only briefly summarized here. Early reports of the preparation of oxirenes (oxidation of propyne [24], reaction of an α-chloro ketone with base [25], and epoxidation of 5-decyne [26]) turned out to have been mistaken. The modern phase of oxirene study began with the demonstration by Strausz and coworkers that a species with this symmetry is involved in the decomposition of α-diazo ketones [27, 28] with eventual formation of ketenes (the Wolff rearrangement; Fig. 3.3). Loss of nitrogen gives an oxo carbene ("ketocarbene") which undergoes 1, 2-oxygen switching through a species with the symmetry of an oxirene, but the labeling experiments do not tell if this is an intermediate or merely a transition state. It was claimed that this reaction led to the infrared spectroscopic detection of perfluorinated oxirenes [29]; this is considered later. An extensive matrix-isolation photolysis study of diazo ketones gave no evidence of the detection of oxirenes [30]. Metal-promoted decomposition of α-diazo ketones evidently does not lead to an oxirene species, probably because metal-containing carbenoids rather than free carbenes are involved [31, 32, 33, 34, 35]. Blaustein and Berson addressed the important point that symmetrization might occur prior to loss of nitrogen, for example through a species like a bicylic diazaoxirane; this possibility was excluded by labeling experiments, at least for the diphenyl compound shown [36].



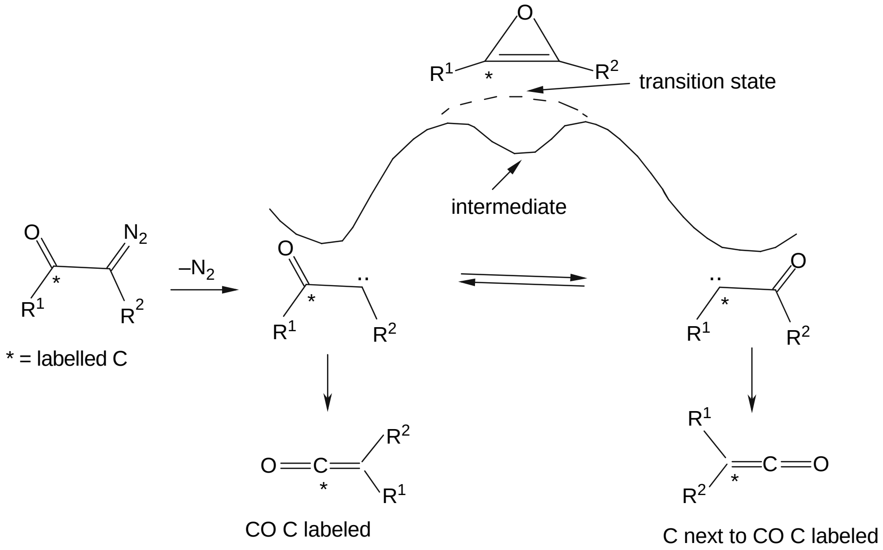


Fig. 3.3 The Wolff rearrangement: formation of a ketene from an α-diazo ketone. Thermal or photochemical decomposition of an α-diazo ketone forms a carbene; labeling shows that the oxygen of the carbene undergoes a 1,2-shift through a symmetrical (or pseudosymmetrical, $R^1 \neq R^2$) oxirene species which may be an intermediate or a transition state. Migration of an R group to the electron-deficient carbon gives a ketene. Metal-promoted decomposition of diazo ketones, which may proceed through metal-containing carbenoids, gives ketenes but apparently does not involve an oxirene species

The standard way of making *oxiranes* (no CC double bond) is by peroxy acid oxidation of alkenes, so the analogous reaction of alkynes would be expected to form oxirenes. The evidence on this point is not definitive. Peroxy acid oxidation of alkynes does indeed yield products which can be interpreted as arising from oxo carbenes, such as ketenes (cf. the Wolff rearrangement, above) and α, β-unsaturated ketones (possibly from a 1, 2-hydrogen shift in a carbene) but the putative carbenes need not arise from oxirenes. For example, peroxy acid oxidation of cyclic alkynes shows intriguing similarities to and differences from the “analogous” diazo ketene reaction, as shown for cyclooctyne in Fig. 3.4 [37]. Suggested explanations were that (1) both types of reactions involve oxo carbenes, but in different conformations and energies, (2) the cycloalkynes form oxirenes which open to carbenes, but the diazo ketones form their products in reactions concerted with loss of nitrogen, (3) the cycloalkynes are oxidized to oxirenes which are trapped intramolecularly without forming carbenes, and (4) either or both types of reaction proceed by more than one mechanism. These alkyne reactions are summarized and discussed in detail elsewhere [38]. In contrast to the ambiguity of product distribution results, kinetic studies of the reaction of 3-chloroperoxybenzoic acid with 3-octyne and with cyclohexene were said, by their similarity of solvent effects, to strongly indicate the formation of an oxirene [39].

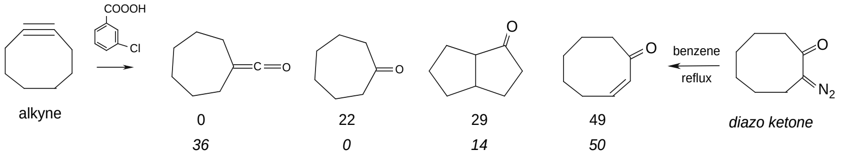


Fig. 3.4 Comparison of peroxy acid oxidation of an alkyne with the “analogous” reaction of a diazo ketone. The relative yields of products from alkyne and from diazo ketone (italics) are shown. The similarities and difference between such reactions has been ascribed to various possibilities (see text)

Besides the carbene isomerization and peroxy acid reactions, another obvious potential route to oxirenes is retrocycloaddition. In principle the heterocycle could be extruded from a formal adduct with a diene (the retro Diels-Alder reaction [40]) or with a CC double bond (a retro [2 + 2] reaction [41]). Because of the high temperatures needed, retro Diels-Alder reactions are actually unrealistic as synthetic routes to oxirenes, but a theoretical study of them can provide useful information (see *Oxirenes After 1981*). The retro Diels-Alder reactions of formal adducts of oxirene and of benzooxirene with a diene should be aided by using a benzene ring to provide the diene moiety, because the activation energy for extrusion of the oxirene should be lowered by the stability of the incipient benzene moiety in the transition state. Compounds **1a** [42] and **2** and **3** [43, 44] on heating largely rearranged to cycloheptatriene derivatives (Fig. 3.5); **3** gave a small amount of ketene, but it is not known if this arises from oxirene, or by prior rearrangement of the epoxide to a ketone. The benzooxirene adduct **4**, a benzene oxide, isomerized by a [1, 5] sigmatropic shift to another benzene oxide [45]. The formal permethyl cyclopentadiene-oxirene adduct **5** (Fig. 3.6) decomposed in the gas chromatograph to the cyclopentadiene and, oddly, 2,3-butanedione; the dione could be an oxidation product of an oxo carbene formed from dimethyl oxirene, but why the carbene should give this rather than dimethylketene is unclear [46].

Much more promising than the retro Diels-Alder reaction for direct observation of oxirenes is a retro [2 + 2] reaction of a formal oxirene-benzene adduct, because these can be effected photochemically; again, the formation of a benzene ring should facilitate the reaction. This approach has, in principle, the great advantage that the photolysis could be conducted at low temperature in a matrix isolation experiment [13], perhaps permitting the observation of the spectra of the oxirene. Warrener and coworkers prepared and photolyzed the very promising-looking **6**, but instead of extruding oxirene, ring-opening to a cyclooctatriene occurred [47] (Fig. 3.7). Attempts to make oxirene under matrix isolation conditions by photochemical extrusion of CO_2 or COS from **7**, **8**, and **9** failed [48]. That **10** is a good source of thiirenes attests to the greater stability of this system compared to the oxirene one [49]. Other attempts to generate oxirenes by reverse cycloaddition, under matrix isolation conditions, failed [50].

Another kind of elimination reaction which could in principle form oxirenes is β-elimination. No systematic study of simple β-elimination of halooxiranes seems

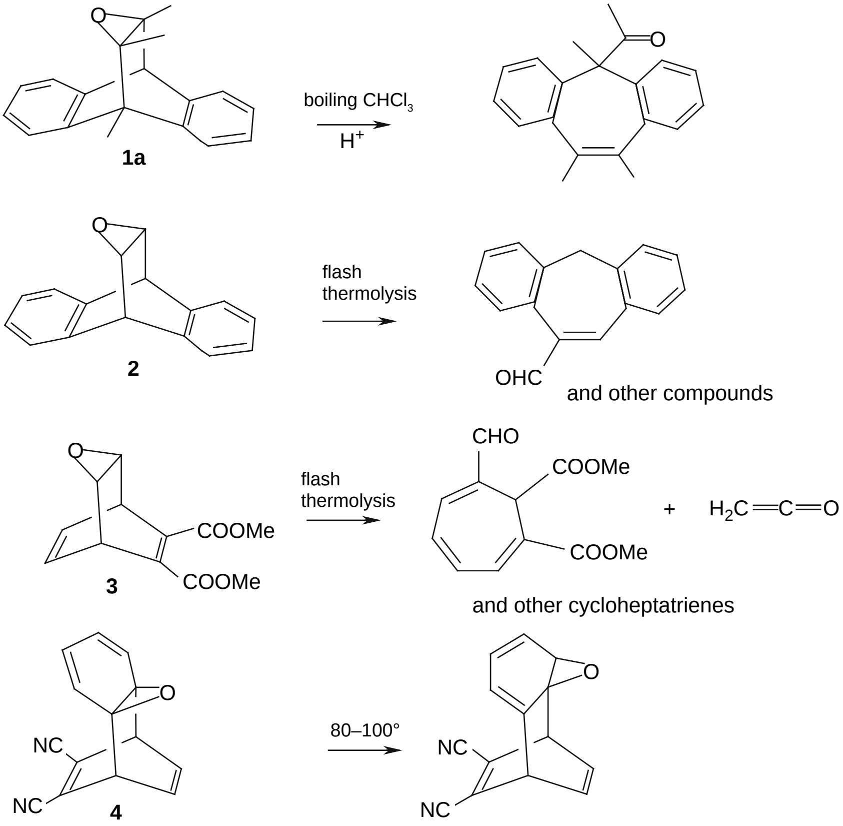
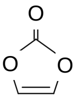


Fig. 3.5 Attempted retro Diels-Alder reactions on formal adducts of an oxirene or benzooxirene with benzene. The adducts prefer to isomerize rather than extrude an oxirene



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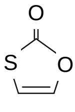

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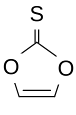

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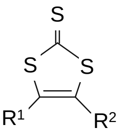

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to have been carried out, but such reactions with nucleophiles usually give products expected from substitution on an isomeric halo ketone [51], and in at least one case a likely oxo carbene-derived product was formed [52]. More propitious for the actual detection of oxirenes than base-induced elimination is Norrish type II elimination, the formation of an alkene by photochemical abstraction of a γ-hydrogen by a ketone carbonyl oxygen followed by cleavage of the resulting 1,4-diradical [53]. The reaction is illustrated (Fig. 3.8) for the ketonyloxirane **11**, the photolysis of which Padwa and coworkers rationalized as proceding through phenyloxirene [54]. Repetition of this experiment under matrix isolation conditions with scrutiny for

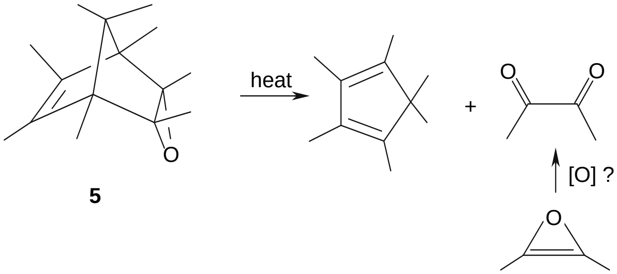


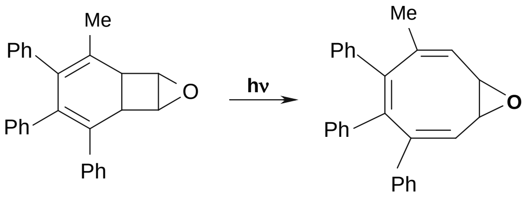
Fig. 3.6 The methylated formal cyclopentadiene-oxirene adduct was reported to decompose in the gas chromatograph to hexamethylcyclopentadiene and 2,3-butanedione. Again, oxirene-diene adducts are reluctant to extrude the heterocycle

infrared bands attributable to the oxirene (below) may be worthwhile, although that the ketonyloxirane **12** (Fig. 3.9) gave enone **13** but no **14** militates against formation of ethylpropyloxirene [55].

A few attempts to test for the involvement of a benzooxirene are outlined in Figs. 3.9 and 3.10. Neither the phenol derivative **15** [56] nor the naphthols **16**/**17** [57] showed evidence of oxygen migration in reactions that may have generated carbenes (Fig. 3.9). Photodecomposition of the labeled diazo ketone **18** gave only ketene **19**, indicating that a benzooxirene did not participate (Fig. 3.10).

The qualitative concepts (above) of strain [1, 2, 3, 4, 5] and antiaromaticity [6, 7] cast light on the reasons for the elusiveness of oxirenes. In principle, the place of oxirene among its molecular siblings C_2H_2O can be illuminated quantitatively by quantum mechanical (QM) calculations. In principle: QM calculations are not infallible oracles, as shown by the contrast between some predictions for oxirene from the earliest calculations and those of later investigations at higher levels of theory. One of the earliest QM studies of oxirene, by Dewar and Ramsden [58], using an early semiempirical method, predicted that the heterocycle is a true intermediate lying 100 kJ mol^{-1} below the oxo carbene, and that this should isomerize to oxirene without a barrier. An early ab initio study gave similar results [59]. More sophisticated ab initio calculations indicated that oxirene is much less stable than these pioneering studies suggested [59]. Although oxirene was predicted to be a true intermediate, it was calculated by Tanaka and Yoshimine [60] in their comprehensive study of the C_2H_2O energy surface to isomerize to ketene with a barrier of only 8 kJ mol^{-1}, with the carbene structure being merely a transition state in this process

Fig. 3.7 Photolysis of the formal benzene-oxirene adduct **6** resulted in ring-opening rather than oxirene extrusion. Formal oxirene adducts are reluctant to extrude the heterocycle



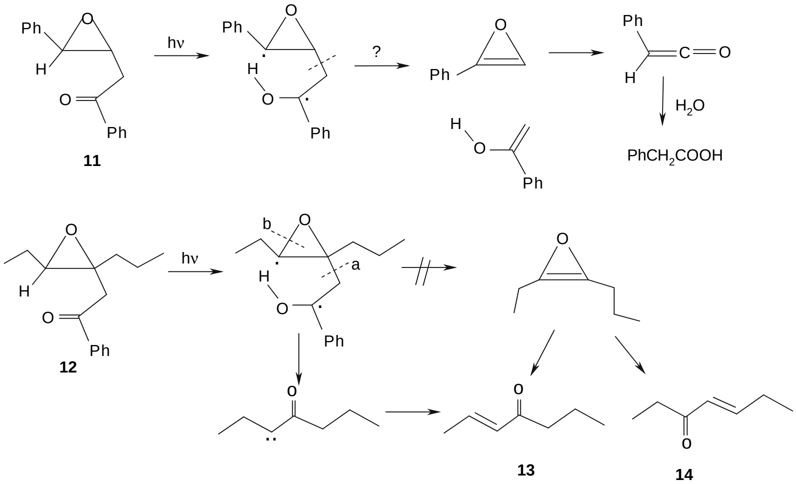


Fig. 3.8 Photolysis of the ketonyl oxirane **11** led to formation of, amongst other products, phenylketene (isolated as the phenylacetic acid). The reaction was rationalized as a Norrish type II process: abstraction of a γ-hydrogen by a ketone carbonyl group, giving a 1,4-diradical which fragments to an alkene (in this case phenyloxirene) and the enol of a ketone. However, photolysis of **12** gave **13**, presumably derived from the oxo carbene, but no **14**, which argues against the (pseudo)symmetrical ethylpropyloxirene and suggests that in the diradical bonds a and b cleave simultaneously

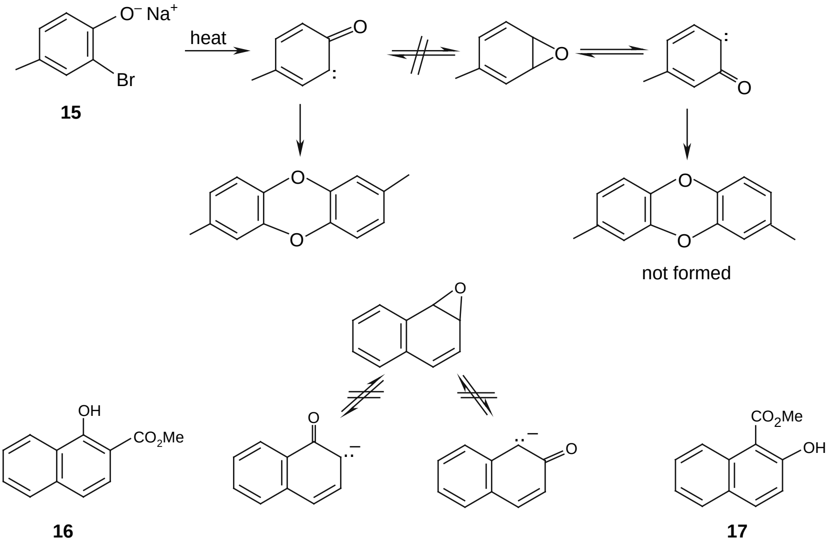


Fig. 3.9 Elimination reactions on phenol derivatives give products which seem to arise from oxo carbenes, but the carbenes do not appear to equilibrate through oxirenes

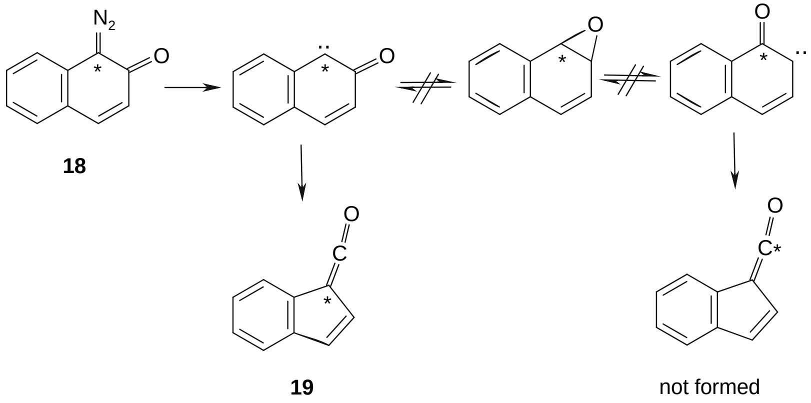


Fig. 3.10 The diazo ketone underwent the Wolff rearrangement, presumably to give initially a carbene, but the position of the isotopic label in the ketene indicated that a species with oxirene symmetry did not intervene

(there is experimental evidence that methanoylcarbene is indeed of very low kinetic stability or even just a transition state [61]). This corresponds to a room temperature halflife of about 10^{-12} seconds [62], only about the time for ten vibrations of a typical bond, a fragility which might challenge even matrix isolation methods. Other ab initio explorations of C_2H_2O isomers gave generally similar results to those of Tanaka and Yoshimine, albeit with somewhat higher, but still low, barriers for rearrangement to the carbene: the Strausz group obtained 31 kJ mol^{-1} [28], and Radom and coworkers reported 32 kJ mol^{-1} [63]. We turn now to more recent developments in oxirene chemistry.

Oxirenes After 1981

This section presents the notable developments in oxirene chemistry since those reported in the 1983 review [23], i.e. since 1981. The radical cation of oxirene was predicted by HF, MP2 and MP3 calculations to be an observable species [64]. This found support in the reported generation of methyloxirene by neutralization-reionization mass spectrometry [65]. Diazoacetone was ionized, generating the methyloxirene radical cation, which was neutralized with mercury atoms to give methyloxirene; this decomposed rapidly to methylketene, 2-propenal and methoxyethyne or 1-propynol (Fig. 3.11). An earlier, similar attempt to demonstrate that the parent oxirene is a true intermediate had failed: the radical cation was generated from vinylene carbonate, oxazole, and isoxazole, but its neutralization provided no sign of an oxirene intermediate [66].

Apart from the neutralization-reionization mass spectrometric study above, there have apparently been only two plausible claims of the observation of oxirenes. The

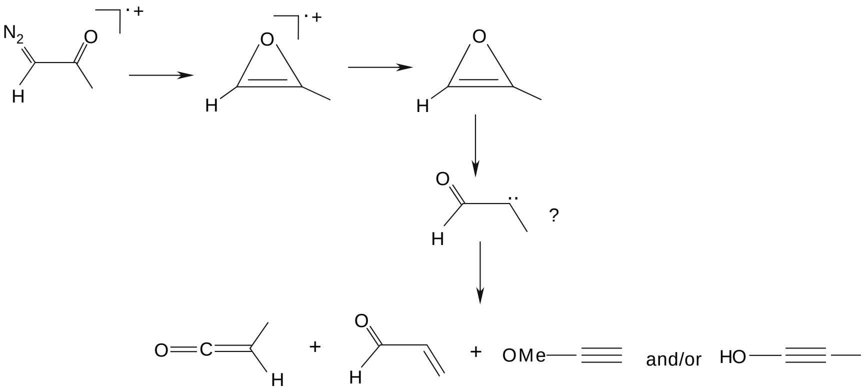


Fig. 3.11 Ionization of diazoacetone in a mass spectrometer evidently gave the radical cation of methyloxirene. The oxirene apparently has a finite lifetime as shown by its neutralization and reionization. The carbene shown is speculative

first was made by Torres et al. in 1983 [29]. They reported the matrix isolation of bis(trifluoromethyl)- and perfluoromethylethyloxirene. The second plausible claim was the reported matrix isolation of dimethyloxirene, by Bachmann et al., in 1990 [67]. These two groups reported bands which they ascribed to the double bond stretch of oxirenes formed by photolysis of diazoketones; the question of the IR spectrum of oxirenes is addressed below in connection with calculations by the author.

On the theoretical front, oxirene has been examined at high computational levels to probe the questions: whether it is a true minimum or only a transition state [68, 69], its role in the Wolff rearrangement [70], and the effects of substituents on its stability [71]. Calculations by the author also shed light on the IR spectrum of oxirenes and their stability [72]. In papers with the vigorous titles “Does oxirene exist?” and “To be or not to be”, the key problem of the kind of species that oxirene is, namely a relative minimum or a transition state (we know that a species with oxirene *symmetry* exists [27, 28]) was attacked straightforwardly [68, 69]. This was done by calculating the IR spectrum and noting whether or not an imaginary frequency was present (relative minima – true molecules – show no imaginary frequencies while transition states have one imaginary frequency [73]). The frequencies were calculated at systematically higher and higher levels; at the highest level, CCSD(T) with a very big basis set, oxirene was still a minimum, but the continued fall in the lowest frequency, corresponding to ring-opening to the oxo carbene, left open the possibility that the species is really a transition state. In closely related work, the role of oxirene in the Wolff rearrangement was examined [70]. The best results predicted that the heterocycle is an intermediate, with a barrier of 2 kJ mol^{-1} separating it from the oxo carbene, which is also an intermediate, separated by a barrier of 21 kJ mol^{-1} from ketene, which lies 325 kJ mol^{-1} below oxirene (Fig. 3.12). However, the accuracy of such calculations leaves open the possibility

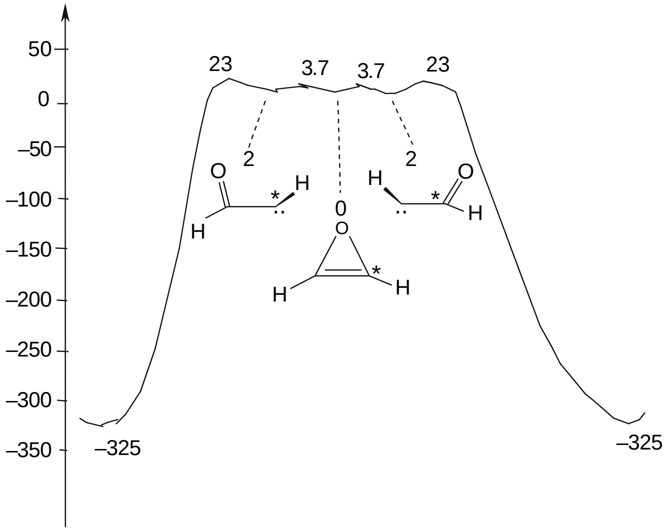


Fig. 3.12 The best results calculated for the species in the Wolff rearrangement, by Scott et al. [70]. The numbers are relative energies in kJ mol^{-1}. The accuracy of the calculations does not rule out the possibility that oxirene is only a transition state connecting equivalent-energy carbenes and scrambling the label, or that the carbene is not really a stationary point (neither a minimum nor a transition state) on the potential energy surface

that oxirene is actually a transition state representing a very small barrier between equivalent-energy carbene structures.

A systematic study of the effect of substituents on oxirene stability was carried out by Fowler et al. [71], who in a "periodic scan" examined the oxirenes XCH(O)CHX with X=BH_2, CH_3, NH_2, and F. They concluded that only dimethyloxirene was clearly a relative minimum (a true molecule); all the others were transition states (with difluorooxirene a possible borderline case). The unique stabilization by the methyl group was ascribed to a subtle effect in which its C–H antibonding orbitals removed electron density from the sigma framework of the ring, raising the frequency of the vibrational mode corresponding to ring opening. Dimethyloxirene should be stabler than the parent oxirene too.

A computational study by the author and coworkers compared the energetics of oxirene extrusion with that of other alkenes, in the generation of alkenes by the retro Diels-Alder reaction [72]; Fig. 3.13 shows the retro Diels-Alder reactions that were studied. That thermal extrusion is not a feasible route to a highly sensitive molecule like oxirene was not in serious doubt; the main value of the calculations lies rather in the information they provide on the stability of oxirene (ancillary calculations, below, also gave useful information on the rearrangement and spectra of oxirene and dimethyloxirene). Comparing bond orders in transition states (TSs) with those in reactants showed that the TS for cyclopropene extrusion was about 74% along the reaction path, while that for oxirene extrusion was about 83% along the way. The later TS for the heterocycle is expected since, other things being equal,

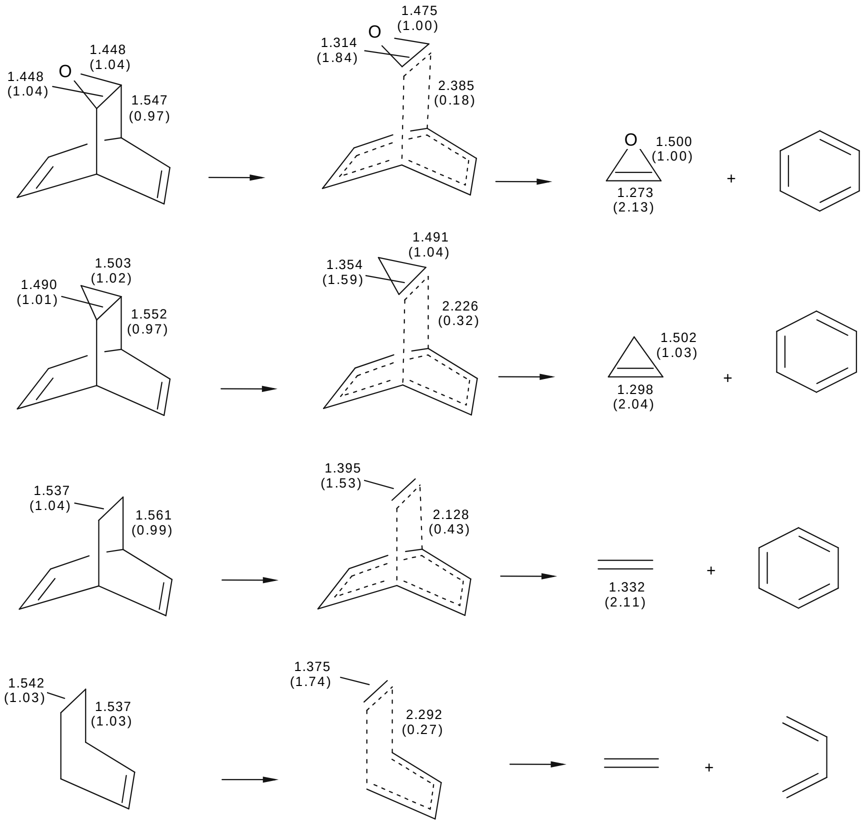


Fig. 3.13 The retro Diels-Alder reaction generating oxirene (and benzene) was compared with analogous reactions for cyclopropene and ethene, and with the prototype retro Diels-Alder reaction [72]. The level is MP2(fc)/6-31G(df, p). Bond lengths (Å) are shown, and in parentheses Löwdin bond orders for HF/3-21G calculations on the MP2(fc)/6-31G(df, p) geometries

it should be harder to expel a higher-energy molecule. Comparing the activation energy of oxirene extrusion with that of cyclopropene extrusion, we concluded that oxirene suffers from an antiaromatic destabilization of 214.2−95.9 = 118 kJ mol^{-1} (Fig. 3.14). This can be compared with the experimental/calculated value of 201–230 kJ mol^{-1} for another icon of antiaromaticity, cyclobutadiene [74], and suggests that in this regard the effect of an oxygen lone pair and a CC double bond is considerably less than that of two CC double bonds. Cyclobutadiene is highly reactive, but in quite a different way than oxirene: it is prone to bimolecular reactions, such as dimerization, while oxirene is “of itself” reactive, isomerizing unimolecularly. A purist in chemical terminology might say that cyclobutadiene is stable but reactive, while oxirene is unstable (to such a degree that its bimolecular reactivity has never been observed!).

Our calculations [72] for the oxirene potential energy surface were at a somewhat lower level (CCSD(T)/6-31G(df, p)//MP2(fc)/6-31D(df, p) cf. CCSD(T)/6-311

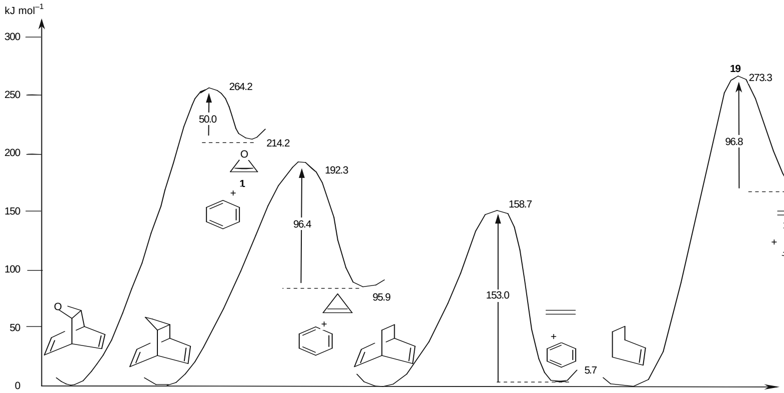


Fig. 3.14 Energetics of the retro Diels-Alder extrusion of oxirene and other alkenes, calculated at the CCSD(T)/6-31G(df, p)//MP2(fc)/6-31G(df, p) level with HF/3-21G ZPE corrections [72]

G(df, p)) than those of Scott et al. on the Wolff rearrangement [70], and allow a comparison of oxirene with dimethyloxirene (Fig. 3.15 cf. Fig. 3.16). For oxirene, the two sets of calculations ([72] cf. [70]) agree that oxirene rearranges with a very small barrier of 1–3 kJ mol^{-1}. Our results, single point CCSD(T) energies on an MP2 potential energy surface, predict direct conversion to ketene with the carbene not being a stationary point, while on the CCSD(T) surface of Scott et al. the carbene, an intermediate 4 kJ mol^{-1} below oxirene, rearranges to ketene with a barrier of 20 kJ mol^{-1}. In fact, soon after the calculations of Scott et al., experiments by Tanigaki and Ebbesen (transient grating spectroscopy, related to flash photolysis, of methanoyldiazomethane, i.e. formyldiazomethane) gave a good indication that the oxo carbene is indeed a detectable intermediate with a halflife of 0.9 ns in dichloromethane solution at room temperature [75, 76]. This corresponds to a barrier of about 22 kJ mol^{-1} [62], essentially the same as calculated in [70]. These flash photolysis experiments are agnostic on the question of the existence of oxirene (earlier flash photolysis work had led to the suggestion that benzooxirenes had been detected [77, 78], but the spectra in question were shown to be due to ketenes [79]). The salient conclusion from the calculations of Scott et al. (note Fig. 3.12) and the experiments of Tanigaki and Ebbesen is that methanoylcarbene is probably a real intermediate in the Wolff rearrangement, and that it is energetically almost indistinguishable (ca. 2 kJ mol^{-1}) from oxirene; the oxirene structure interconverts enantiomeric carbene structures and may be a real intermediate or may be only a transition state, i.e. the central dip in the curve in Fig. 3.12 may or may not represent reality. The notable difference between the MP2 [72] and CCSD(T) [70] potential energy surfaces lies in their curvature near the point representing the carbene: the MP2 surface does not have a stationary point there and oxirene goes to ketene with almost no barrier, while on the CCSD(T) surface the carbene is a relative minimum and it (and thus oxirene, which if it exists is very close in energy to the carbene) goes to ketene with a barrier of about 20 kJ mol^{-1}.

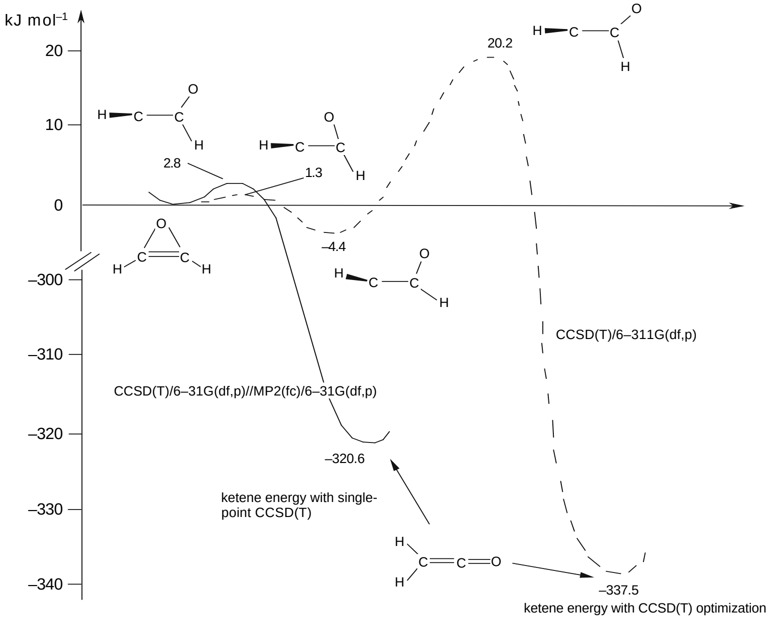


Fig. 3.15 The potential energy surface for the conversion of oxirene to ketene, at two levels, CCSD(T)/6-31G(df, p)//MP2(fc)/6-31G(df, p) (with MP2(fc)/6-31G(df, p) ZPE) [72] and the CCSD(T)/6-311G(df, p) level [70]; cf. Fig. 3.12

The retro Diels-Alder study also included a look at the dimethyloxirene potential energy surface (Fig. 3.16). As expected from the periodic scan work [71], dimethyloxirene is calculated to have a higher barrier (16 kJ mol^{-1}) than the parent oxirene (3 kJ mol^{-1}) for rearrangement (CCSD(T)/6-31G(df, p)//MP2(fc)/ 6-31G(df, p), Fig. 3.16 cf. Fig. 3.15). Unlike the case of methanoylcarbene, acetylmethylcarbene, the oxo carbene from dimethyloxirene was, at our level of calculation (CCSD(T)/6-31G(df, p)//MP2(fc)/6-31D(df, p)), a relative minimum (which mirrors reality [67]), lying 11 kJ mol^{-1} above the oxirene. We were unable to rigorously locate the transition state connecting the oxirene and carbene. Closing the carbene CCO angle stepwise and optimizing each of these structures with the angle fixed gave as the highest point on the “coordinate driving” curve gave a structure only marginally above the oxirene in energy. Coordinate driving is not guaranteed to find a transition state [80], so this activation energy for the carbene-to-oxirene rearrangement is tentative. These correlated ab initio calculations place the carbene 11 kJ mol^{-1} above dimethyloxirene (Fig. 3.16), in contrast to the semiempirical (MNDOC-BWEN) calculations of Bachmann et al. [67], which put the oxirene ca. 29 kJ mol^{-1} above the carbene, with a barrier of ca. 9 kJ mol^{-1} for the isomerization. In agreement with the matrix isolation experiments, methyl migration in the carbene leading to dimethylketene is predicted, surprisingly, to have a lower barrier than hydrogen migration forming (either conformer of) butenone.

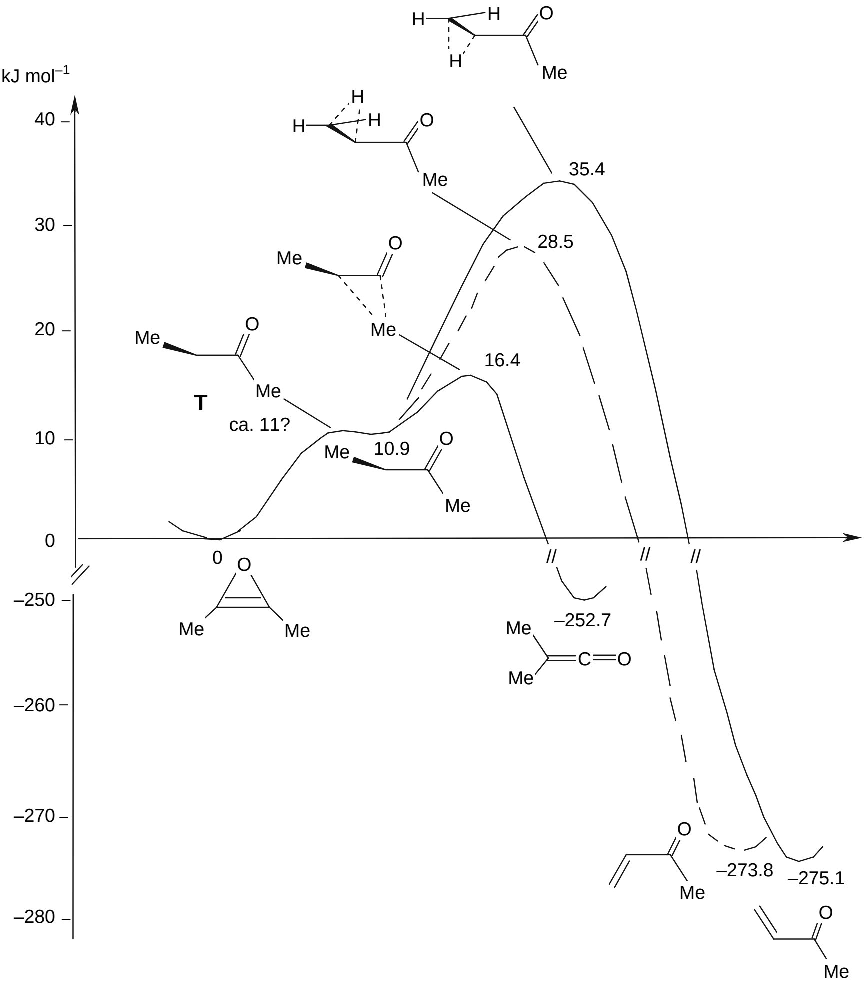
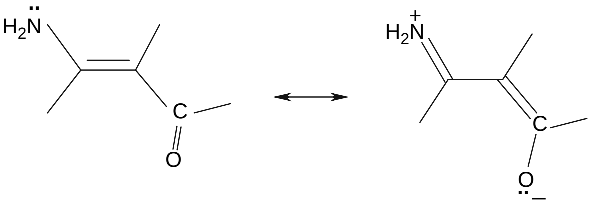


Fig. 3.16 The dimethyloxirene potential energy surface. The level is CCSD(T)/6-31G(df, p)//MP2(fc)/6-31G(df, p) (with MP2(fc)/6-31G(df, p) ZPE), except for the transition state **T**, which is not fully optimized, but was obtained as the maximum-energy point from a series of ring-closings of the carbene CCO angle ("coordinate driving") [72]

A few reports of the observation of the IR spectra of oxirenes prompted us to include in the retro Diels-Alder paper results from our calculations of vibrational frequencies. Bachmann et al. assigned to the CC stretch of dimethyloxirene an IR band at 2137 cm^{-1} and to dimethyloxirene-d_6 a band at 2127.6 cm^{-1}; the putative oxirenes, stable below 25 K, arose from UV irradiation of the undeuterated and the deuterated carbenes from 3-diazo-2-butanone and its deuterated derivative [67]. HF/3-21G calculations on dimethyloxirene and HF/6-31G** calculations on oxirene were said to support these assignments. Our MP2(fc)/6-31G(df, p) frequencies, corrected by a factor of 0.94 [81], are 1974 cm^{-1} and 1969 cm^{-1} for dimethyloxirene and dimethyloxirene-d_6, respectively. Both observed bands are thus ca. 160 cm^{-1} higher than for our calculated CC stretch; this is outside the expected maximum discrepancy of about 50–100 cm^{-1}. One might conjecture that the 2127.6 cm^{-1} band of the deuterated species could actually be due to a CD, rather than CC, stretch of dimethyloxirene-d_6, since in our calculated spectrum the second-strongest band (relative strength 49%) is due to a CD stretch appearing at 2108 cm^{-1}; however, the calculated IR spectrum of undeuterated dimethyloxirene shows no bands near 2137 cm^{-1}. Furthermore, because of symmetry, both CC stretches should be very weak or undetectable. It may be worth noting that dimethylketene in an argon matrix shows one or more bands (varying in position with the matrix sites in which it is trapped) at ca. 2130–2119 cm^{-1} [82]; my HF/6-31G* and B3LYP/6-31G* calculations gave 2115 and 2207 cm^{-1}, respectively, as the corrected [81] wavenumbers for the only prominent band of dimethylketene.

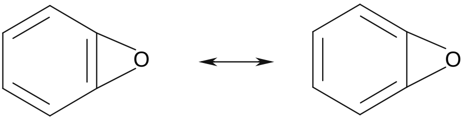
The first plausible claim of the preparation of oxirenes was the report by Torres et al. of the observation of IR bands attributed to perfluroalkyloxirenes when the appropriate diazoketones were irradiated under matrix isolation conditions [29]. The spectrum attributed to bis(trifluoromethyl)oxirene (perfluorodimethyloxirene) was reported in somewhat greater detail than that assigned to perfluoroethylmethyloxirene. For bis(trifluoromethyl)oxirene, at the MP2(fc)/6-31G* level (we used the smaller basis set on the relatively large perfluoro molecule after confirming that the calculated IR spectra of oxirene and dimethyloxirene changed little on going from the MP2(fc)/6-31G(df, p) to the MP2(fc)/6-31G* levels), there was no band reasonably corresponding to the observed 1325 cm^{-1} band. These results with dimethyloxirene and the perfluoalkyloxirenes lead us to conclude that the isolation of an oxirene has not yet been clearly demonstrated.

Besides oxirene and dimethyloxirene, the author investigated the potential energy surfaces of fluorooxirene, the amino/aldehydo push-pull oxirene, and a series of benzooxirenes. As part of a survey of the C_2F_2O potential energy surface, fluorooxirene (CCSD(T)/6-31G(df, p)//MP2(fc)/6-31G(df, p) level) was found to be merely a transition state connecting enantiomeric F–C–CFO carbenes [83], in agreement with the periodic scan results of Fowler et al. [71]. The push-pull concept has been widely investigated [84, 85, 86, 87]; the idea is that an electron-donating group (an electron source) on one end of a double bond and an electron-donating group (an electron sink) on the other end should lower the electron density in the bond, making it more like a single bond, for example:



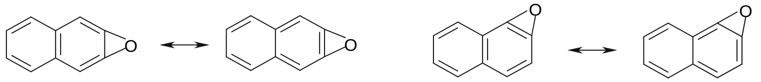
Consequences of this include, at least potentially, a high dipole moment and a reduced barrier to rotation around the double bond. One might expect that a push-pull oxirene would be stabilized relative to the parent by virtue of the diminished electron density in the double bond: antiaromatic destabilization in the oxirene system arises from the presence of four π-electrons, and the shift toward two π-electrons implied by the dipolar resonance structure should correspond to less instability. With this in mind, an oxirene substituted with the amino and methanoyl (formyl) groups was studied [88]. The calculational level was relatively low; in particular, the stabilizing effect of *f* functions on oxirenes was not then realized [68, 69, 70, 71]. Nevertheless, the results do suggest the lack of a stabilizing effect: as the theoretical level was improved, the push-pull oxirene went from being a minimum (semiempirical AM1), to an inflection point (HF/3-21G) to a mere transition state (HF/6-31G* and MP2(fc)/6-31G*). Repetition of this work at a higher level may be worthwhile.

Apart from substitution with discrete groups, oxirenes might potentially be stabilized by fusion to a benzenoid ring, as in benzooxirene; delocalization of the π-electrons of benzene should stabilize the oxirene moiety by diminishing the double bond character in that ring (cf. the rationale for stabilization of push-pull oxirenes, above):



Benzooxirene was found to be a true intermediate at the MP2(full)/6-31G* level [89]. This probably reflects reality since his level appears to *underestimate* the stability of oxirenes – it predicted the parent oxirene to be a transition state and the dimethyl derivative to be a relative minimum, whereas at a considerably higher computational level [71] the parent, like dimethyloxirene, is a relative minimum. On the QCISD(T)/6-31G*//MP2(full)/6-31G* potential energy surface the relative energies of benzooxirene, the transition state for its opening to the oxo carbene, and the carbene were 0, 24.6, and -17.8 kJ mol^{-1}; one might however be inclined to put more quantitative trust in calculations by the CCSD(T) method using a basis set with *f* functions, as was done for the Wolff rearrangement [70]. The molecule is evidently slightly nonplanar, which is not unexpected for a bicyclo[m.n.o]alkene [90].

Calculations comparing the benzooxirenes **20**–**24** (Fig. 3.17) revealed an interesting pattern of reactivity [91]. The rationale behind this study was that higher benzooxirenes, derived from naphthalene, anthracene, etc., can have the oxirene ring fused on linearly or angularly, as shown here for naphthalene: the tendency to maintain the maximum amount of benzenoid character should make the linear systems have dimethyleneoxirane, rather than oxirene, character, while the converse should be the case for the angularly fused molecules:



This hypothesis was tested by calculating the bond orders in **20–24**, and by comparing the activation energies for the transformation of each of the five oxirenes into the oxo carbenes (the subsequent conversion of the carbenes into ketenes was also examined). Briefly: the linear molecules **21** and **23** have bond orders of about 1.2 for the “oxirene” ring CC bond, and the angular molecules **22** and **24** have oxirene ring CC bond orders of about 1.65 (benzooxirene itself showed an “oxirene” CC bond order of 1.35). Thus to a first, rough, approximation, in the linear molecules the three-membered ring is an oxirane and in the angular molecules it is an oxirene. The calculated activation energies (by a DFT method that with oxirene itself gave a barrier similar to that reported [70] for CCSD(T)/6-311G(df, p) calculations) reinforce these conclusions: the linear systems, which are not “really”

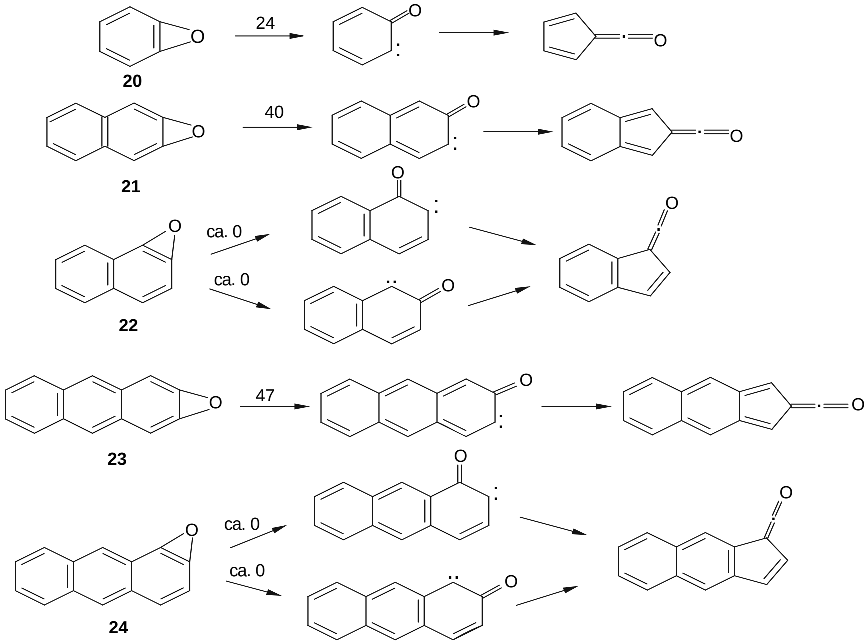


Fig. 3.17 The reactivity of a series of benzooxirenes was studied by semiempirical, ab initio and DFT methods [91]. The numbers over the arrows are the activation energies (kJ mol^{-1}) for conversion to the oxo carbenes, calculated by a DFT method. **21**–**24** are drawn with a resonance form that maximizes the number of benzenoid rings; this forces the formal oxirene rings to be formally dimethyleneoxirane moieties in the linear **21** and **23**, and oxirene moieties in the angular **22** and **24**. Comparing the linear with the angular molecules, former have much higher calculated barriers to rearrangement

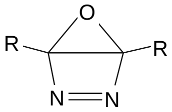
oxirenes, have much higher calculated barriers to rearrangement. Purely empirically, the barriers were linearly correlated with the oxirene bond orders, and using this, extrapolation gave a barrier of ca. 50 kJ mol^{-1} for tetracene, which seems to be the limit in the series. This is probably not high enough for isolation at room temperature,[2] but the compound should be readily observable by matrix isolation, and perhaps even less extreme low-temperature methods.

In an ab initio study of the reaction of triplet oxygen atoms with ethyne oxirene was not considered [92], but a theoretical study of the reaction of singlet and triplet oxygen atoms with ethyne suggested that triplet oxirene might be "stable" compared to the singlet [93]. The reaction of ozone with ethyne was examined by ab initio methods and concluded to be "very complicated" with oxirene possibly being formed from the oxo carbene but, because of its facile reversion to the carbene, being only of peripheral mechanistic interest here [94].

On the experimental front, photolysis of an ozone/2-butyne mixture in an argon matrix was said to give no spectroscopic evidence for the formation of dimethyloxirene [82] (it was concluded, with the aid of ab initio calculations, that triplet oxygen atoms reacted to form species which quickly undergo spin flipping to singlet intermediates). However, in view of questions about the IR spectrum of dimethyloxirene (above), it would be worthwhile to reexamine these spectra.

Synthesis

The isolation of a simple oxirene, such as the parent or the dimethyl derivative, will clearly require matrix isolation techniques, and in this connection the most promising method for characterization is IR spectroscopy. Such a study should be preceded by an as definitive as possible calculation of the IR spectrum of the target oxirene, and the experiments on photolysis of diazoketones [29, 30, 67], vinylene carbonates and related compounds [48], ozone/butyne [82], and perhaps Norrish type II reactions of oxiranyl ketones [53] should be reexamined in this light. It is hard, however, to avoid the feeling that some new route to the oxirene system may be needed to create this photochemically in a reasonably clean manner, simplifying its spectroscopic identification. One possibility is the 2, 3-diaza-5-oxa-bicyclo[2.1.0]pent-2-ene system (cf. [36]), the synthetic realization of which may itself be no trivial matter.



Because oxirene itself hovers on the edge of reality and may even be a mere transition state, efforts to unambiguously characterize an oxirene should first be directed at dimethyloxirene, which has been convincingly shown to very likely isolable in principle.

Conclusions

Labeling experiments show that oxirene species (transition states and/or intermediates) are almost certainly involved in the photochemical and some thermal reactions of diazo ketones, reactions which lead ultimately to ketenes (the Wolff rearrangement). The key species is either a transition state which rearranges by ring-opening to an oxo carbene with a barrier of no more than a few kJ mol^{-1}, or even just a transition state. Methyloxirene, but not, under these conditions, oxirene, has been reported to have been detected by neutralization-reionization mass spectrometry. Reliable calculations indicate that dimethyloxirene is probably a genuine intermediate with a significant barrier to rearrangement, but this author has reservations about the reported matrix isolation IR spectrum of this molecule. The IR detection of perfluoroalkyloxirenes from diazo ketone photolysis in matrix isolation experiments has been reported, but disagreements with the calculated spectra make these attributions, too, questionable. Unambiguous spectroscopic observation of an oxirene will require a definitive calculated spectrum (probably IR) for comparison with an observed spectrum. Some new precursor to oxirenes may be needed for the clean and clear generation of the system, probably photochemically in a cryogenic matrix.

Notes

1. D. Hellwinkel, "Systematic Nomenclature of Organic Chemistry", Springer, New York, 2001. Note that Chemical Abstracts names for *oxiranes* (no CC double bond) sometimes end in -oxirene, e.g. 1a,9a-dihydro-1a,9b-diphenylphenanthro[9,10-*b*]oxirene, for (using standard numbering) 9,10-diphenylphenanthrene-9,10-oxide.
2. Some barriers/room temperature halflives for unimolecular reactions: (a) Decomposition of pentazole and its conjugate base: 75 kJ mol^{-1}/10 minutes and 106 kJ mol^{-1}/2 days, respectively. V. Benin, P. Kaszynski, J. G. Radziszki, J. Org. Chem., 2002, *67*, 1354. (b) Decomposition of $(CF_3CO)OOO(COCF_3)$: 86.5 kJ mol^{-1}/1 minute. S. v. Ahsen, P. Garciá, H. Willner, M. B. Paci, G. Argüello, Chem. Eur. J., 2003, *9*, 5135. (c) Isomerization of (*E*)-cycloheptene to (*Z*)-cycloheptene: 71 kJ mol^{-1}/tens of seconds, Y. Inoue, T. Ueoka, T. Hakushi, J. Chem. Soc., Perkin Trans. 2, 1983, 983.

References

1. "Advances in Strained and Interesting Organic Molecules", B. Halton, ed., JAI Press, Stamford, Connecticut, 2000; vol. 8.
2. W. Sander, Angew. Chem. Int. Ed. Engl., 1994, *33*, 1455.
3. Chem. Rev., 1989, *89*(5), whole issue.
4. K. Wiberg, Angew. Chem. Int. Ed. Engl., 1986, *25*, 312.
5. J. F. Liebman, A. Greenberg, Chem. Rev., 1976, *76*, 311.
6. P. v. R. Schleyer, Chem. Rev., 2001, *101*, 1115.
7. A. de Meijere, R. Haag, F.-M. Schüngel, S. I. Kozhushkov, I. Emme, Pure Appl. Chem., 1999, *71*, 253.
8. N. Ya Dem'yanov, M. N. Doyarenko, Bull. Acad. Sci. Russ., 1922, *16*, 297.
9. M. J. Dem'yanov, M. Dojarenko, Ber., 1923, *56*, 2200.

10. M. J. Schlatter, J. Am. Chem. Soc., 1941, *63*, 1733.
11. K. B. Wiberg, W. J. Bartley, J. Am. Chem. Soc., 1960, *82*, 6375.
12. W. M. Stigliani, V. W. Laurie, J. C. Li, J. Chem. Phys., 1975, *62*, 1890.
13. R. S. Sheridan, Org. Photochem., 1987, *8*, 159.
14. F. A. Carey, R. J. Sundberg, “Advanced Organic Chemistry”, Fourth Edn., Kluwer, New York, 2000; pp. 405–416.
15. E. D. Glendenning, A. E. Reed, J. E. Carpenter, F. Weinhold, J. P. Foster, NBO Version 3.1(as implemented in Gaussian 03).
16. J. P. Foster, F. Weinhold, J. Am. Chem. Soc., 1980, *102*, 7211.
17. A. E. Reed, F. Weinhold, J. Chem. Phys., 1983, *78*, 4066.
18. A. E. Reed, R. B. Weinstock, F. Weinhold, J. Chem. Phys., 1985, *83*, 735.
19. S. W. Staley, T. D. Norden, J. Am. Chem. Soc., 1984, *106*, 3699.
20. W. E. Billups, L.-J. Lin, E. W. Casserly, J. Am. Chem. Soc., 1984, *106*, 3698.
21. G. Maier, M. Hoppe, K. Lanz, P. Reisenauer, Tetrahedron Lett., 1984, *25*, 5645.
22. P. Burk, J.-L. Abboud, I. A. Koppel, J. Phys. Chem., 1996, *100*, 6992and refs. 21, 22, 26, 29–33 therein.
23. E. Lewars, Chem. Rev., 1983, *83*, 519.
24. M. Berthelot, Bull. Soc. Chim. Fr., 1870, *14*, 113.
25. W. Madelung, M. E. Oberwegner, Liebigs Ann. Chem., 1931, *490*, 201.
26. H. Schubach, V. Franzen, Liebigs Ann. Chem., 1952, *557*, 60.
27. O. P. Strausz, I. G. Csizmadia, J. Font, J. Am. Chem. Soc., 1968, *90*, 7360.
28. M. Torres, E. M. Lown, H. E. Gunning, O. P. Strausz, Pure Appl. Chem., 1980, *52*, 1623.
29. M. Torres, J. L. Bourdelande, A. Clement, O. P. Strausz, J. Am. Chem. Soc., 1983, *105*, 1698.
30. G. Maier, H. P. Reisenauer, T. Sayraç, Chem. Ber., 1982, *115*, 2192.
31. S. A. Matlin, P. G. Sammes, J. Chem. Soc., Perkin Trans. 1, 1973, 2851.
32. S. A. Matlin, P. G. Sammes, J. Chem. Soc., Perkin Trans. 1, 1972, 2623.
33. S. A. Matlin, P. G. Sammes, J. Chem. Soc., Chem. Commun., 1972, (1), 11.
34. U. Timm, K.-P. Zeller, Chem. Ber., 1978, *111*, 1549.
35. H. Okuno, S. Kondo, Y. Izawa, J. Am. Chem. Soc., 1980, *102*, 7123.
36. M. A. Blaustein, J. A. Berson, Tetrahedron Lett., 1981, *22*, 1081.
37. P. Concannon, J. Ciabattoni, J. Am. Chem. Soc., 1973, *95*, 3284.
38. E. Lewars, Chem. Rev., 1983, *83*, 519, 521–525.
39. K. Ibne Rasa, Y. H. Pater, J. Ciabattoni, J. O. Edwards, J. Am. Chem. Soc., 1973, *95*, 7894.
40. H. Kwart, K. King, Chem. Rev., 1968, *68*, 415.
41. R. N. Warrener, E. E. Nunn, M. N. Paddon-Row, Aust. J. Chem., 1979, *32*, 2659.
42. H. Hart, J. B.-C. Jiang, M. Sasoka, J. Org. Chem., 1977, *42*, 3840.
43. E. G. Lewars, G. Morrison, Can. J. Chem., 1977, *55*, 966.
44. E. G. Lewars, G. Morrison, Can. J. Chem., 1977, *55*, 975.
45. F.-G. Klärner, E. Vogel, Angew. Chem., Int. Ed. Engl., 1973, *12*, 840.
46. H. Hart, S.-M. Chen, Tetrahedron Lett., 1975, (28), 2363.
47. R. N. Warrener, R. A. Russell, R. Y. S. Tan, Aust. J. Chem., 1981, *34*, 855.
48. M. Torres, A. Clement, O. P. Strausz, J. Org. Chem., 1980, *45*, 2271.
49. M. Torres, A. Clement, H. E. Gunning, O. P. Strausz, Nouv. J. Chem., 1979, *3*, 149.
50. G. Maier, T. Sayraç, H. P. Reisenauer, Chem. Ber., 1982, *115*, 2202.
51. C. Herzig, J. Gasteiger, Chem. Ber., 1982, *115*, 601, especially ref. 20 therein.
52. R. N. McDonald, R. N. Steppel, R. C. Cousins, J. Org. Chem., 1975, *40*, 1694.
53. P. J. Wagner “CRC Handbook of Organic Photochemistry and Photobiology”, C. R. C., Boca Raton, FL, 1995; p. 449.
54. A. Padwa, D. Crumrine, R. Hartman, R. Layton, J. Am. Chem. Soc., 1967, *89*, 4435.
55. R. A. Cormier, Tetrahedron Lett., 1980, *21*, 2021.
56. J. I. G. Cadogan, J. T. Sharp, M. J. Trattles, J. Chem. Soc., Chem. Commun., 1974, (21), 900.
57. H. F. Gruetzmacher, J. Huebner, Liebigs Ann. Chem., 1971, *748*, 154.
58. M. J. S. Dewar, C. A. Ramsden, J. Chem. Soc. Chem. Commun., 1973, (18), 688.

59. A. C. Hopkinson, J. Chem. Soc., Perkin Trans. 2, 1973, 794.
60. K. Tanaka, M. Yoshimine, J. Am. Chem. Soc., 1980, *102*, 7655.
61. A. Krantz, J. Chem. Soc., Chem. Commun., 1973, (18), 670.
62. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; p. 284.
63. W. J. Bouma, R. H. Nobes, L. Radom, C. E. Woodward, J. Org. Chem., 1982, *47*, 1869.
64. W. J. Bouma, P. M. W. Gill, L. Radom, Org. Mass. Spectrom., 1984, *19*, 610.
65. F. Turacek, D. E. Drinkwater, F. W. McLafferty, J. Am. Chem. Soc., 1991, *113*, 5958.
66. C. E. C. A. Hop, J. L. Holmes, J. K. Terlouw, J. Am. Chem. Soc., 1989, *111*, 441.
67. C. Bachmann, Y. N’Guessan, F. Debû, M. Monnier, J. Pourcin, J.-P. Aycard, H. Bodot, J. Am. Chem. Soc., 1990, *112*, 7488.
68. G. Vacek, J. M. Galbraith, Y. Yamaguchi, H. F. Schaefer, R. H. Nobes, A. P. Scott, L. Radom, J. Phys. Chem., 1994, *98*, 8660.
69. G. Vacek, B. T. Colegrove, H. F. Schaefer, Chem. Phys. Lett., 1991, *177*, 468.
70. A. P. Scott, R. H. Nobes, H. F. Schaefer, L. Radom, J. Am. Chem. Soc., 1994, *116*, 10159.
71. J. E. Fowler, J. M. Galbraith, G. Vacek, H. F. Schaefer, J. Am. Chem. Soc., 1994, *116*, 9311.
72. C. Delamere, C. Jakins, E. Lewars, Can. J. Chem., 2002, *80*, 94.
73. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 2.
74. A. A. Deniz, K. S. Peters, G. J. Snyder, Science, 1999, *286*, 1119.
75. J. P. Toscano, M. S. Platz, V. Nicolaev, Y. Cao, M. B. Zimmt, J. Am. Chem. Soc., 1996, *118*, 3527.
76. J. P. Toscano, M. S. Platz, V. Nicolaev, J. Am. Chem. Soc., 1995, *117*, 4712.
77. K. Tanigaki, T. W. Ebbesen, J. Phys. Chem., 1989, *93*, 4531.
78. K. Tanigaki, T. W. Ebbesen, J. Am. Chem. Soc., 1987, *109*, 5883.
79. J. Andaos, Y. Chiang, C.-G. Huang, A. J. Kresge, J. C. Sciano, J. Am. Chem. Soc., 1993, *115*, 10605.
80. S. S. Shaik, H. B. Schlegel, S. Wolfe, “Theoretical Aspects of Physical Organic Chemistry”, Wiley, New York, 1992; pp. 73–75.
81. A. P. Scott, L. Radom, J. Phys. Chem., 1996, *100*, 16502.
82. J. K. Parker, S. R. Davis, J. Phys. Chem. A, 1999, *103*, 7280.
83. E. Lewars, J. Mol. Struct. (Theochem), 2002, *579*, 155.
84. A. Forni, R. Destro, Chem. Eur. J., 2003, *9*, 5528.
85. C. F. Bernasconi, M. Ali, J. C. Gunter, J. Am. Chem. Soc., 2003, *125*, 151.
86. I. Alkorta, C. Wentrup, J. Elguero, J. Mol. Struct. (Theochem), 2003, *585*, 27.
87. R. Benassi, C. Bertarini, E. Kleinpeter, F. Taddei, S. Thomas, J. Mol. Struct. (Theochem), 2003, *498*, 201.
88. E. Lewars, J. Mol. Struct. (Theochem), 1997, *391*, 39.
89. E. Lewars, J. Mol. Struct. (Theochem), 1996, *360*, 67.
90. H.-V. Wagner, G. Szeimies, J. Chandrasekhar, P. v. R. Schleyer, J. A. Pople, J. S. Binkley, J. Am. Chem. Soc., 1978, *100*, 1210.
91. E. Lewars, Can. J. Chem., 2000, *78*, 297.
92. B. S. Jursic, J. Phys. Chem. A, 1999, *103*, 5773.
93. Y. Girard, P. Chaquin, J. Phys. Chem. A, 2003, *107*, 10462.
94. D. Cremer, R. Crehuet, J. Anglada, J. Am. Chem. Soc., 2001, *123*, 6127.

Chapter 4
Nitrogen Pentafluoride and Related Compounds

Introduction

Between nitrogen pentafluoride and related species, and the helium compounds of Chapter 5, there is is a curious link, beyond the fact that both species are experimentally unknown: the two classes appear to violate a cherished valence rule. The octet rule, which supposedly summarizes the appetite for electrons of atoms of the first full row of the periodic table (“first-row atoms” to computational chemists), decrees that the elements from lithium to neon cannot have more than eight electrons in their valence shells. Hydrogen and helium might be said to be subject to an analogous, duplet, rule, stating that their valence shells are limited to two electrons. Yet plausible computations indicate that compounds can exist which appear to defy these rules. In this chapter we examine molecules in which nitrogen and some nearby elements formally violate the octet rule, and consider whether this transgression is real.

Molecules that seem to violate the octet (or duplet) rule are *hypercoordinate,* because the “central” atom is bonded to an unconventionally high number of “ligands”. The simplest hypercoordinate, neutral, even-electron compounds of the first full row can be conceptually obtained by adding a hydrogen molecule to the normal hydrides (Fig. 4.1). Let us examine a related molecule which has substantially weathered *in silico* the tests that have been applied to its putative existence, namely nitrogen pentafluoride.

Nitrogen Pentafluoride, the Octet Rule, and Hypervalency

The only reason why the hypothetical NF_5 is fascinating is because it seems to violate the octet rule. The idea of a connection between chemical properties and the number eight goes back to Mendeleev’s periodic table of 1869 and even to its tentative precursors [1], but the modern formulation of the rule apparently began with Abegg’s realization that eight electrons in the outer shell of an atom in a compound constitutes a particularly stable arrangement [2, 3]. The rule was recognized in much

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_4,

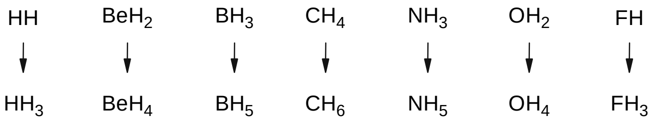
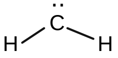


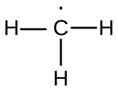
Fig. 4.1 The simplest neutral, even-electron hypercoordinate first-row molecules can be considered to result from combining a normal hydride with a hydrogen molecule

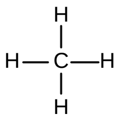
the modern form by G. N. Lewis, at least by 1902 (initially couched in a quaint – to our eyes – cubic geometrical format), but not published until 1916 [4, 5, 6]. The contemporaneously-published but less-well-known work of Kossel invokes a "rule of eight" in which ionic compounds are formed by atoms losing or gaining electrons to achieve an octet [7]. The word *octet* in connection with the special stability this number of electrons bestows may have been first used by Langmuir [8], who explicitly discussed ionic ("electrovalent") and "covalent" bonding. Langmuir clearly states the octet rule as we now understand it: "In the column marked *S* is given the maximum number of pairs of electrons which an atom is capable of sharing with a single other atom [3 pairs for N]" (p. 927 of [8]) and asserts that "in the second short period...the maximum covalence remains constant at 4" (p. 928 of [8]); on this same page he makes it clear that for bonding to an element like fluorine the "covalence" is the same as the coordination number. Lewis did not take kindly to the publicizing by Langmuir of a theory which he, Lewis, regarded as essentially his own [9].

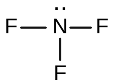
Did chemists regard as sacrosanct the stricture against the presence of more than eight electrons in the valence shell of the atoms lithium to neon? Certainly in 1923 Lewis did not so regard it: "When I claimed that nitrogen is never more than quadrivalent I did not mean to deny the theoretical possibility of a compound such as NF_5...What I maintained...is that in any compound now known the nitrogen atom is never attached to more than four bonds." (p. 111 of [5]). We shall see that Lewis crafted better than he knew: even for NF_5, if it can be made, the octet rule will evidently not be violated (!), which brings us to the term hypervalency.

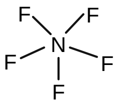
A hypervalent compound is typically considered to be one in which the "central" atom has in its valence shell more than eight valence electrons, as in NF_5 or the known PF_5 and SF_6, which appear to have 10, 10, and 12 electrons, respectively, in their valence shells [10]. The valence of an atom may reasonably be taken as the number of electrons it uses in bonding, as expressed in a Lewis structure. Thus carbon in CH_2, CH_3 and CH_4 is taken, uncontroversially, to be di-, tri- and tetravalent, respectively. Nitrogen in NF_3 is trivalent, and in NF_5 would be pentavalent, according to simple Lewis structures:











Note that there is no question that NF_5 is hypercoordinate, but whether it really is hypervalent is linked to the question of octet rule violation (in the Lewis structure shown nitrogen has ten electrons in its valence shell). To appreciate the theoretical the basis of the octet rule, and to understand its (real or apparent) violations, we take a look at quantum chemistry, which exposes its underlying basis and indicates two possible ways to transcend its limitations. To review a standard elementary picture of bond formation: an atom like nitrogen has available for bonding one 2s and three 2p orbitals. These four atomic orbitals can be mixed (hybridized) by linearly combining their wavefunctions, a mathematical artifice that may sometimes be convenient but does not represent a real physical process and is never essential [11]; the result is four hybrid sp^3 orbitals tetrahedrally arrayed. Since in this scheme only four atomic orbitals are available for bonding, the maximum number of atoms that can bond covalently to nitrogen should be four; if each of the atoms bonding to nitrogen contributes one electron, as does a fluorine atom, the maximum number is three (Fig. 4.2). The two possible ways to exceed a coordination number of four for nitrogen (or another second-row atom) are (1) to expand the octet by drawing on atomic orbitals beyond the 2s and 2p class, (2) a subtle approach: using eight electrons to do the work of ten.

Expanding the octet with d atomic orbitals. For elements of the second full period, like silicon and sulfur, the formation of pentacoordinate and hexacoordinate species

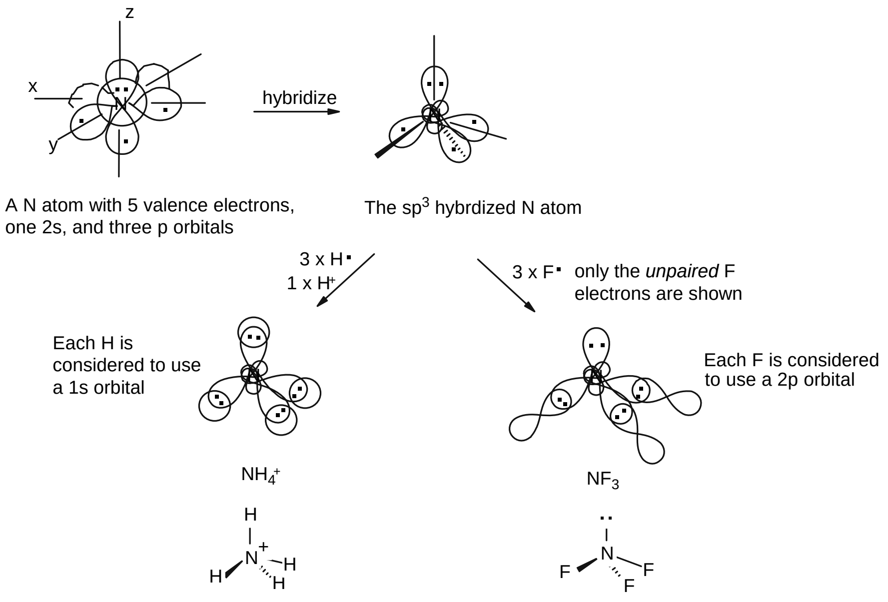


Fig. 4.2 Conventional model of the formation of tetracoordinate and tricoordinate molecules by nitrogen. One 2s and three 2p orbitals give four sp^3 orbitals which, with eight electrons, create four or three (with an electron pair left over as a lone pair) conventional (two-center, two-electron) bonds

like SiF_5^- and SF_6 was long explained by invoking the participation of 3d orbitals, an approach which originated with Pauling [12]. Hybridizing one 3d orbital of appropriate symmetry with three 2p and one 2s orbital supposedly provides five sp^3d orbitals which are disposed in a trigonal bipyramidal geometry; with the five valence electrons of nitrogen and five electrons provided by five fluorine atoms (each using, say, a 2p orbital to bond), we have 5 atomic orbitals on nitrogen and ten electrons to place in them, so five two-center, two-electron (2c-2e) bonds, i.e. five conventional bonds, are formed, in this model (Fig. 4.3). In this model nitrogen violates the octet rule and is pentavalent.

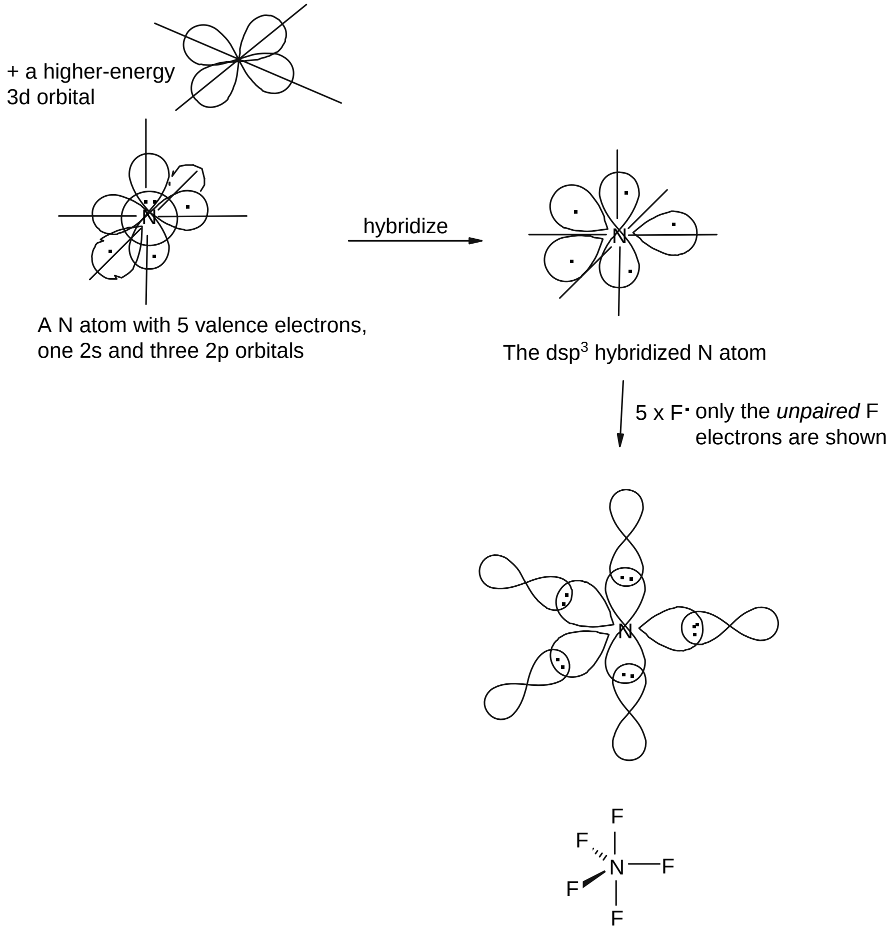


Fig. 4.3 Conventional model of the formation of a (hypothetical) pentacoordinate molecule by nitrogen. A nitrogen 3d orbital is hybridized with one 2s and three 2p orbitals to give five sp^3d orbitals which, with ten electrons, create five conventional (two-center, two-electron) bonds

Using eight electrons to do the work of ten. However, invoking d orbitals for the chemistry of main-group elements like nitrogen or sulfur is now out of favor [13]. This is because of the realization that, e.g. for nitrogen, the 3d orbitals are so much higher in energy than 2s and 2p ones that they will not mix (hybridize) appreciably with the latter two kinds; an equivalent way of expressing this is to say that when 3d orbitals are added to a diagram showing the correlation of atomic with molecular orbitals, these d orbitals are but little perturbed[1] (Fig. 4.4). A more pictorial and perhaps more chemically intuitive depiction of the model of Fig. 4.4 is shown in Fig. 4.5. The theory behind the molecular orbital energies, coefficients and nodes here is quite analogous to the situation in the propenyl (allyl) species in simple Hückel theory [14, 15, 16]. Here three of the nitrogen valence electrons are taken to bond to three equatorial fluorines using normal (two-center two electron) bonds, which contribute six electrons to the valence shell of nitrogen in NF_5; the other two nitrogen valence electrons bond the remaining two fluorines using a molecular orbital encompassing the three atoms (a three-center two-electron, 3c-2e MO). Each axial fluorine could be said to be held to nitrogen by one electron, and although there are five bonds to the central atom, nitrogen has only eight valence electrons, so it clearly does not violate the octet rule. Its valence here is trickier to assign; if we take the equatorial bonds to be normal two-electron bonds and the axial bonds to be one-electron bonds, then we have three full and two half bonds, i.e. four "full" bonds to nitrogen, which then from the discussion of the term valence above is tetravalent here. Figure 4.4 concurs with this: four electron pairs are in bonding MOs.

What is the evidence for this model rather than the sp^3d expanded octet one? First we should ask, in what sense is it meaningful to talk about the participation

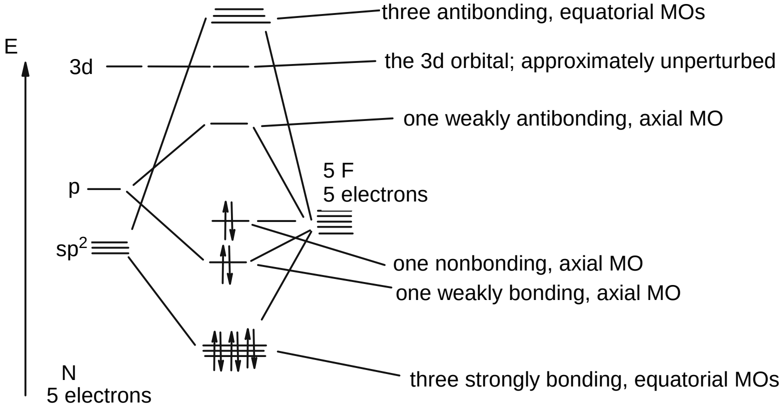


Fig. 4.4 Diagram correlating the atomic orbitals (AOs) of nitrogen and of five fluorines with the molecular orbitals (MOs) of NF_5. The 2s and the three 2p AOs of nitrogen are taken here as providing three sp^2 and one p AO, but a diagram with one 2s and three 2p AOs would be equally valid. The nitrogen 3d AO is (approximately) unperturbed because it is too high in energy to interact much with any of the fluorine 2p orbitals; thus it is essentially superfluous. Compare this diagram with Fig. 4.5

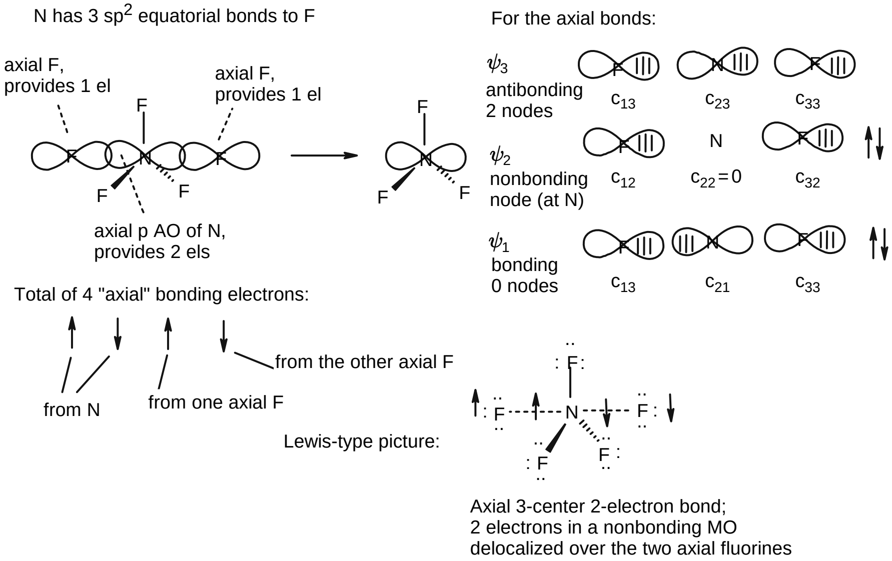
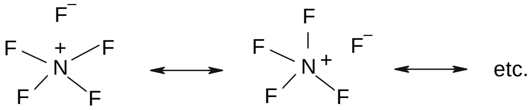


Fig. 4.5 A more pictorial (cf. Fig. 4.4) diagram correlating the atomic orbitals (AOs) of nitrogen and of five fluorines with the molecular orbitals (MOs) of NF_5. The two axial fluorines are bonded to the nitrogen by a three-center, two-electron bond corresponding to the molecular orbital (MO) ψ_1. This MO has electron density on all three atoms (we ignore the equatorial bonds and atoms now) as shown by the fact that the AO coefficients in this MO are all nonzero. The other two “axial” electrons reside in the MO ψ_2; this is nonbonding as shown by the fact that the nitrogen coefficient in this MO is zero, i.e. ψ_2 contributes electron density only to the two axial fluorines. The antibonding MO ψ_3 is empty. The octet rule is clearly not violated

or otherwise of d orbitals? The case can be made that orbitals do not really exist, but rather are pictorial/mathematical conveniences [17]. Pursuing this controversy would take us far afield, but it is worthwhile grappling with the question, how in this connection some kind of contact with experimental observations might be achieved (we do not wish to be seen as arguing about how many angels can dance on the head of an orbital); how can the orbital model touch base with reality? Consider an atom for which the calculated energy gap between d orbitals and, say, 2p or sp^3 orbitals is too big to permit appreciable interaction; suppose we nevertheless find here the formation of a compound which appears to violate the octet rule; then we can conclude that d orbitals are not involved. The demotion of the importance of d orbital participation began in the 1960s with the discovery of xenon compounds [18], which forced chemists to rethink the d-orbital/expanded bonding model. This is clearly pointed out by Malm et al.: “The chemical stability of the xenon compounds seems to violate one of the oldest and most accepted rules of valence theory. Indeed, rigid adherence to the octet rule has, until recently, effectively inhibited both theoretical and experimental study of rare gas compounds”.[2] These authors go on show that not only is the 5p-5d energy gap for xenon prohibitively large (16.6 eV), but the existence of XeF_6, with 14 valence electrons, would need “an impossibly large amount of energy” for the several promotions required, and they propose bonding by multicenter molecular orbitals, analogously to the situation in Fig. 4.5, concluding that “The semiionic [below] description of the ground state of the xenon fluorides implies that the octet rule is still preserved...”.[3]

Preserving the octet rule by using multicenter bonds, as in Fig. 4.5, can alternatively be viewed in simple resonance language (although this is probably less satisfying than the molecular orbital model):



Here none of the canonical forms contributing to the resonance hybrid violates the octet rule. Each N–F bond is (perhaps naively) one-fifth ionic, i.e. semiionic. This simple model implies polar bonds, and so has the advantage of rationalizing the fact that a big difference in electronegativity between the central atom and the ligand favors hypercoordination. Thus PF_5 is much stabler (presumably!) than NF_5, in accord with the fact that phosphorus is more electropositive than nitrogen. In the major computational paper on NF_5 [19], the importance of polar bonds for hypercoordination is alluded to.[4] Note that this resonance picture also shows nitrogen as being tetravalent. In a long, recondite paper on the octet rule and molecular orbitals, Halgren et al. reserve the term hypervalent for molecules which are hypercoordinate *and* violate the octet rule [20], so in the currently favored approach, where four electrons do the work of five, nitrogen in NF_5 is not hypervalent. Including d functions in a basis set for calculations on hypercoordinate compounds may improve the accuracy of the results (this can easily be tested by comparison with known molecules), but this does not mean that *physical* d orbitals (whatever that may mean) are involved: the orbitals may merely be acting as polarization functions, skewing the s and p orbitals in more propitious directions [19].

The Predicted Properties of NF_5

The most comprehensive theoretical study of nitrogen pentafluoride so far comes from Bettinger et al., [19]. They report an investigation of this molecule at several high levels: CASSCF, MRCI, B3LYP, MP2, and CC;[5] with variants of these methods and of basis sets, some species were studied at 15 different levels. The calculated structure and, of prime interest, the calculated thermodynamic and kinetic stabilities, are given. In contrast to some earlier studies (*Synthesis*, below), these workers are optimistic about the possibility of preparing NF_5.

Structure. The calculated structure, a trigonal bipyramid, was in detail only moderately dependent on the method: the axial bond lengths varied from 1.568 to 1.608 Å, and the equatorial ones from 1.307 to 1.399 Å. Calculations up to the CCSD(T)/TZ2P (a triply-split-valence basis set with two sets of polarization functions [21, 22,

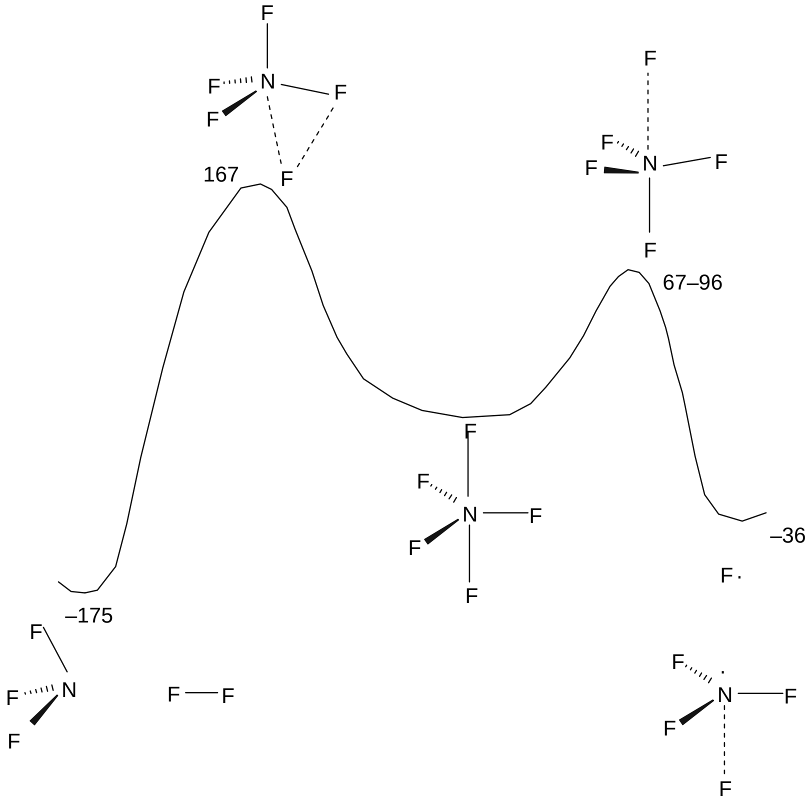


Fig. 4.6 Typical calculated barriers and reaction energies (kJ mol^{-1}, NF_5 set to zero) for two plausible decomposition routes of NF_5. For details of variability with level of calculation and for energies, enthalpies and free energies, see [19]

23]) were mutually reasonably consistent. These authors eschew the violation of the octet rule and favor an electronic structure based on a three-center 2-electron model for the apical bonds, as described above (cf. Figs. 4.4 and 4.5). At all levels this basic trigonal bipyramidal structure was a relative minimum on its potential energy surface, as shown by the absence of imaginary frequencies. These methods thus all agree that the molecule can exist, and so (if we trust the calculations!) the synthesis of this compound is impeded only by our ingenuity. The axial bonds are longer than the equatorial, as expected from the three-center two-electron model, since the axial bonds are essentially F(p)–N(p) one-electron bonds, while the equatorial bonds are F(p)–N(sp^2) two-electron bonds. Mixing in s character strengthens and shortens a bond [24], and a two-electron bond should obviously be stronger and shorter than a one-electron bond, other things being equal.

Thermodynamic and kinetic stabilities. Further information on the challenge to our ingenuity posed by the synthesis of nitrogen pentafluoride was provided by calculated results for its thermodynamic and kinetic stabilities. The reaction energy and barrier were obtained for two plausible decomposition modes, namely the obvious conversion to NF_3 and F_2, and the homolytic breaking of an (longer and presumably weaker) axial bond to give the NF_4 radical and a fluorine atom (Fig. 4.6). The reaction that is more favored thermodynamically (by 175 kJ mol^{-1}), $NF_5 \rightarrow NF_3 + F_2$, has the higher barrier (167 kJ mol^{-1}), which is perhaps counterintuitive, but not very unusual. The $NF_5 \rightarrow NF_4\cdot + F\cdot$ reaction, only 36 kJ mol^{-1} exothermic but with a barrier of only 67–96 kJ mol^{-1}, represented the lowest-energy pathway found for the decomposition of NF_5. If this calculated barrier is correct then NF_5 *once prepared* should be easily isolable. It is even possible that the compound would be somewhat stable at room temperature since the threshold for this is a barrier of about 100 kJ mol^{-1},[6] with a halflife at the upper end of perhaps several days. The low stability of NF_5 compared to PF_5 has been attributed [19] to the lower polarity of the N–F bonds, alluded to above, and the smaller size of nitrogen, which squeezes the fluorines into contact. However, these factors may not make nitrogen hypercoordination impossible, and even NF_6^- has not been ruled out [25].

Related Nitrogen Compounds

Ewig and van Wazer have studied NF_5 and the effect of sequentially replacing fluorines by hydrogen [26]. Like Bettinger et al., they find that NF_5 is a relative minimum on its potential energy surface, and so (according to the reasonable levels used, up to MP2/6-31+G*) capable of existence. They also investigated the derivatives with from one to five hydrogens in place of fluorine. Two were found to be, like NF_5 "structurally stable": NF_4H and NF_3H_2; the structures of the three species are shown in Fig. 4.7. Hydrogen wants to be equatorial: attempted optimization at correlated levels, e.g. MP2/6-31G*, with the alternative (axial) placement of hydrogen in the input structure, led to pseudorotated structures with equatorial hydrogen.[7,8] The preference of electropositive groups for the equatorial positions of trigonal bipyramids has long been known, and was given some theoretical justification by early computations which indicated that these orbitals are more electronegative than the axial orbitals.[9] This is readily rationalized by the model of Fig. 4.5, in which the equatorial orbitals of nitrogen are sp^3 and the axial are p, because mixing in s character increases the electronegativity of an orbital [24].

Ewig and van Wazer did not find any relative-minimum structures in this series with more than two hydrogens. In the author's hands, too, at the MP2/6-311++G**

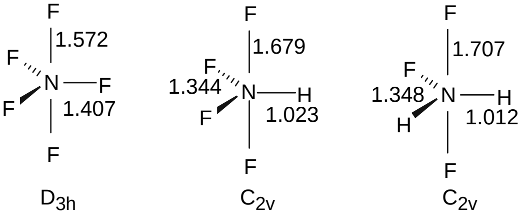


Fig. 4.7 Calculated geometries of the three NF_nH_{5-n} molecules that were found to be stationary points ("structurally stable") at the MP2/6-31++G** level [26]

level, NF_2H_3 (Fs axial, D_{3d}) had one imaginary frequency for expulsion of F^-, NFH_4 resembled an $NH4^+F^-$ ion pair (C_{3v}) and showed two imaginary frequencies for twisting around axes perpendicular to the N–F axis, and NH_5 (D_{3d}) had an imaginary frequency for expelling H^-. Why are hydrogens destabilizing here? This is expected from the resonance picture above, since N^+ F^- is natural (fluorine is more electronegative than nitrogen), while neither N^+ H^- or N^- H^+ are very reasonable (the former makes the more electropositive atom negative, the latter violates the octet rule). A rigorous explanation (the resonance picture does seem to smack of hand-waving) of the destabilizing effect of hydrogens on these molecules would require examination of the lowest-energy transition state for decomposition, since we are concerned with *how readily* they fall apart (kinetics), not *whether* they do so (thermodynamics). Nevertheless, thermodynamics may provide some indication of the factors at work here, in the recognition that replacing fluorines by hydrogens takes us away from the possibility of decomposition to $NF_4{}^+F^-$ with the high-energy $NF_4{}^+$ (see below) and toward $NH_4{}^+F^-$ and $NH_4{}^+H^-$ (granted that the latter should form NH_3 and H_2) with the stable, low-energy $NH_4{}^+$. Of course this kind of argument supposes that the transition state for decomposition resembles the products.

Hypercoordinate Compounds of Other Nonmetals

Ewig and van Wazer studied hypercoordinate hydrides of phosphorus, sulfur and chlorine at the MP2 level with fairly big basis sets [27]. They concluded from the absence of imaginary frequencies that these molecules should be able to exist: PH_5, SH_4, SH_6, ClH_3, and ClH_5. They state that “three-center bonding does not stabilize the structure of PH_5, is slightly stabilizing in the sulfur hydrides, and is relatively important only in ClH_3 and ClH_5.”

Synthesis

There have been a few suggested approaches to and reported attempts at the synthesis NF_5. Michels and Montgomery calculated $NF_5 \rightarrow NF_3 + F_2$ to be exothermic by 149 kJ mol^{-1} [28] (cf. 175 kJ mol^{-1} for Bettinger et al. [19]), and suggested that “successful synthesis of NF_5 thus requires preparation of the reactants with sufficient internal energy to overcome the endothermicity of the $NF_3 + F_2$ reaction.” These workers reported that “nearly 300 kJ mol^{-1} can be realized by shortening the axial bonds by 0.2 Å.” and suggested that vibrationally or possibly electronically excited NF_3 may offer a route to NF_5. This indicates that the irradiation of a mixture of NF_3 and F_2 with UV light, possibly under matrix isolation conditions [29], is worth exploring. The possibility of success here cannot be dismissed, although ones hopes are tempered by the fact that radiolysis [30, 31] or photolysis [32] of NF_3–F_2 mixtures failed to demonstrate formation of NF_5. Note that NF_5 decomposition is too unfavorable energetically to permit isolation or even detection of NF_5 as an equilibrium, minor component of the reaction mixture: using the calculated free energy of reaction at 298 K (-173 kJ mol^{-1}; using the enthalpy value of -149 or -175 kJ mol^{-1} would not alter the conclusion) the equilibrium constant at room temperature is calculated to be 5×10^{-31}, fewer than one molecule in a mixture of a mole each of reagents (even $\Delta G^{o}_{298} = -100$ kJ mol^{-1} corresponds to $K_{eq} = 3 \times 10^{-18}$).

Another approach to NF_5 is the reaction $NF_4^+ + F^- \rightarrow NF_5$. Heating NF_4^+ salts with a source of F^-, e.g. AsF_6^-, BF_4^-, or HF_2^-, failed to provide evidence for NF_5 [33, 34, 35, 36]. In fact, labeling studies on the reaction of NF_4HF_2 using ^{18}F-labeled HF_2^- showed that attack by HF_2^- on NF_4^+ occurs only on F, not on N [36]. Since this is contrary to expectations based on polarity, Christe et al. took this as confirming that it is mainly steric constraints that prevent the formation of pentacoordinate nitrogen species, not only "stable" molecules, but even transient intermediates [36, 37], but their pessimism was not shared by Ewig and van Wazer [26, 38]. In a very important paper, Christe and Wilson concluded from a Born-Haber cycle that covalent and ionic ($NF_4^+F^-$) NF_5 are comparable in energy, and reacted NF_4^+ with F^- ions (from the salts NF_4BF_4 and Me_4NF) [39]. Even at temperatures as low as -142°C the products were NF_3 and F_2, which was interpreted as showing that crystalline $NF_4^+F^-$ is unstable even at -142°C. Christe et al. took this and other considerations cited in the paper as showing that covalent NF_5 suffers from severe crowding, which "would make its synthesis experimentally very difficult."

Where does all this leave us in the search for a viable route to nitrogen pentafluoride? The reaction of NF_3 with atomic fluorine does not seem promising, because $NF_4\cdot$ is only weakly bound, and the $NF_4\cdot + F\cdot$ reaction is thermodynamically disfavored [19]. The photolysis experiments with $NF_3{-}F_2$ should be repeated, now that the IR spectrum of NF_5 can be reliably predicted. The known UV spectra of NF_3 and F_2 and the TDDFT-calculated UV[10] of NF_5 could be used as guides to the appropriate wavelength for irradiation. We are hoping that although the $NF_3 + F_2 \rightarrow NF_5$ reaction with electronic ground-state reactants is depressingly endergonic ($\Delta H^{o}_{298} = -172$, $\Delta G^{o}_{298} = -225$ kJ mol^{-1}) [19], here we may be able to invoke the assistance of an excited state.

Conclusions

Of the obvious routes to nitrogen pentafluoride, the $NF_3 + F_2 \rightarrow NF_5$ reaction will not work, as it is very unfavorable thermodynamically. The other superficially promising approach, the reaction of the known NF_4^+ with fluoride ion (as HF_2^-) gave as the only detectable result attack by F^- on the F, rather than the N, of the cation. Photochemical reaction of NF_3 with F_2, although it has been tried, seems worth repeating.

Bettinger et al. were optimistic that nitrogen pentafluoride can very likely exist, and their calculations indicated that it might even persist for a reasonable time at room temperature [19], and this optimism was shared by van Wazer and coworkers [25, 26, 38]. Christe and coworkers, in contrast, believe that for steric reasons it is difficult if not impossible to attach five fluorines to a nitrogen atom [36, 37, 39].

Accurately accounting for nonbonded interactions between atoms or groups by quantum mechanical calculations requires quite high levels of theory [40], and one cannot assert unequivocally that this was attained even in the notable paper of Bettinger et al. The possibility of the existence of nitrogen pentafluoride can neither be affirmed nor denied with confidence.

Notes

1. Ref. [13], Chapter 6.
2. Ref. [18], p. 214.
3. Ref. [18], p. 234.
4. Refs. 27–29, 30 in [19].
5. CASSCF (complete active space self-consistent field), MRCI (multireference configuration interaction), B3LYP (Becke three-parameter Lee-Yang-Parr), MP2 (Møller-Plesset), and CC (coupled-cluster) are methods for handling electron correlation. This is in contrast to the Hartree-Fock or SCF method of ab initio calculations, which is often said not to treat electron correlation (here each electron sees all the others just as an average electron cloud). *Methods* (CASSCF, etc.) are used with a *basis set* to perform a quantum chemical (ab initio, or DFT) calculation. A basis set is a collection of mathematical functions (of spatial coordinates *x,y,z*); a weighted average of these functions leads to the molecular wavefunction, from which in principle all molecular properties can be calculated. See I. N. Levine, “Quantum Chemistry”, Fifth Edn., Prentice Hall, Upper Saddle River, NJ, 2000; Chapters 15, 16, 17.
6. Some barriers/room temperature halflives for unimolecular reactions: (a) Decomposition of pentazole and its conjugate base: 75 kJ mol^{-1}/10 minutes and 106 kJ mol^{-1}/2 days, respectively. V. Benin, P. Kaszynski, J. G. Radziszki, J. Org. Chem., 2002, *67*, 1354. (b) Decomposition of (CF_3CO)OOO($COCF_3$): 86.5 kJ mol^{-1}/1 minute. S. v. Ahsen, P. Garciá, H. Willner, M. B. Paci, G. Argüello, Chem. Eur. J., 2003, *9*, 5135.
7. Cf. the strong preference for axial positions found for fluorine etc. in trigonal bipyramidal phosphorus compounds: R. R. Holmes, “Pentacoordinated Phosphorus”, ACS, Washington, DC, 1980; vol. II.
8. For a study of pseudorotation and prediction of a preference of electronegative atoms for axial positions in PX_3H2 and PX_4H see: A. Rauk, L. C. Allen, K. Mislow, J. Am. Chem. Soc., 1972, *94*, 3035.
9. See Note 8.
10. TDDFT: (a) M. E. Casida, “Recent Developments and Applications of Modern Density Functional Theory”, J. M. Seminario, ed., Elsevier, Amsterdam, 1996, and refs. Therein. (b) R. E. Stratman, G. E. Scuseria, M. J. Frisch, J. Chem. Phys., 1998, *109*, 8218. (c) K. B. Wiberg, R. E. Stratman, M. J. Frisch, Chem. Phys. Lett., 1998, *297*, 60.

References

1. R. Morris, “The Last Sorcerers: The Path from Alchemy to the Periodic Table”, Joseph Henry Press, Washington, DC, 2003.
2. W. B. Jensen, J. Chem. Educ., 1984, *61*, 191.
3. R. Abegg, Zeitschrift für anorganische Chemie, 1904, *39*, 330.
4. G. N. Lewis, J. Am. Chem. Soc., 1916, *38*, 762.
5. G. N. Lewis, “Valence and the Structure of Atoms and Molecules”, The Chemical Catalog Company Inc., 1923 (Dover reprint with “Introduction” by K. S. Pitzer, Dover, New York, 1966).

6. E. Scerri, “The Periodic Table: Its Development and Significance”, Oxford University Press, Oxford, 2007; Chapter 8.
7. W. Kossel, Ann. Phys., 1916, *49*, 229.
8. I. Langmuir, Am. Chem. Soc., 1919, *41*, 868.
9. A. N. Stranges, “Electrons and Valence”, Texas A&M University Press, TX, 1982.
10. K.-y. Akiba, ed., “Hypervalent Compounds”, Wiley, New York, 1998.
11. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 96–101.
12. L. Pauling, “The Nature of the Chemical Bond”, Cornell University Press, Third Edn., 1960; Chapter 5.
13. J. K. Burdett, “Chemical Bonds. A Dialog”, Wiley, New York, 1997.
14. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003, section 4.3.
15. A. Rauk, “Orbital Interaction Theory of Organic Chemistry”, Wiley, New York, 2001.
16. J. D. Roberts, “Notes on Molecular Orbital Calculations”, W. A. Benjamin, New York, 1961.
17. Computational Chemistry List (CCL), http://www.ccl.net, archives for 2005, February–May.
18. J. G. Malm, H. Selig, J. Jortner, S. A. Rice, Chem. Rev., 1965, *65*, 199.
19. H. F. Bettinger, P. v. R. Schleyer, H. F. Schaefer, J. Am. Chem. Soc., 1998, *120*, 11439.
20. T. A. Halgren, L. D. Brown, D. A. Kleier, W. N. Lipscomb, J. Am. Chem. Soc., 1977, *99*, 6793.
21. K. Raghavachari, J. B. Anderson, J. Chem. Phys., 1996, *100*, 12960.
22. M. Head-Gordon, J. Chem. Phys., 1996, *100*, 13213.
23. D. Feller, K. A. Peterson, J. Chem. Phys., 1998, *108*, 154.
24. M. B. Smith, J. March, “Advanced Organic Chemistry”, Wiley, New York, 2001; pp. 15–24 and refs. therein.
25. C. S. Ewig, J. R. van Wazer, J. Am. Chem. Soc., 1990, *112*, 109.
26. C. S. Ewig, J. R. van Wazer, J. Am. Chem. Soc., 1989, *111*, 4172.
27. C. S. Ewig, J. R. van Wazer, J. Am. Chem. Soc., 1989, *111*, 1552.
28. H. H. Michels, J. A. Montgomery, J. Chem. Phys., 1990, *83*, 1805.
29. R. S. Sheridan, Org. Photochem., 1987, *8*, 159.
30. A. R. Miller, R. R. Tsukimura, R. Velten, Science, 1967, *155*, 688.
31. C. T. Goetschel, V. A. Campanile, R. M. Curtis, K. R. Loos, C. D. Wagner, J. N. Wilson, Inorg. Chem., 1972, *11*, 1696.
32. K. O. Christe, C. J. Schack, R. D. Wilson, Inorg. Chem., 1976, *15*, 1275.
33. I. J. Solomon, J. N. Keith, A. Snelson, J. Fluorine Chem., 1972/73, *2*, 129.
34. K. O. Christe, R. D. Wilson, I. B. Goldberg, Inorg. Chem., 1979, *18*, 2572.
35. J. N. Keith, I. J. Solomon, I. Sheft, H. Hyman, Inorg. Nucl. Chem. - Herbert H. Hyman Mem. Vol., 1976, 143.
36. K. O. Christe, W. W. Wilson, G. J. Schrobilgen, R. V. Chitakal, G. A. Olah, Inorg. Chem., 1988, *27*, 789.
37. K. O. Christe, Chem. Eng. News, 1990, *April*, 3.
38. C. S. Ewig, J. R. van Wazer, Chem. Eng. News, 1990, *April*, 3.
39. K. O. Christe, W. W. Wilson, J. Am. Chem. Soc., 1992, *114*, 9934.
40. A. K. Rappé, E. R. Bernstein, J. Phys. Chem. A, 2000, *104*, 6117.

Chapter 5
Helium Compounds

Introduction

Helium and its siblings, neon, argon, krypton, xenon and radon, were once called the inert gases, but with the forging of a well-documented and fairly abundant chemistry of krypton and especially xenon, the term noble appears to have displaced inert. The history [1, 2] of the unveiling[1] of the dormant chemical proclivities of these heavier noble gases (radon chemistry has been less well explored, for obvious reasons) is well-documented, and will be only briefly mentioned here, along with some discussion of neon and argon. This will help to put helium chemistry in perspective. By chemical compounds we mean here real compounds, with an ionic or covalent bond. Entities in which noble gas atoms are associated with other atoms or molecules by van der Waals attraction or by mere physical incarceration were long the only, meager, some would say spurious, examples of noble gas chemistry: atom pairs (e.g. He–He, He–CH_4) [3], hydrates [4, 5], and fullerenes with encapsulated atoms [6, 7]. We will also pass over species that have long been known but were essentially confined to mass spectrometric studies, like HHe^+ [8] and He_2^+ [9]. These will be regarded here as belonging to the (no offense intended to theoretical or physical chemists) trivial chemistry of the noble gases.

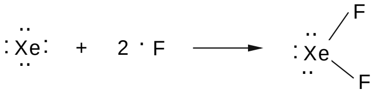
Overview of the Chemistry of Neon, Argon, Krypton, Xenon, (Radon)

(This overview is not intended to be comprehensive, but rather to put the reactivity of helium in perspective.) The chemistry of xenon is now quite abundant, and that of krypton limited but significant [10, 11, 12, 13]; were it not for its short halflife (ca. 4 days for the stablest isotope) and the difficulty of obtaining it in quantity, radon would undoubtedly have at least as rich a chemistry as xenon. The rationale behind the historic experiment that led Bartlett (in H. G. Wells's *War of the Worlds* the Martians were evidently ahead of Bartlett in noble gas chemistry, as shown by their nefarious use of an element that "[possibly] combines with argon to form a

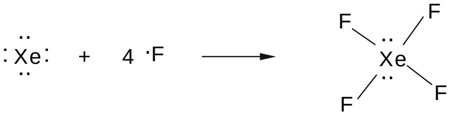
E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_5,

compound which acts at once with deadly effect...") to the first reaction of xenon [1, 2] was that the ionization energies (IEs) of xenon 12.13 (eV) and dioxygen (12.07) eV are essentially the same, and dioxygen was known to form the compound $O_2^+PtF_6^-$ with the powerful oxidant PtF_6. Although the reaction of xenon with PtF_6 turned out to be more complex than expected [14], the principle should be valid, as reaction is presumably initiated by electron abstraction by PtF_6. The IE of krypton (14.00 eV) is significantly higher than that of xenon, but close enough to suggest that it may be somewhat comparable to xenon in reactivity. In fact, any good inorganic textbook discloses that there is an abundance of xenon compounds, and a limited, but significant, number of krypton compounds. Some simple compounds of xenon are the fluorides XeF_2, XeF_4 and XeF_6 and the oxides XeO_3 and XeO_4. Krypton compounds include KrF_2 and the KrF^+ and $Kr_2F_3^+$ ions, as well as $Kr(OTeF_5)_2$ (with a Kr–O bond) and $[(RCN)KrF]^+[AsF6]^-$ (with a Kr–F and a Kr–N bond). HKrF has been prepared in a cryogenic matrix [15].

Using IE as a guide to the reactivity of the noble gases does not imply that we are considering only compounds with an Ng^+ (noble gas cation): intuitively, one sees that in a series like this the tendency to share electrons, that is covalent bond formation, should be positively correlated with the ease with which an atom is willing to relinquish some hold on its valence electrons. Talk of valence electrons brings us to a brief look at bonding in xenon and krypton compounds. A naive picture of this would be, for xenon difluoride and xenon tetrafluoride (similarly for krypton):



and



This would mean that there are 10 electrons in the valence shell of the Ng atom in xenon difluoride or krypton difluoride and 12 or 14 electrons for xenon tetrafluoride or hexafluoride, and even more for the octafluoroxenate ion, $[XeF_8]^{2-}$. Since one s and three p orbitals can accommodate only eight electrons, this would require the participation of d orbitals. In fact, the currently favored model uses only s and p atomic orbitals [16]. For example, XeF_2 can be constructed with a three-center-two-electron (3c-2e) bond, like NF_5 (Chapter 4, Fig. 4.5) without using d orbitals (Fig. 5.1). Perhaps one should not worry much about which orbitals are involved, because as has been pointed out, "bonding is not an observable quantity; only bonding distancies and electron density are amenable to observation" although

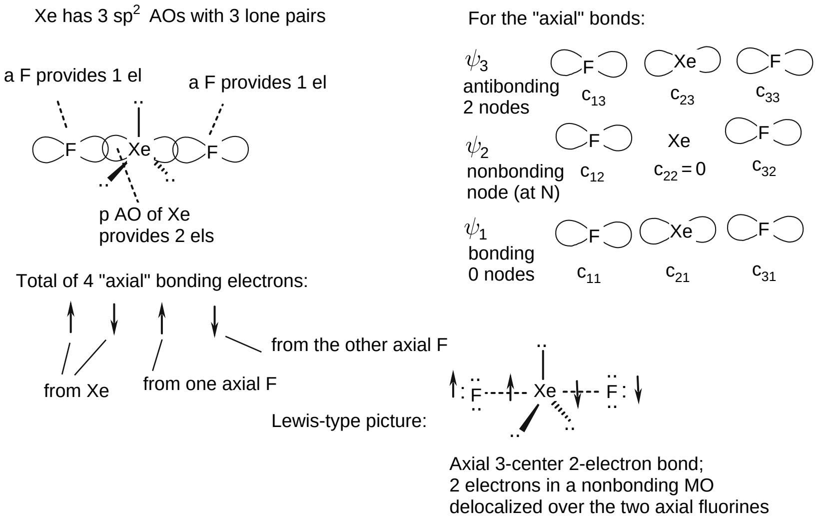


Fig. 5.1 Correlating the atomic orbitals (AOs) of xenon and of two fluorines with the molecular orbitals (MOs) of XeF_2. The two fluorines are bonded to the xenon by a three-center, two-electron bond corresponding to the molecular orbital (MO) ψ_1. This “axial” MO has electron density on all three atoms as shown by the fact that the AO coefficients in this MO are all nonzero. The other two “axial” electrons reside in the MO ψ_2; this is nonbonding as shown by the fact that the xenon coefficient in this MO is zero, i.e. ψ_2 contributes electron density only to the two fluorines. The antibonding MO ψ_3 is empty. The octet rule is clearly not violated. The situation is analogous to that in NF_5 (Chapter 4, Fig. 4.5)

“for solely didactic reasons” we can talk about the participation or not of d orbitals [17]. Orbitals, too, are perhaps not observables [18]; this may be controversial [19].

Neon and argon have so far revealed a far sparser chemistry than xenon and even krypton. This is in accord with their IEs (eV): Ne, 21.6; Ar, 15.8; Kr, 14.0, Xe, 12.1. In fact, the noble gases tend to be regarded as belonging to two classes, the heavier, with xenon (reactive) and krypton (somewhat reactive) and the lighter, with argon, neon and helium (all very unreactive). A review to ca. 1989 of the chemistry of these latter three elements is thus limited very largely to theoretical analyses and computational predictions of their putative compounds; it summarizes, among other things, work of the 1980s on helium, neon and argon by Frenking and coworkers (refs. 4–15 therein) and serves as a valuable guide to experimentalists [20]. At the time of that review, the authors were able to state “... are there any compounds containing either helium, neon or argon? ... There are no revolutionary research reports on chemical reactions involving He, Ne or Ar ...”. Let us review briefly the state (purely computational at that time) of the chemistry of neon and argon as of 1989, and then survey the progress in the ca. eight years since then in the computational and experimental study of their reactivity. This will set the stage for an examination of the potential chemistry of helium.

Argon fluoride salts have been considered as possibly capable of existence. Candidates were [ArF][PF_6] [21], [ArF][BF_4] [22], [ArF][SbF_5] and [ArF][AuF_6] [23]. Frenking and Cremer [20] point out that the creation of the ArF^+ cation poses a formidable challenge because SbF_6 and AuF_6, the neutrals corresponding to the antimony and gold counterions, probably could not oxidize argon atoms (contrast the pathbreaking reaction of xenon with PtF_6). They suggest that these argon fluoride salts are probably at the limit of "possible neutral, chemical compounds of the noble gas atoms. Unless one includes" NgBeO.[2] These hypothetical compounds owe their possible existence to the very strong electron-pair acceptor ability of BeO, which is known to bond strongly to CO and to N_2. The reservation about including NgBeO compounds among molecules with a genuine covalent bond to the Ng atom stems from the finding that although these argon, neon, and even helium compounds are computed to be thermodynamically stable, the bonding is very weak (calculated dissociation energies 29, 9, and 3 kJ mol^{-1}), and an atoms-in molecules (AIM) [24, 25, 26] analysis indicated that the bonding was dipole-induced dipole, rather than covalent.[3]

Reserving helium chemistry for the next section, let us survey here the advances in the chemistry of argon and neon since the reactivity of these was reviewed in 1990 [20]. The first genuine argon molecule was reported in 2000. HArF was convincingly shown by Khriachtchev et al., by IR analysis, to be formed by photolysis of HF in an argon matrix [27]. From a detailed examination of the IR spectrum of the species, with the aid of isotopic substitution, these workers concluded that the molecule is linear and subject to both ionic and covalent bonding, with significant but not dominating HAr^+F^- character. Thus, as the authors pointed out, the bonding here is not at all as in the hypothetical argon fluoride salts mentioned above. HArF decomposed above 27 K, but this may have been due to reactions with impurities in the matrix rather than to its inherent kinetic instability. The molecule was calculated to be thermodynamically unstable with respect to Ar and HF by 5.87 eV (566 kJ mol^{-1}). Interestingly, HArF [27] was reported before HKrF [15]. Note that in the context of such compounds "stable" means observable, even if temperatures near 0 K are required for their isolation. Khriachtchev et al. have recently presented evidence for the insertion of Ar, Kr and Xe into the HC bond of HCCCN and HCCNC [28].

Li et al. presented computational evidence that the anions $FHeO^-$, $FArO^-$, and $FKrO^-$ are local minima (stable toward dissociation), and that the neutrals LiFArO (a trapezium-like structure) and LiFKrO (linear) can exist [29]. The former was calculated to lie 720 kJ mol^{-1} below Li^+ and $FArO^-$, and 84 kJ mol^{-1} below LiF and ArO; the latter was calculated to lie 649 kJ mol^{-1} below Li^+ and $FKrO^-$, and 46 kJ mol^{-1} below LiF and KrO.

Neon seems to be an anomaly in the series helium to xenon. One expects a monotonic gradation of properties, with helium the least and xenon the most reactive. While no genuine compounds of helium or neon appear to be known yet, there is some computational evidence that neon is more recalcitrant than helium to form compounds. For the (admittedly borderline) molecules NgBeO, the calculated dissociation energies were (kJ mol^{-1}) He, 12.9; Ne, 9.2; Ar, 29.[4] In their study of

$FNgO^-$ and LiFNgO, Li et al. tacitly ignored neon [29]. In computational studies, Wong [30] found HHeF to be a bound species presumably capable of being synthesized, although Lundell et al. [31] were cautious about the ability of this compound to exist. Gerber has presented computational evidence that HHeF [32, 33] and HArCCCCH [34] can exist under high pressure in solid helium. Wong [30] and Lundell et al. [31] found HNeF to be unbound and thus not capable of existence. There is at present only computational evidence for the possibility of real helium compounds (below), and no evidence, computational or experimental, for neon compounds (apart from possible cations of primarily mass spectrometric significance). The order of increasing reactivity thus seems to be Ne, He, Ar, Kr, Xe, (then, very likely, Rn). Why should neon be the odd one out? Wong suggested that in HNeF the longer H...F distance (compared to HHeF) makes the HNg^+ ion pair attraction weaker than for the helium case (these molecules seem to have a largely ionic Ng–F bond; see below). If this is so, then for them, at least, the sizes of the atoms may be the cause of the neon-helium anomaly. Frenking and coworkers have suggested repulsive p–π interactions as a destabilizing factor in certain (computed) neon cations [35]. Of the elements Ne, Ar, Kr, Xe, and Rn, only neon has not yet been shown to form compounds (other than relatively trivial species like the protonated atom or van der Waals molecules; even neon clathrates are apparently unknown too), and computational studies are not encouraging with regard to the ability of this element to enter into serious chemical combination.

Helium Compounds

Helium and neon are the only elements, apart from the more short-lived transuranium elements, for which no compounds have yet been reported. As indicated above, neon may turn out, surprisingly, to be less reactive than helium, and in this sense it may be more challenging, experimentally and theoretically, than helium. However, we focus here on helium because (1) it is the prototypical noble element, and has stood, even after the inauguration of “inert” gas chemistry, as a symbol of inertness, (2) there would be little to say about neon as, unlike helium, it has almost no computational chemistry: all attempts to adduce evidence for the possible existence of genuine neon compounds have apparently failed. Gerber has recently reviewed theoretical and experimental work on the elements helium to xenon [32, 33]. The pioneering work on helium chemistry, by Frenking and coworkers, was first reported mainly in 1987 [36] and more extensively in 1990 [20].

For the honor of being a representative of neutral covalent helium compounds, there seem to be in the literature only two serious (HeLiH may be very slightly – ca. 0.4 kJ mol^{-1} – bound)[5] candidates: HHeF which, as briefly mentioned above, has been examined computationally, and HeBeO.[6] Despite doubts [31], the evidence, on the whole, is that HHeF can exist [30], at least under pressure in solid helium [32, 33] (conditions which, it must be conceded, would require somewhat specialized experimental equipment). Let us examine theoretical rationales for the possible existence of HHeF. In the simplest electronic picture, helium would use 1s-2p hybridization to make available two orbitals for its two electrons, permitting two normal two-electron bonds, one to hydrogen and one to fluorine; this would rationalize the possibility of molecules like HHeF. However, the 2p orbital of helium is considered to be too high in energy and too much bigger than the 1s orbital for the two to mix (hybridize) effectively [37]. This is the orbital background to the duplet analogue of the octet rule. Bearing in mind that bonding schemes are perhaps more rationalizations than objective phenomena, an alternative view of the electronic situation in HHeF is one analogous to that discussed above for XeF_2: similarly to the case of the xenon molecule (Fig. 5.1), for HHeF (Fig. 5.2) we combine a hydrogen 1s, a helium 1s and a fluorine 2p (three atomic orbitals) to give three molecular orbitals, one bonding, one nonbonding, and one antibonding. Using the four available electrons (Fig. 5.2), the bonding and nonbonding molecular orbitals are filled to give provide bonding by a three-center-two-electron (3c-2e) bond. Of course the problem with this picture is that it requires that a fluorine 2p atomic orbital mix with a helium 1s orbital. In contrast, the 3c-2e bond of NF_5 (Chapter 4) is based on a nitrogen 2p and two fluorine 2p orbitals and here there is no enormous disparity in energy or size. In the context of the orbital model this is probably a fundamental problem with helium covalent bonding, and is one

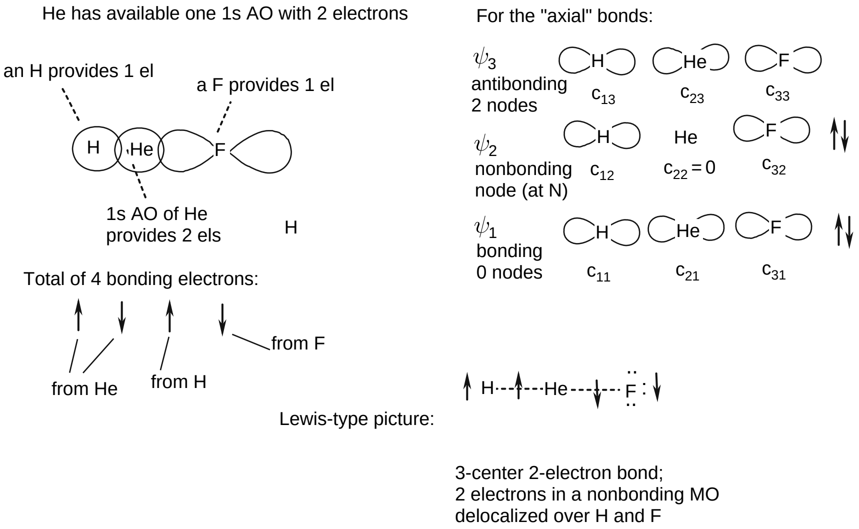
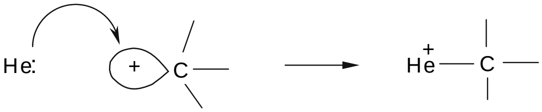


Fig. 5.2 Speculative view of covalent bonding in HHeF, correlating the atomic orbitals (AOs) of helium, hydrogen and fluorine with the molecular orbitals (MOs) of HHeF. The hydrogen and fluorine are bonded to helium by a three-center, two-electron bond corresponding to the molecular orbital (MO) ψ_1. This MO has electron density on all three atoms as shown by the fact that the AO coefficients in this MO are all nonzero. The other two electrons reside in the MO ψ_2; this is nonbonding as shown by the fact that the helium coefficient in this MO is zero, i.e. ψ_2 contributes electron density only to the H and F. The antibonding MO ψ_3 is empty. The duplet rule (the analogue of the octet rule for hydrogen and helium) is clearly not violated. The situation is analogous to that in XeF_2 (Fig. 5.1), and in NF_5 (Chapter 4, Fig. 4.5)

way of seeing why such compounds are likely to be rather fragile. The only other neutral helium compound for which good computational evidence exists seems to be HeBeO.[7] However, the bonding here is said to be "caused by strong charge induced dipole interactions without covalent contributions." Evidently a dipole induced on the He atom by BeO attracts the He toward Be.

Not limiting ourselves to neutral species, other possibilities appear. Li et al. showed that the anion $FHeO^-$ may lie in a deep energy well, with a covalent He–O bond and a large contribution from an F^- HeO canonical form [29]. Investigation of the effect of Li^+ as a counterion or possibly as a candidate for covalent bonding showed that LiFHeO has a "negligible dissociation barrier" to formation of LiOF + He (although the argon and krypton compounds were stable).

An intriguing possibility is the existence of organohelium compounds. A simple way to think of the bonding here is to imagine a helium atom acting as a Lewis base and donating its electron pair into the vacant orbital on a carbocation Lewis acid:



This is fundamentally the basis of the assertion by Koch et al. that "helium is capable of forming strong bonds with carbon" [36] (this statement is qualified by "in cations"; we examine the qualification below), although these workers rally for their support sophisticated atoms-in-molecules analyses. Let us examine the bonding of helium to carbocations. In ethyne, ethene and methane, carbon bonds to *hydrogen* using sp, sp^2, and sp^3 orbitals, with respectively 50, 33 and 25% s character. The C–H bond is progressively weaker in this series, as shown by the homolytic (the usual criteria of bond strengths) dissociation energies (kJ mol^{-1}) [38]:

HCCH	548
H_2CCH_2	460
CH_4	435

From this we might expect carbon-helium bonding to be strongest in the helium analog of HCCH, which by analogy with $H:^-$ + ^+CCH we can imagine being formed from He: + ^+CCH. Tests of potential helium compounds suggest that the fairly fast B3LYP/6-31G** level [39] is adequate for preliminary studies (although to assert with real confidence that a hypothetical helium molecule can exist one would certainly want to go to a higher level, e.g. optimization with the CCSD(T) method using a bigger basis set [40]); results reported without a reference are based on work at this level by the author. For example, the B3LYP/6-31G** level reproduces reasonably well the (computationally!) established geometries of $HeCCH^+$,[8] HHeF [30], and HeBeO.[9] Consider a helium atom donating an electron pair into the vacant

Table 5.1 Results of calculations on $HeCCH^+$ at various levels. "Minimum, yes" means that the species was a (relative) minimum on the potential energy surface. The energy differences in the last column are positive, showing that according to these calculations the combination of CCH^+ with He is exergonic. Zero-point energies are included in these calculations

Level	Minimum?	Shape	Energy	$E(CCH^+ + He)$	$E(CCH^+ + He) - E(HeCCH^+)$
					Hartrees ($kJ\,mol^{-1}$)
HF/6-31G*	yes	linear	−78.35354	−78.27548	0.07806 (205)
HF/6-31G**	yes	linear	−78.38123	−78.27770	0.10353 (272)
MP2/6-31G*	yes	bent	−78.77418	−78.73714	0.03704 (97.2)
MP2/6-31G**	yes	bent	−78.79950	−78.75812	0.04138 (108.6)
B3LYP/6-31G*	yes	bent	−79.05647	−79.02751	0.02896 (76.0)
B3LYP/6-31G**	yes	bent	−79.06458	−79.02945	0.03513 (92.2)

sp orbital on CCH^+ (the ethynyl cation). The results of optimization/frequency calculations are shown in Table 5.1 and the B3LYP/6-31G** structure of $HeCCH^+$ is shown in Fig. 5.3. At all six levels of calculation the ethynylhelium cation $HeCCH^+$ is a relative minimum and lies below the separated ethynyl cation and helium atom. The effect of the change in basis set (putting three p orbitals on helium and hydrogen) is small, but adding electron correlation beyond the Hartree-Fock level reduces the CCH^+/He binding energy by a factor of about 2–3, although the two species remain quite strongly bound, at about 100 $kJ\,mol^{-1}$ (MP2/6-31G**, 109 $kJ\,mol^{-1}$, B3LYP/6-31G**, 92 $kJ\,mol^{-1}$). This heterolytic dissociation energy is about one-fourth the homolytic dissociation energy of a typical covalent bond. In contrast, the homolytic process

$$\overset{+}{He}-C\equiv C-H \longrightarrow \overset{+}{He}\cdot + \cdot C\equiv C-H$$

is calculated (B3LYP/6-31G**) to require 1284 (*sic*) $kJ\,mol^{-1}$, in keeping with the intuitive expectation that formation of a helium atom and a carbocation should be the more favorable process. At all six levels the C–He bond is ca. 1.1 Å long, similar to a C–H bond, and the Löwdin bond order [41] of the B3LYP/6-31G** structure is 0.82 (cf. the C–H bond order of 0.94 in ethyne), indicating essentially a covalent single bond. Visualization of the molecule as a space-filling model shows the C–He van der Waals surfaces of carbon and helium overlapping well: to the same extent, visually, as do C and H (Fig. 5.3). The calculated C–He stretching frequency is 1373 cm^{-1}.

We can compare bonding of helium to CCH^+ with bonding to $HCCH_2{}^+$ and to $CH_3{}^+$, that is, to the ethenyl and the methyl cations, using again the B3LYP/6-31G** level. The results of geometry optimizations are shown in Fig. 5.3 and Table 5.2. For the ethenylhelium cation, the C–He bond length is 2.528 Å, the Löwdin bond order is only 0.03, and the stretching frequency is 126 cm^{-1}. A space-filling representation shows only slight C–He van der Waals-type overlap. For the methylhelium cation the C–He bond length is 1.668 Å, the Löwdin bond order is 0.35, and the stretching frequency is 285 cm^{-1}. A space-filling representation suggests quite good C–He

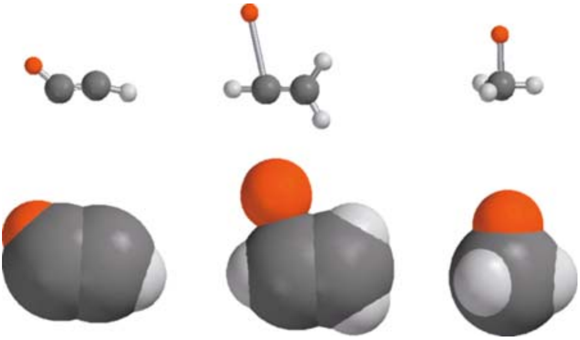


Fig. 5.3 The geometries of the cations $HeCCH^+$, $HeCHCH_2^+$, and $HeCH_3^+$, calculated at the B3LYP/6-31G** level. The top row shows ball-and-spoke models and the bottom row space-filling models. The space-filling models give a quick impression of the extent of covalent bonding, from the extent of overlap of the van der Waals surfaces

van der Waals overlap. $HeCCH^+$ is evidently much more strongly bonded than the other two, as expected from analogy with C–H bonding, but, unexpectedly, $HeCH_3^+$ seems to be much more robust than $HeCHCH_2^+$. Energy calculations agree fairly well with this. Consider the stability of the helium compounds toward dissociation to a helium atom and the organic cation: as noted above, $HeCCH^+$ is fairly strongly bound, $HeCHCH_2^+$ is scarcely bound at all, and $HeCH_3^+$ is very weakly bound. The C–He bond strength does not quite follow that of the C–H, but note that the C–H bond in ethyne is considerably stronger than that in ethene, while that in ethene is not much stronger than that in methane.

It would be nice if the promising ethynylhelium cation could be elaborated into a neutral molecule, thus moving away from the realm of ion chemistry to something one might bottle, even if only at low temperature. Interestingly, the neutrals H–He–CCH and H–He–CC–He–H are real molecules (no imaginary frequencies) at the B3LYP/6-31G** level (Fig. 5.4). Although there is no obvious orbital reason why a hydride ion should bond to $HeCCH^+$, or two hydrides to $HeCCHe^{++}$ (the *dication* is evidently quite strongly bound)[10] to give these molecules, a simple rationalization of their possible existence is given by a resonance picture involving a contribution from a protonated helium and deprotonated (or doubly deprotonated) ethyne canonical

Table 5.2 Results of calculations on $HeCCH^+$, $HeCHCH_2^+$, and $HeCH_3$+ at the B3LYP/6-31G** level. The energy differences in the last column are positive, showing that according to these calculations the combination of the cation with He is exergonic. Zero-point energies are included in these calculations

Molecule(HeR^+)	Energy(HeR^+)	E(R^+ + He)	E(R^+ + He) − E(HeR^+) Hartrees (kJ mol^{-1})
$HeCCH^+$	−79.06458	−79.02945	0.03513 (92.2)
$HeCHCH_2^+$	−80.46384	−80.46379	0.00005 (0.13)
$HeCH_3^+$	−42.36271	−42.36031	0.00240 (6.3)

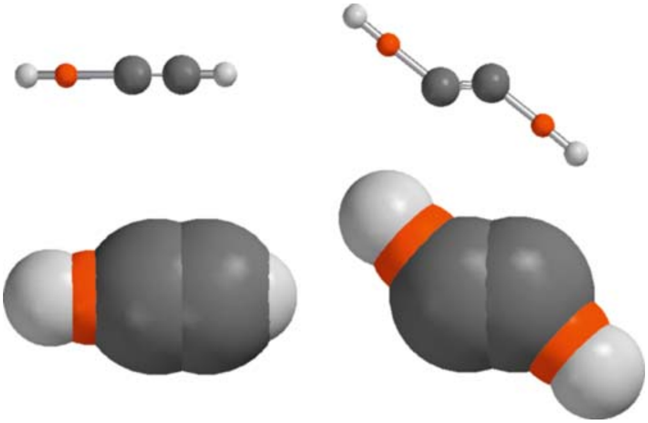


Fig. 5.4 The geometries of the neutral molecules HHeCCH and HHeCCHeH calculated at the B3LYP/6-31G** level. The top row shows ball-and-spoke models and the bottom row space-filling models. The space-filling models give a quick impression of the extent of covalent bonding, from the extent of overlap of the van der Waals surfaces. The HHeCCH geometry is quantified in Fig. 5.5

form, HHe^+ ^-CCH; the two ionic species are of course stable entities in their own right. These neutral molecules are not as strongly bound as the cationic species: for H–He–CCH the bond lengths/bond orders are H–He 0.987/0.48, He–C 1.636/0.33; for H–He–CC–He–H the bond lengths/bond orders are H–He 1.080/0.38, He–C 1.659/0.30. This compares with the He–C bond length of 1.1 Å and bond order of 0.82 for $HeCCH^+$, above. Some salient features of the energetics of H–He–CCH are shown in Table 5.3. HHe^+ and ^-CCH are calculated to react exergonically to form H–He–CCH (i.e. the decomposition of H–He–CCH to HHe^+ and ^-CCH is endergonic) and also exergonically to form He + HCCH, but the latter reaction is about twice as favorable thermodynamically. The decomposition of H–He–CCH to He and HCCH is evidently very favorable (unlike the endergonic decomposition to HHe^+ and ^-CCH), as expected, being exergonic by 707 $kJ\,mol^{-1}$. The stability of H–He–CCH may depend on the barrier to decomposition to He and HCCH,

Table 5.3 Results of calculations comparing the reaction of HHe^+ with ^-CCH to give the neutral molecule H–He–CCH (**a**) and to give He + HCCH (**b**). Although the energy differences in the last column are positive in both cases, showing that according to these calculations formation of H–He–CCH and of He + HCCH from $HHe^+ + {}^-CCH$ are both exergonic processes, the formation of He + HCCH is much more favorable thermodynamically. Zero-point energies are included in these calculations. A simple thermodynamic cycle shows that the reaction HHeCCH → He + HCCH is exothermic by $1485 - 778 = 707\,kJ\,mol^{-1}$

Molecule(M)	Energy(M)	$E(HHe^+ + {}^-CCH)$	$E(HHe^+ + {}^-CCH) - E(M)$
			Hartrees ($kJ\,mol^{-1}$)
(**a**)			
H–He–CCH	−79.94066	−79.64438	0.29628 (778)
(**b**)			
He + HCCH	−80.20989	−79.64438	0.56551 (1485)

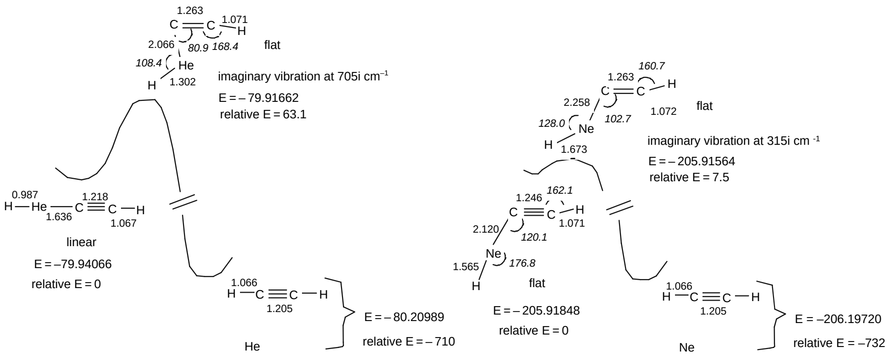


Fig. 5.5 Energy profile for the decomposition of HHeCCH to HCCH and He, and HNeCCH to HCCH and Ne, at the B3LYP/6-31G** level. Bond lengths are in Å and *angles* in degrees. Energies are in hartrees and relative energies in kJ mol^{-1}. Zero-point energies are included

and a transition state for this process was found; the reaction profile is shown in Fig. 5.5. The calculated activation energy for ejection of a helium atom is surprisingly large, 63 kJ mol^{-1}. The analogous neon molecule also existed at the same computational level (Fig. 5.5), but the activation energy for its loss of the noble gas atom is only 7.5 kJ mol^{-1}, so again neon is, counterintuitively, more reluctant than helium to react. The relative energies (not shown in Fig. 5.5) of the argon molecule HArCCH, its transition state for decomposition to Ar + HCCH, and the these products are 0, 114 and -634 kJ mol^{-1}, at the B3LYP/6-31G** level. We must bear in mind that the B3LYP/6-31G** level is only modestly high by current standards, and at higher levels the stability of HHeCCH, not to mention HNeCCH, could turn out to be illusory. Nevertheless, even if this should prove to be the case, modifications of these ethyne-based structures might conceivably be able to persuade helium, at least, to enter into combination.

Synthesis

No “nontrivial” helium compounds are known experimentally. Frenking and coworkers suggested that “the easiest way to obtain helium-containing cations should be by using tritiated compounds as precursors since He^+ is formed as the result of radioactive decay of tritium” [36]. Trace amounts of an ion corresponding in mass to CH_3He^+ have been reported from the decay of CH_3T [42], but it seems unlikely that the decay of tritium compounds, with a halflife of 12 years, would allow the accumulation of a sufficient amount of a helium compound for other than mass spectrometric detection. The energetics of radioactive decay may also create molecules in an excited state which would promote decomposition. The reported detection of an organohelium ion from reaction of He^+ with graphite employed a method that likely suffers from much the same problems [43].

An approach to organohelium cations that may appear simplistic but is at least worth examination is reaction of helium with carbocations in superacid [44] solution. A related tactic, less versatile perhaps but more likely to yield success, is the generation of an ionized fullerene derivative with a helium atom trapped inside [45], for example by ionization of, say, $C_{60}H_{59}Br$ with He inside ($He@C_{60}H_{59}Br$), or by protonation of a helium-containing fullerene [46, 47]. The fullerene approach has the advantage that the helium atom is confined in the vicinity of the carbocation center and so has little choice but to bond if it is indeed capable of doing so. The bonding situation in a pair of neutral noble gas atoms trapped in neutral C_{60} has been recently examined computationally by Krapp and Frenking [48]. They conclude that $Ar_2@C_{60}$, $Kr_2@C_{60}$ and Xe_2C_{60} have Ng–Ng and Ng–C bonds, but He_2 and Ne_2 in C_{60} are van der Waals dimers.

The synthesis of neutral helium compounds like HHeF [30, 31, 32, 33, 34] seems most likely to succeed if pursued by some kind of matrix isolation approach. After all, it was thus that the first argon compound was prepared, by the (deceptively simple?) ploy of photolyzing HF in solid argon. HF cannot be photolyzed in solid helium in ordinary commercial matrix isolation equipment, since helium is liquid even at 0 K unless under pressure. Worse, Gerber's work [32, 33, 34] suggests that helium compounds may require entombment in solid helium at very high pressure to stabilize them. Such an experiment may however be possible using a diamond anvil cell, a device in which a modest force is concentrated onto a small cell area, creating pressures up to about three million atmospheres (300 GPa) [49]. Whether this mating of theory and experiment will finally persuade helium to shed its coyness remains to be seen.

Notes

1. (a) The first noble gas reaction, of xenon, was reported by Neil Bartlett on 19 July 1962, at the Second International Fluorine Chemistry Meeting, Estes Park, Colorado. The first publication was: N. Bartlett, Proc. Chem. Soc., 1962, 218. The reaction took years to clarify. (b) In 1933 Pauling suggested that krypton and xenon compounds could exist: L. Pauling, J. Am. Chem. Soc., 1933, *55*, 1895.
2. Ref. [20], p. 88.
3. Ref. [20], pp. 85–87.
4. See Note 3.
5. Ref. [20], p. 87.
6. See Note 3.
7. See Note 3.
8. Ref. [20], p. 63.
9. See Note 3.
10. Ref. [20], pp. 63–65.
11. A. Krapp, G. Frenking, unpublished (2007). I thank Professor Frenking for a manuscript of this paper.

References

1. R. Dagani, Chemical and Engineering News, 2002, October 7, 27.
2. P. Ball, "Elegant Solutions", Royal Society of Chemistry, Cambridge, UK, 2005; Chapter 8.
3. G. Calderoni, F. Cargoni, A. Famulari, M. Raimondi, J. Phys. Chem., 2002, *106*, 5521, and refs. therein.

4. T. Maekawa, J. Chem. Eng. Data, 2003, *48*, 1283.
5. B. J. Anderson, J. W. Tester, B. L. Trout, J. Phys. Chem. B, 2004, *108*, 18705.
6. C. M. Stansky, R. J. Cross, M. Saunders, M. Murata, Y. Murata, K. Komatsu, J. Am. Chem. Soc., 2005, *127*, 299.
7. G.-W. Wang, X.-H. Zhang, H. Zhan, Q.-X. Guo, Y.-D. Wu, J. Org. Chem., 2003, *68*, 6732.
8. T. R. Hogness, E. G. Lunn, Phys. Rev., 1925, *26*, 50.
9. O. Tüxen, Z. Physik, 1936, *103*, 463.
10. C. K. Jørgensen, G. Frenking, "Noble Gases and High-Temperature Chemistry, Structure and Bonding *73*", Springer-Verlag, Berlin, 1990.
11. P. Laszlo, G. J. Schrobilgen, Angew. Chem. Int. Ed. Engl., 1988, *27*, 479.
12. C. E. Housecroft, A. G. Sharpe, "Inorganic Chemistry", Prentice Hall, NJ, 2005; Chapter 17.
13. F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, "Advanced Inorganic Chemistry", Wiley, New York, 1998; Chapter 14.
14. L. Graham, O. Graudejus, N. K. Jha, N. Bartlett, Coord. Chem. Rev., 2000, *197*, 321.
15. M. Pettersson, L. Khriachtchev, A. Lignell, M. Räsänen, J. Chem. Phys., 2002, *116*, 2508.
16. W. Kutzelnigg, Angew. Chem. Int. Ed. Engl., 1984, *23*, 272.
17. J. F. Lehmann, G. J. Schrobilgen, K. O. Christe, A. Kornath, R. J. Suotamo, Inorg. Chem., 2004, *43*, 6905.
18. S. S. Zumdahl, "Chemical Principles", Fourth Edn., Houghton Mifflin, Boston, 2004; pp. 673–675.
19. J. Itatani, J. Levesque, D. Zeidler, H. Niikura, H. Pépin, J. C. Kiefer, P. B. Corkum, D. M. Villeneuve, Nature, 2004, *432*, 867.
20. G. Frenking, D. Cremer, Structure and Bonding (Berlin, Germany), 1990, *73*(Noble Gas High Temp. Chem.), 17.
21. J. F. Liebman, J. F. Allen, J. Chem. Soc., Chem. Commun., 1969, 1355.
22. C. K. Jørgensen, Z. Anorg, Allg. Chem., 1986, *549*, 91.
23. G. Frenking, W. Koch, C. Deakyne, J. F. Liebman, N. Bartlett, J. Am. Chem. Soc., 1989, *111*, 31.
24. R. F. W. Bader, "Atoms in Molecules: A Quantum Chemical Theory", Clarendon, Oxford, UK, 1990.
25. R. F. W. Bader, P. L. A. Popelier, T. A. Keith, Angew. Chem. Int. Ed. Engl., 1994, *33*, 620.
26. R. G. Parr, P. W. Ayers, R. F. Nalewajski, J. Phys. Chem. A, 2005, *109*, 3957.
27. L. Khriachtchev, M. Pettersson, N. Runeberg, J. Lundell, M. Räsänen, Nature, 2000, *406*, 874.
28. L. Khriachtchev, A. Lignell, H. Tanskanen, J. Lundell, H. Kiljunen, M. Räsänen, J. Phys. Chem. A, 2006, *110*, 11876.
29. T.- H. Li, C.-H. Mou, H.-R. Chen, W.-P. Hu, J. Am. Chem. Soc., 2005, *127*, 9241.
30. M. W. Wong, J. Am. Chem. Soc., 2000, *122*, 6289.
31. J. Lundell, G. M. Chaban, R. B. Gerber, Chem. Phys. Lett., 2000, *331*, 308.
32. R. B. Gerber, Khimiya be Yisra'el, 2005, *18*, 7.
33. R. B. Gerber, Annu. Rev. Phys. Chem., 2004, *55*, 55.
34. L. Sheng, A. Cohen, R. B. Gerber, J. Am. Chem. Soc., 2006, *128*, 7156.
35. G. Frenking, W. Koch, F. Reichel, D. Cremer, J. Am. Chem. Soc., 1990, *112*, 4240.
36. W. Koch, G. Frenking, J. Gauss, D. Cremer, J. R. Collins, J. Am. Chem. Soc., 1987, *109*, 5917.
37. L. Pauling, "The Nature of the Chemical Bond", Third Edn., Cornell University Press, Ithaca, New York, 1960; Chapter 5.
38. F. R. Carey, R. J. Sundberg, "Advanced Organic Chemistry. Part A", Kluwer, New York, 2000; p. 14.
39. E. Lewars, "Computational Chemistry", Kluwer, Boston, 2003; Chapter 7.
40. I. N. Levine, "Quantum Chemistry", Fifth Edn., Prentice Hall, Engelwood Cliffs, NJ, 2000; sections 15.19, 17.1, 17.2.
41. L. C. Cusachs, P. Politzer, Chem. Phys., 1968, *1*, 529.

42. A. H. Snell, F. Pleasonton, J. Phys. Chem., 1958, *62*, 1377.
43. S. Young, M. J. Coggiola, Int. J. Mass Spectrom. Ion Proc., 1986, *74*, 137.
44. M. B. Smith, J. March, “March’s Advanced Organic Chemistry”, Wiley, New York, 2001; pp. 219–225.
45. G.-W. Wang, X.-H. Zhang, H. Zhan, Q.-X. Guo, Y.-D. Wu, J. Org. Chem., 2003, *68*, 6732.
46. D. D. DesMarteau, Science, 2000, *289*, 72.
47. C. A. Reed, K.-C. Kim, R. D. Bolskar, L. J. Mueller, Science, 2000, *289*, 101.
48. A. Krapp, G. Frenking, Chem. Eur. J., 2007, *13*, 8256.
49. R. J. Hemley, H.-K. Mao, G. Shen, J. Badro, P. Gillet, M. Hanfland, D. Häusermann, Science, 1997, *276*, 1242, and refs. therein.

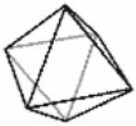
Chapter 6
Tetrahedrane

Introduction

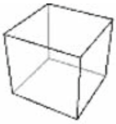
Tetrahedrane, **1**, C_4H_4 or $(CH)_4$ is interesting for at least four reasons:

(1) *Esthetic considerations*: it is the molecular counterpart of the simplest of the five platonic solids, the tetrahedron, the octahedron, the cube or hexahedron, the icosahedron, and the dodecahedron.[1] The (hydro)carbon counterparts of these geometric figures are:

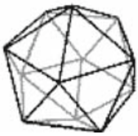
1
C_4H_4
tetrahedrane



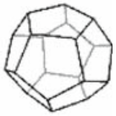
C_6
octahedrane



C_8H_8
cubane



C_{12}
icosahedrane



$C_{20}H_{20}$
dodecahedrane

Of the five mathematical objects, only tetrahedrane, cubane and dodecahedrane can be translated into conventional organic molecules with tetrahedrally bonded four-coordinate carbon. Octahedrane, which would actually be an allotrope of carbon, requires pyramidally disposed bonds on tetrahedral carbon, and icosahedrane, another putative allotrope, demands pyramidal pentacoordinate carbon. In view of the apparent stability of (the yet-unknown; Chapter 2) pyramidane, the possible existence of octahedrane cannot be simply dismissed, although calculations are so far not of good augur for its experimental realization.[2] Icosahedrane requires pentacoordinate carbon vaguely reminiscent of that in certain nonclassical carbocations of which CH_5^+ might be considered a prototype [1, 2]; the possible existence of this structure as a neutral or even a cationic entity seems remote. Structures with features like those in octahedrane and icosahedrane are, however, common in boron hydrides and carboranes [3]. Derivatives of tetrahedrane have been synthesized (see below), and cubane [4, 5, 6] and dodecahedrane [7, 8, 9] are known compounds.[3]The

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_6,

chemical relevance of the platonic solids, with emphasis on tetrahedrane and dodecahedrane, is nicely summarized in a review by Grahn [10].

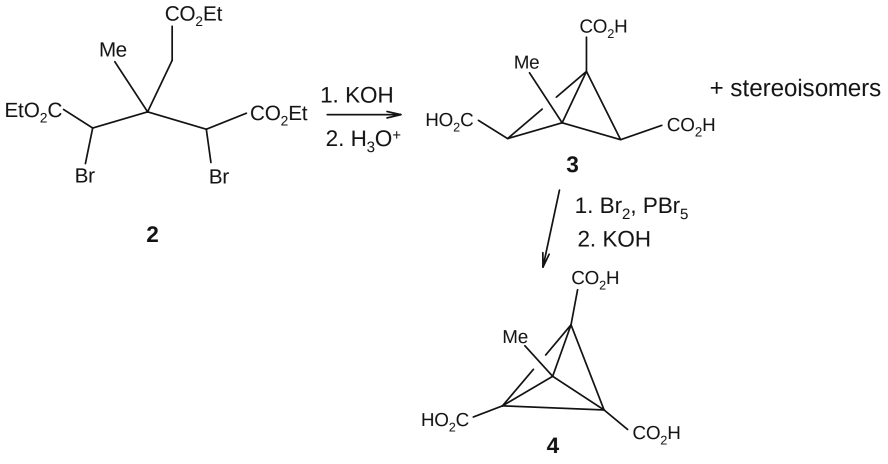
(2) *A test of the limits of the structural theory of organic chemistry*: ever since Baeyer introduced the concept of angle strain [11], chemists have wondered how much distortion of bond angles can be packed into a molecule. Cyclopropane is the simplest example of a strained organic molecule and tetrahedrane is composed of four fused cyclopropane rings. Can such a molecule exist? If so, how stable would it be?

(3) *A challenge to synthesis*: this is a consequence of the expected high strain in tetrahedrane. Novel reactions and extraordinary experimental skill are often needed to construct highly strained molecules.

(4) *Exotic chemistry*: the concatenation of strained rings in tetrahedrane may not only thwart conventional routes to its realization, but could also confer unusual properties, such as anomalous reactivity, acidity or basicity, and ionization energy, to name some possibilities.

Counterfeit Chemistry: A Fictional Synthesis of a Tetrahedrane

The first report of the synthesis of this ring system, a claim of perhaps only modest credibility even at the time, evidently appeared in 1913, and was elaborated on in 1920, in two papers by Thorpe and Beesley, who claimed the formation of the tetrahedrane **4** by dehydrobromination from the bicyclobutane **3** [12, 13]:



2

3

4

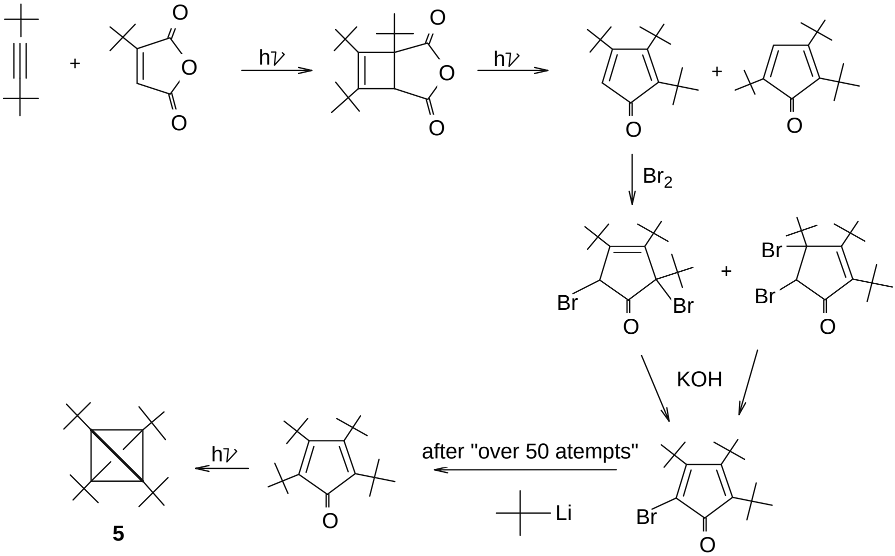
methyltetrahedranetricarboxylic acid

The reports were fraudulent. The unmasking of this deception is described by Wiberg in a synopsis [14] evidently based on a paper by Larson and Woodward [15] and information in the Ph.D. thesis of Larson, a student of R. B. Woodward's, who attempted to repeat the alleged synthesis [16]. Woodward, skeptical of the reported results, tracked down Beesley in Mexico and was told by the latter that he had fabricated the research. It is wryly amusing that the preliminary report of 1913 was followed by the full paper/fabrication in 1920, a delay allegedly caused by the Great War, but perhaps long enough to concoct ten pages of experimental data. The report was taken seriously enough for Ingold to write a theoretical analysis of tetrahedrane in terms of what would now be called bent bonds, published as an addendum to the 1920 paper [13]. Much later, a reinvestigation of a butadiene derivative (2-methyl-1,3-butadiene-1,3,4-tricarboxylic acid) considered by Woodward as a possible product from dehydrobromination of the dibromo triester **2**, was reported [17] (Wiberg pointed out that it may really be possible to prepare a bicyclobutane from **2**, although such an attempt has apparently not been reported [14]).

Real Syntheses of Tetrahedranes

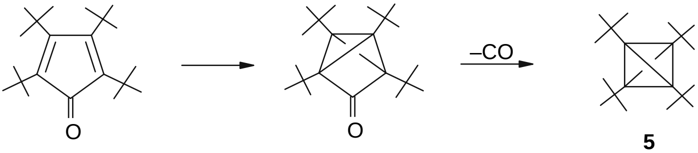
Tetra-t-*butyltetrahedrane, Synthesis*

The first genuine tetrahedrane synthesis was reported in 1978 by the Maier group: the preparation of tetra-*t*-butyltetrahedrane, **5** [18]. This synthesis, which demanded astonishing persistence and experimental skill (the experimental details are reported in a 1981 paper [19]) is sketched here.



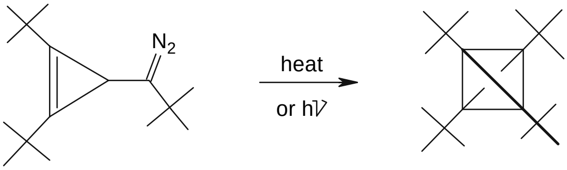
5

This outline omits details, sometimes at first frustrating and often baffling, of some reactions, particularly the introduction of the fourth *t*-butyl group into the cyclopentadienone, and the photochemical isomerization of tetra-*t*-butylcyclopentadienone, which involved various intermediates and byproducts, and demanded the judicious choice of reaction conditions. Under certain conditions irradiation of tetra-*t*-butylcyclopentadienone gave, besides relatively prosaic byproducts (a tricyclic ketone, a ketene, and an alkyne) a hydrocarbon $C_{20}H_{36}$ whose properties did not initially appear to be entirely propitious for its identification as the desired tetrahedrane: it was stable in air at room temperature. On the other hand, the IR showed no notable functional groups and the UV displayed only weak absorption; the ^{1}H NMR spectrum showed only *t*-butyl protons and the ^{13}C NMR spectrum revealed three kinds of carbons, at $\delta = 32.26$, 28.33, and 10.20, the two first two characteristic of the *t*-butyl group and the third of carbons in cyclopropane or cyclobutane hydrocarbons. These spectra are those expected for tetra-*t*-butyltetrahedrane, but the stability of the compound was, from experience with strained molecules, at odds with this structure. Some reassurance came from the thermal behavior: the colorless crystals, mp 135° with red coloration (below), could be isomerized quantitatively at 130° in perdeuterated hexamethyltrisilacyclohexane (Cyclosilan) to an orange–red substance that appeared to be tetra-*t*-butylcyclobutadiene. The cyclobutadiene structure was later proved by X-ray analysis [20], and the photoelectron spectra of both isomers supported the assigned structures [21]. This facile isomerization suggests the conversion of one (*t*-BuC)$_4$ compound into another, and besides cyclobutadiene the only "rational" C_4 molecule with equivalent carbons is tetrahedrane. "Any remaining doubt" [22] about the tetra-*t*-butyltetrahedrane structure was removed in 1984 with the publication of an X-ray crystallographic analysis [23]. This revealed the tetrahedrane shown in Fig. 6.1 (for calculations on the geometries of **5** and other tetrahedranes and the corresponding cylobutadienes, see [24]). It was considered "plausibel" that the formation of the tetrahedrane proceeded by isomerization of the cyclopentadienone to a tricyclopentanone (detected by IR) and loss of CO:



5

After much effort, a shorter and higher-yield to **5** was developed. Conditions were found (eventually!) under which tetra-*t*-butylcyclopropenyldiazomethane lost nitrogen to give tetra-*t*-butyltetrahedrane by carbene insertion into the double bond [25, 26, 27]:



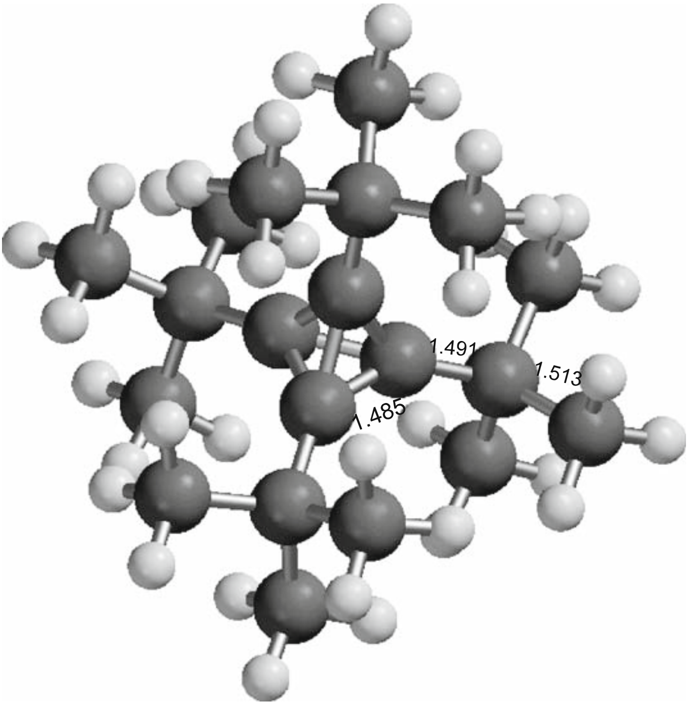
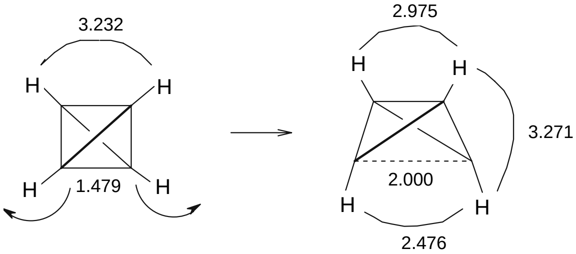


Fig. 6.1 Tetra-*t*-butyltetrahedrane and (average) bond lengths revealed by X-ray crystallographic analysis. The structure shown is actually a B3LYP/6-31G*-optimized geometry with T symmetry calculated by the author and closely resembles the X-ray structure shown in [23]. The X-ray results indicate that rather than the slightly higher-symmetry Td molecules the crystals may consist of enantiomeric T-symmetry (arising from slight elongation of one CH bond on each *t*-butyl group) molecules. The B3LYP/6-31G* bond lengths differ from the average X-ray ones shown thus, X-ray/B3LYP: 1.485/1.494, 1.491/1.505, 1.513/1.545

*Tetra-*t*-butyltetrahedrane, Properties*

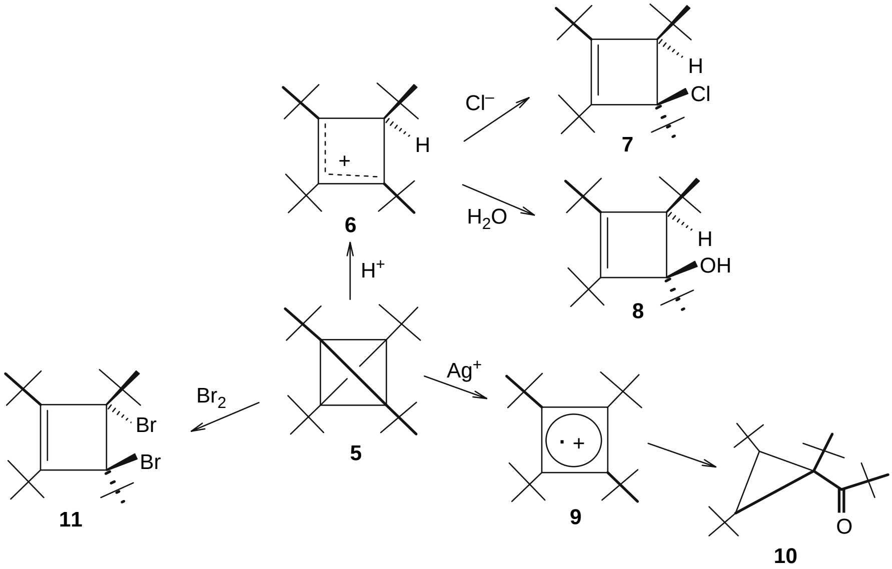
The ability of the bulky *t*-butyl groups to diminish reactivity toward external reagents (below) is obvious, but how do they impose on **5** its astonishing stability toward release of strain by unimolecular CC bond cleavage (discussed later for tetrahedrane itself)? This was ascribed by Maier to a “corset effect” (Korsettprinzip) [18, 22]: placing four groups on the corners of a tetrahedron puts them as far apart as possible, disposing them equispaced on the surface of a sphere. Breaking a CC bond may bring two pairs of pendant groups closer, e.g. B3LYP/6-31G* indicates for a CC stretch from the equilibrium length of 1.479 to 2.000 Å (using H for simplicity) the change shown.

The term corset is apparently based on the idea that the restraining device resists (lateral?) motion, although Hopf, in his review of the tetrahedrane problem [28], assures us that a corset does not actually work in the same manner as the *t*-butyl groups of **5** [29]. For the effect to work, the groups must be so big that the steric



strain felt on forcing them closer offsets the release of ring strain in the transition state for bond cleavage; if this condition is met the barrier for ring opening to a diradical (through which the tetrahedrane is believed to isomerize to the cyclobutadiene; below for the parent molecule) will be raised and the substituted tetrahedrane will be stabler than the parent. Of course, one has to somehow arrive at the substituted system, and the groups desired in this product can influence the reactivity of putative precursors and possibly thwart a synthesis. Thus, an attempt to make the tetraadamantyl analogue of **5** failed, not because of a breakdown of the corset effect, but because of an untoward steric effect in a potential precursor of tetraadamantyltetrahedrane; as Maier points out, sterically "everything [must fit] nicely together" [22]. Another case of nice fitting is that of the trimethylsilyl group, discussed below. Decades ago, Dewar and Baird [30, 31] predicted that tetrahedrane would probably be unable to exist, isomerizing with essentially no barrier to cyclobutadiene (an "amusing and very unexpected prediction" [30]) and that "substituted tetrahedranes should be even less stable" [30]. Current ab initio calculations (discussed later) are not as pessimistic (less amusing?) toward tetrahedrane as were the semiempirical methods used by Dewar and Baird, and the steric effect of large groups was evidently not considered by those workers. A corollary of the corset postulate and the work of Dewar and Baird is that after tetra-*t*-butyl- and sterically similar tetrahedranes, the stablest tetrahedrane should be tetrahedrane itself! This is counterintuitive, since substitution by methyl or phenyl groups is commonly found to stabilize reactive compounds.

The chemistry of tetra-*t*-butyltetrahedrane has been summarized by Maier in his review [22]; besides thermal and photochemical isomerization to the cyclobutadiene, it is dominated by only two reactions, protonation and oxidation. The molecule is inert to aqueous acids, evidently because the ring CC bonds are shielded by the *t*-butyl groups from the fairly big hydrated H_3O^+; however, anhydrous HCl protonates **5** to give the homocyclopropeny cation **6**, which in an unreactive solvent captures chloride ion to form the chlorocyclobutene **7**, and in the presence of water gives the cyclobutenol **8**. With bromide or iodide as counterion (from HBr or HI) **6** remains as an ion pair. Oxidation of **5** with silver ion leads via the radical cation **9** to the cyclopropenyl ketone **10**, or to **8**, depending on conditions. With bromine as the oxidant, the dibromocyclobutene **11** is formed (possibly via **9**). Compound **5** also reacts with oxygen, forming ketones and peroxides.



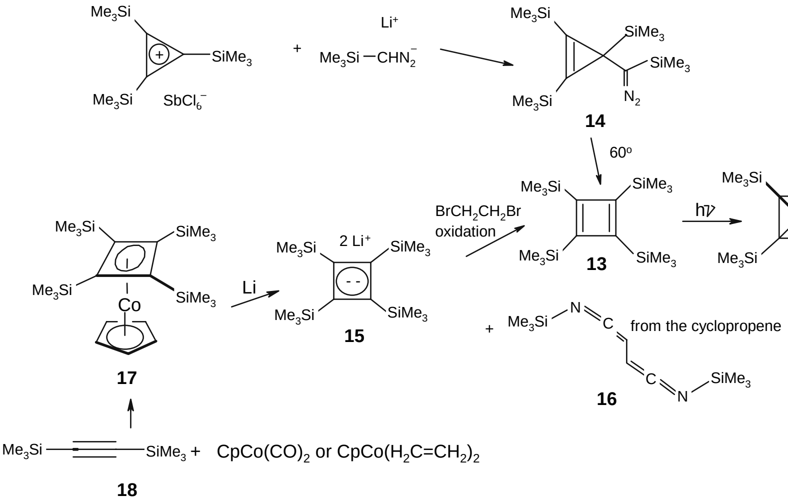
Tetrakis(trimethylsilyl)tetrahedrane, Synthesis

This is another stable tetrahedrane. The synthesis of tetrakis(trimethylsilyl)tetrahedrane, **12**, was reported in 2001 in a communication by Maier and coworkers [32] and in 2002 in a full paper by the groups of Maier and Sekiguchi [33]. Note that between the reports of the tetra-*t*-butyl (1978) [18] and the tetrakis(trimethylsilyl) derivatives (2001) [32] derivatives, seven other isolable tetrahedranes were reported in 1990–1995 by the Maier group; these have, in addition to three *t*-butyl groups, one of the following groups: $SiMe_3$, $SiMe_2Ph$, SiMeOPr-*i*, $SiHMe_2$, $GeMe_3$, $CHMe_2$, and adamantyl.[4] Unlike the first synthesis of the first-ever tetrahedrane, the tetra-*t*-butyl derivative, the preparation of **12** did not go through a cyclopentadienone, but rather through a cyclobutadiene **13** prepared from the cyclopropenyldiazomethane **14** or (apparently better) the cyclobutadiene dianion **15**, via **17**, starting with the alkyne **18** and a cobalt complex.

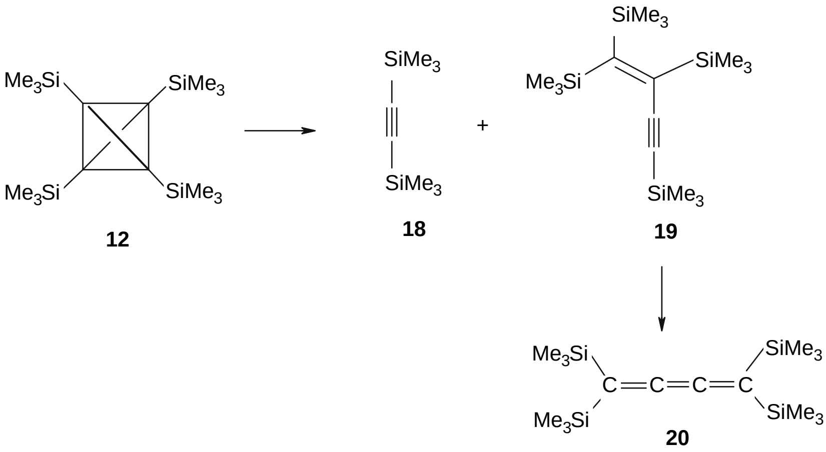
In the 2001 communication [32] the cyclobutadiene **13** made from the cyclopropene **14** was contaminated with the bis(ketenimine) **16**, which complicated positive identification of the tetrahedrane **12** formed when the when the (impure) **13** was photolyzed. The use of pure **13** [34], readily available from the dianion, starting with bis(trimethylsilyl)ethyne and $CpCo(CO)_2$ or $CpCo(H_2C{=}CH_2)_2$, facilitated the preparation and identification of the tetrahedrane [33].

Tetrakis(trimethylsilyl)tetrahedrane, Properties

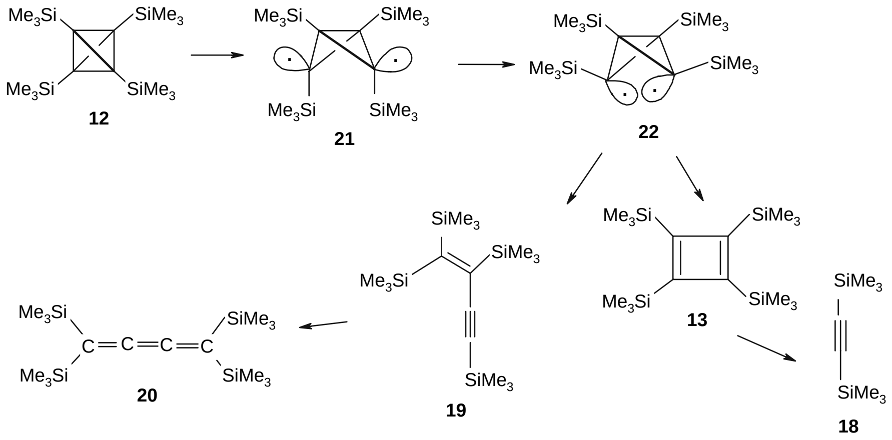
Tetrakis(trimethylsilyl)tetrahedrane (**12**) is a colorless crystalline solid, mp 202°. Unlike tetra-*t*-butyltetrahedrane (**5**), which melts at 135° with isomerization to the



corresponding cyclobutadiene, **12** melts without decomposition. Neat **12** reacts only at 300°, forming bis(trimethylsilyl)ethyne (**18**). At 280° in solution (perdeuterated tetracosane) **12** slowly forms **18** and tetrakis(trimethylsilyl)vinylethyne (**19**), which latter slowly isomerizes to the butatriene (**20**).



As with the isomerization of tetra-*t*-butyltetrahedrane to tetra-*t*-butylcyclobutadiene, the isomerization of **12** to **18**, **19** and **20** likely begins with opening to a diradical (discussed below for the parent) **21** which isomerizes to a diradical **22**; the second diradical isomerizes to the cyclobutadiene **13**, but unlike the case in the tetra-*t*-buty system, the cyclobutadiene is of higher energy than the tetrahedrane, and furthermore can drain away to the low-energy alkyne **18**. A control experiment showed that **19** and **20** do not arise from the cyclobutadiene; **19** was suggested to arise from diradical **22** with trimethylsilyl migration, and the isomerization of **19** to **20** is in accord with the fact that trimethylsilyl groups prefer vinylic positions.



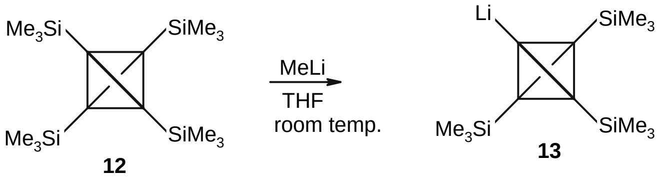
The stability of tetrakis(trimethylsilyl)tetrahedrane is ascribed to a steric (corset) effect, as for the tetra-*t*-butyl compound, and to an electronic effect [32, 33]. The corset effect is expected to be weaker than in the tetra-*t*-butyl molecule, because although $SiMe_3$ is bigger than CMe_3, this is offset by the longer C–Si compared to C–C bond. Offsetting the diminished (as compared to tetra-*t*-butyltetrahedrane) stabilization from the corset effect, there is electronic stabilization due to σ-donation by the silyl groups (silicon being more electropositive than carbon) and a π-acceptor effect due to donation of electrons from the bent (banana) CC bonds [14] of the tetrahedrane system into σ^* CSi bonds [33]. This kind of stabilization had been anticipated in calculations on tetralithiotetrahedrane [35, 36, 37, 38]. Maier et al. extended [33] to silyl-substituted tetrahedranes and cyclobutadienes earlier calculations by Balci et al. on the parent and tetra-*t*-butyl molecules [24]. Using the isodesmic reaction [39, 40]

$$C_4H_4 + 4\,CH_3R \rightarrow C_4R_4 + 4\,CH_4$$

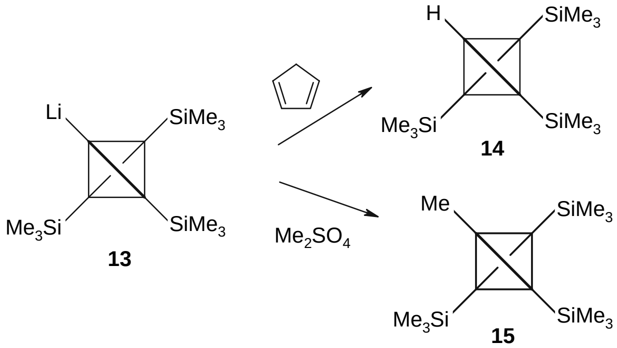
they compared the preference of several groups for attachment to methane or to tetrahedrane/cyclobutadiene. Tetrahedrane is stabilized by *t*-Bu and by Me_3Si groups, while cyclobutadiene is destabilized by *t*-Bu but stabilized by Me_3Si. Of more direct relevance to the experimental results, they also calculated the relative stabilities of the tetrahedrane and the cyclobutadiene for the parent (H), the tetra-*t*-butyl, and the tetrakis(trimethylsilyl) molecules (as well as methyl and silyl substituents). The results of B3LYP/6-31G* calculations were: tetrahedrane/cyclobutadiene, kJ mol^{-1}: H, 102/0; *t*-Bu, −5.0/0; $SiMe_3$, −37/0. Thus the prediction is that for the parent molecule the tetrahedrane is much the higher in energy, for the tetra-*t*-butyl the tetrahedrane is slightly lower, and for the tetrakis(trimethylsilyl) the tetrahedrane is markedly lower. In fact experiment shows, by thermal isomerization (above), that tetra-*t*-butyltetrahedrane is higher in energy than the cyclobutadiene (but the calculated energy difference is only marginally negative and well within the error limit expected for a B3LYP/6-31G* calculation), while the prediction for tetrakis(trimethylsilyl)tetrahedrane is borne out by the refusal of that compound to give the cyclobutadiene as a product of the thermal reaction. These calculations and some by the author are summarized later.

Tetrahedranyllithium (and Compounds Derived Therefrom)

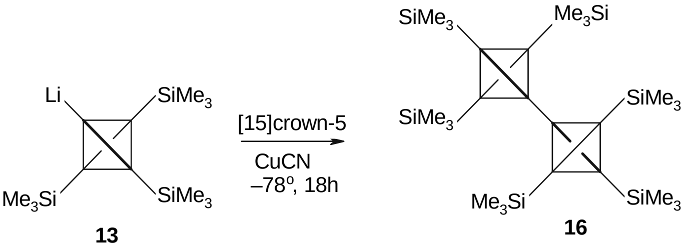
Tetralithiotetrahedrane is apparently unknown.[5] The synthesis of a fully-characterized monolithio tetrahedrane, tris(trimethylsilyl)tetrahedranyllithium (**13**), was reported in 2003 by Sekiguchi and Tanaka [41], who prepared it by reacting tetrakis(trimethylsilyl)tetrahedrane **12** [32, 33] with methyllithium.



The compound is sensitive to air and moisture, but thermally stable. Lithiated tetrahedranes are synthetically important because of the ease with which it should be possible to replace the lithium by other groups. In particular, tetralithiotetrahedrane is potentially a precursor of the parent tetrahedrane, by protonation. In fact, protonation of **13** by the relatively acidic cyclopentadiene gave tris(trimethylsilyl)tetrahedrane (**14**), and reaction with dimethyl sulfate gave methyltris((trimethylsilyl) tetrahedrane (**15**).



Both **14** and **15** are stable to air and heat (up to 100°), which is surprising in view of the failure[6] of so many attempts to make tetrahedranes not fully substituted with *t*-butyl, trimethylsilyl, or similar groups.[7] The stability of **14** and **15** was attributed [41] to the electronic stabilizing effect of the trimethylsilyl groups mentioned above. It was later found that two moieties of **13** could be oxidatively coupled to give the "dimer" **16** [42]. This compound is interesting not only for its stability, but also because it has the shortest-known "normal" (noncyclic, i.e. not bent [14]) single bond between tetracoordinate carbons.



The connecting CC bond in **16** is (from X-ray analysis) 1.436 Å long. This is shorter even than a typical sp^2–sp^2 CC single bond; calculated B3LYP/6-31G* CC bond lengths, which are accurate to within about 0.01 Å [43] are: sp^3–sp^3, 1.535 (butane central bond), sp^2–sp^2, 1.458 (1,3-butadiene), sp–sp, 1.369 (1,3-butadiyne). The short bond in **16** is expected from the high s character of the exocyclic carbon orbitals of the tetrahedrane system.

Calculations on tetra(*t*-butyl)tetrahedrane, tetrakis(trimethylsilyl)tetrahedrane, and the parent tetrahedrane.

The salient questions to be addressed by calculations on a tetrahedrane are:

(1) can it exist at all?
(2) If it can exist, how stable is it?
(3) If it can exist, which is stabler, the tetrahedrane or the cyclobutadiene?

(1) *Can it exist at all?* A reliable answer is usually easy to get with modern computational methods: one simply optimizes the structure at a sufficiently high level and examines the vibrational frequencies (at the same level of course); a real molecule, a relative minimum on the potential energy surface, has all its frequencies real (none of them corresponds to an imaginary number of cm^{-1}) while a transition state or higher-order saddle point has one or more imaginary frequencies [44]. In a worst-case scenario the species may not even be a stationary point; a transition state, on the other hand, may occasionally be separated from proper molecule status just by a change in symmetry or in torsional angle. "A sufficiently high level" is a term not so easy to pin down. A good example of the problems that can arise in seeking to establish the theoretical reality of a species is provided by oxirene (Chapter 3). Calculations at systematically higher levels showed, for the most part, no imaginary frequency, but the fall in the magnitude of the ring-opening vibration with increase in the computational level was disturbing [45, 46]. It is probably true that

a species with no imaginary and no very low (below about $100\,\text{cm}^{-1}$) frequencies at the MP2, B3LYP and, especially, the CCSD(T) levels [47] with a 6-31G* or bigger basis will very likely prove to be a relative minimum (a real molecule). The importance of correlated level calculations in reliably probing the curvature of the potential energy surface (minimum, transition state, or hilltop) has been stressed [48].

(2) *If it can exist, how stable is it?* This is the hardest of the three questions to answer reliably. In principle one computes the energy and frequencies of the reactant and the lowest transition state for unimolecular decomposition and obtains from these data the activation energy of the reaction and from this the rate constant (or, more meaningfully, the halflife of the species) [49]. We are interested here in *kinetic* stability, as it is this, rather than thermodynamic stability (below) that is of prime interest to the synthetic chemist. Many molecules of very low thermodynamic stability have been isolated, particularly with the aid of matrix isolation techniques [50]. Correlated level (e.g. MP2 or DFT) calculations are needed for reasonably accurate results. At the simplest level, the difference in energy of the transition state and the species is the approximate activation energy, which by standard physical chemistry equations provides a rate constant. More reliable results can be achieved with a specialized program which accepts the energies and frequencies and utilizes statistical mechanics RRKM-type theory to calculate a rate constant [51, 52]. In the absence of calculations on the transition state for decomposition, an idea of the stability of the species is afforded by its vibrational frequencies: the absence of low- (below a few hundred cm^{-1}) frequency vibrations corresponding to a decomposition mode suggests substantial stability. This test was used for the stability of azacubanes [53, 54] and N_6 isomers [55, 56, 57] before transition state calculations became routine.

(3) *If it can exist, which is stabler, the tetrahedrane or the cyclobutadiene?* The thermodynamic stability of a synthetic goal is not irrelevant. For example, in those rare cases where the desired species represents the global minimum, isomerization of a prosaic higher-energy molecule may constitute a viable synthesis. Good examples of this are the synthesis of adamantane and related diamond-like polycyclics by the Schleyer group [58]. Even when a desired substance is not actually the global minimum, it may be possible to obtain it by isomerization. Thus, if tetra-*t*-butyltetrahedrane had been the more readily-available of the two, it might have served as a precursor of the cyclobutadiene in a practical synthesis, by virtue of its thermal transformation to the latter (above). A reliable answer to the relative stability question is readily obtained (except of course in borderline cases) merely by comparing the energies of the two species. Again, for a reasonably accurate energy difference correlated level calculations are needed, and although zero-point energies tend to cancel, they are probably best taken into account.

Let us apply these principles to tetra-*t*-butyltetrahedrane, tetrakis(trimethylsilyl) tetrahedrane, and tetrahedrane itself. Unreferenced calculations are by the author, and some of these results are summarized in Table 6.1. Note that calculations designed to address kinetic stability directly, by examining transition states for interconversion of diradicals (below), seem to be limited to the parent molecule.

Table 6.1 Energies from B3LYP/6-31G* calculations on tetrahedranes and cyclobutadienes (by the author, using Gaussian 03). Note that for the tetra-*t*-buty and the tetrakis(trimethylsilyl) systems the tetrahedrane is calculated to lie below the cyclobutadiene in energy, but for the parent molecules the tetrahedrane is calculated to lie above the cyclobutadiene

Tetrahedrane/cyclobutadiene	Energies, hartrees			Energy of tetrahedrane−Energy of cyclobutadiene, hartrees/kJ mol^{-1}		
	Raw ab initio	ZPE-corrected	Sum of electronic and thermal free E	Raw ab initio	ZPE-corrected	Sum of electronic and thermal Free E
tetra-*t*-butyl, tet.	−783.68343	−783.16956	−783.21923			
tetra-*t*-butyl, CBD	−783.68073	−783.16344	−783.21115	−0.00270/−7.1	−0.00612/−16.1	−0.00808/−21.2
tetrakis(trimethylsilyl), tet.	−1789.41042	−1788.93988	−1789.00561			
tetrakis(trimethylsilyl), CBD	−1789.39652	−1788.92483	−1788.98929	−0.01390/−36.5	−0.01505/−39.5	−0.01632/−42.9
parent, tet.	−154.63669	−154.57680	−154.59951			
parent, CBD	−154.67546	−154.61426	−154.63826	0.03877/101.8	0.03746/98.4	0.03875/101.8

Tetra *t*-butyltetrahedrane, B3LYP/6-31G* Calculations

Can it exist at all? This molecule is a potential energy surface minimum. All the frequencies below 500 cm^{-1} correspond to torsional or bending modes of the *t*-butyl groups, rather than involving the tetrahedrane nucleus. Thus higher-level calculations are unlikely to reveal imaginary frequencies, and there was from theory every reason to anticipate that this molecule can exist.

How stable is it? Were high-level calculations possible before the synthesis of this compound (reported in 1978), significant kinetic stability would have been suggested by the above-mentioned absence of low-frequency vibrations corresponding to isomerization. Furthermore, the anticipated corset effect would have been reason to expect greater kinetic stability than for the parent.

Which is stabler, the tetrahedrane or the cyclobutadiene? As mentioned above, B3LYP/6-31G* calculations place the tetrahedrane very slightly lower (5.0 kJ mol^{-1}) than the cyclobutadiene [33]. The possible error in such calculations is considerably bigger than 5 kJ mol^{-1}, so the experimental fact that the tetrahedrane isomerizes thermally to the cyclobutadiene is no surprise. Also, the calculations apply to a gas-phase reaction, but under the experimental conditions a crystal lattice breaks down and reaction occurs in a solution of molten reactant and product.

Tetrakis(trimethylsilyl)tetrahedrane, B3LYP/6-31G* Calculations

Can it exist at all? Like tetra-*t*-butyltetrahedrane this is a potential energy surface minimum and lacks frequencies below 500 cm^{-1} corresponding to vibrations of the tetrahedrane nucleus, indicating (cf. tetra-*t*-butyltetrahedrane, above) a secure minimum. Such calculations would have provided, prior to its synthesis, good evidence that the molecule can exist.

As for tetra-*t*-butyltetrahedrane, the absence of low-energy tetrahedrane-deforming vibrations suggests significant kinetic stability.

As stated above, B3LYP/6-31G* calculations place tetrakis(trimethylsilyl)tetrahedrane about 37 kJ mol^{-1} below the cyclobutadiene [33]. This calculated energy difference would have made one reasonably confident of the greater thermodynamic stability of the tetrahedrane.

The Parent Tetrahedrane, Calculations

Some of the earliest ab initio calculations on tetrahedrane are by Kollmar, who also refers to earlier semiempirical work [59]. Can it exist? B3LYP/6-31G* calculations (e.g. by the author) show a potential energy surface minimum with no vibrations below 500 cm^{-1} for deformation of the C_4 nucleus (in fact no vibrations at all below 500^{-1}). This indicates a robust minimum on the potential energy surface.

As is the case for the two substituted tetrahedranes, the absence of low-frequency vibrations corresponding to a reaction mode indicates for the parent reasonable kinetic stability. More definitive information on this comes from calculations that directly address the energy barriers on the route from tetrahedrane to cyclobutadiene. Maier et al. have reported MP2/6-311G** calculations for this reaction [33]. Their results, summarized in Fig. 6.2, predict that the critical step for the stability of tetrahedrane (**5**) along the path leading to the much lower-energy cyclobutadiene (**19**) (and presumably the critical step for the kinetic stability of tetrahedrane) is not, as might have been expected, cleavage of a CC bond to give a diradical (**17**), but rather conversion of the diradical **17** into the diradical **18.** The designation here of **17** and **18** as *exo, exo* and *endo, endo* follows Lautz[8] and Maier et al. [33], who base it on the orientation of the orbitals rather than the hydrogens (Fig. 6.2). That the diradical **17**, rather than **18**, is the proximate product of ring-opening of tetrahedrane is perhaps counterintuitive, but was supported by IRC [60] calculations.[9] The calculated barrier for this step, the inversion of stereochemistry at the radical centers, was 136 kJ mol^{-1}. If this is indeed a fairly reliable value for the rate-limiting step in the isomerization of **5** to **19**, then tetrahedrane is by no means highly unstable kinetically, and may even be isolable at room temperature![10] Some caution is warranted concerning this MP2 barrier, as the standard method of handling diradicals is by means of CASSCF calculations [61]. The authors were aware of this, and Lautz reported[11] that unrestricted MP2 (UMP2) calculations were done as a check on these restricted MP2 results,[12] with no change in energies, and

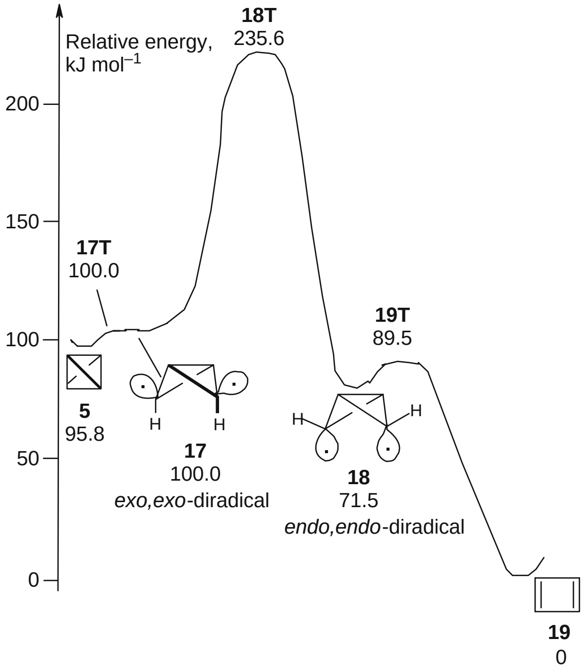


Fig. 6.2 Potential energy surface for isomerization of tetrahedrane (**5**) into cyclobutadiene (**19**), calculated at the MP2/6-311G** level; adapted from Maier et al. The transition-state structures were not depicted [33]. Diradical **17** may not really be an intermediate, so **5** may in fact isomerize directly to **18**

that CASSCF calculations supported the MP2 results; the latter technique, however, was said to be very sensitive to the choice of the active space, and the energies from these attempts were not reported. That cyclobutadiene is thermodynamically much stabler than tetrahedrane is scarcely in doubt: the MP2/6-311G** calculations place the polycycle 96 kJ mol^{-1} higher, and B3LYP/6-31G* concurs, putting it 98 kJ mol^{-1} higher (ZPE corrected energies). However, it is by no means clear that, as has been asserted [28] tetrahedrane has very low kinetic stability. Indeed, recent calculations at several levels (B3LYP and coupled cluster, with reasonably big basis sets) all concur with the above-mentioned results of Maier et al. [33] and Lautz[7] in assigning it a barrier to rearrangement of ca. 130–150 kJ mol^{-1} (this paper also recounts an unsuccessful attempt to make tetrahedrane from cyclopropene and atomic carbon) [62].

Some Calculated Properties of Tetrahedrane

Other than its kinetic and thermodynamic stability (above), several properties of tetrahedrane are of interest, and can be readily calculated by current computational chemical techniques. Here we will look at four: strain, ionization energy, acidity, and basicity.

(1) *Strain*. The idea of molecular strain began as a qualitative notion more than a century ago, providing chemists with an intuitive way to anticipate and rationalize stability and reactivity [63]. Originally formulated for molecules with “abnormally” small bond angles, the concept has been broadened to encompass torsional and steric strain [64]. The basic meaning of the concept of angle strain is well grasped by trying to build a model of a strained molecule with the usual framework-type plastic components (which may not survive the attempt). At the very least, molecular strain is a heuristic which one invokes naturally when considering the chemistry of certain compounds. With the rise of computational chemistry it became possible to assign numbers to strain, that is, to calculate strain energies, for unknown molecules. There are two methods: (a) One is to calculate the heat of formation of the molecule and to compare this with the heat of formation of an imaginary ideal unstrained molecule, this unstrained value being obtained by adding tabulated heats of formation for the groups present. (b) The other method is to use isodesmic-type reactions to break bonds in the molecule giving a strainless, acyclic molecule, and to calculate the energy released in this reaction or sequence of reactions. Examples of method (a) are given in the calculation of strain energies for pyramidane, $C(CH)_4$ (Chapter 2) [65] and of a bevy of unusual-looking molecules [66]. In an extensive series of calculations on strained molecules using the group equivalents approach, Wiberg et al. reported a strain energy of 586 kJ mol^{-1} for tetrahedrane [67]. Using the measured heat of combustion and group equivalents, the strain energy of tetra-*t*-butyltetrahedrane was estimated to be 541 kJ mol^{-1}, and was thought to be about the same as the parent [22].

The use of isodesmic-type reactions (method (b)) to calculate the strain energy of tetrahedrane is shown (calculations by the author); it is instructive to examine the process in stages, opening it to bicyclobutane and then to the angle-strain-free butane. The level is B3LYP/6-31G*, and ZPE is not included:

(1) opening tetrahedrane to bicyclobutane
tetrahedrane [−154.63679]+2 ethane [2(−79.83014)] → bicyclobutane [−155.94805] + butane (C_{2h}, *anti*) [−158.45804]

$$\begin{aligned}\Delta H_1 &= -155.94805 + (-158.45804) - [-154.63679 + 2(-79.83014)] \\ &= -314.40609 - [-314.29707] = -0.10902 = -286.29\,\mathrm{kJ\ mol^{-1}}\end{aligned}$$

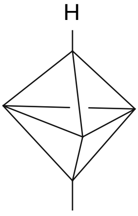
(2) opening bicyclobutane to butane
bicyclobutane [−155.94805] + 4 ethane [4(−79.83014)] → 3 butane [(−158.45804)]

$$\begin{aligned}\Delta H_2 &= 3(-158.45804) - [-155.94805 + 4(-79.83014)] = \\ &= -475.37412 - [-475.26861] = -0.10551 = -277.07\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}\text{So strain energy of bicyclobutane} &= -\Delta H_1 = 277.1\,\mathrm{kJ\ mol^{-1}} \\ \text{and strain energy of tetrahedrane} &= -(\Delta H_1 + \Delta H_2) \\ &= 286.29 + 277.07 = 563.4\,\mathrm{kJ\ mol^{-1}}\end{aligned}$$

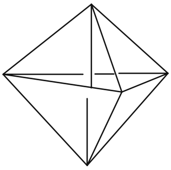
This is not very different from the Wiberg et al. value of 586 kJ $\mathrm{mol^{-1}}$ (above) and in the same range as other calculated values (527–586 kJ $\mathrm{mol^{-1}}$ [68]). It is instructive to compare the strain in tetrahedrane with that in cyclobutane and bicyclobutane. Comparing the strain energy per bond, which affords a fairer comparison than the total strain energy, and using the values in [67], in kJ $\mathrm{mol^{-1}}$: cyclobutane, 110.9/4 = 27.7; bicyclobutane, 267.4/5 = 53.5 kJ $\mathrm{mol^{-1}}$; tetrahedrane, 585.8/6 = 97.6 kJ $\mathrm{mol^{-1}}$. Making a bond in butane to create cyclobutane raises the strain energy per bond from ~ 0 kJ $\mathrm{mol^{-1}}$ to 28 kJ $\mathrm{mol^{-1}}$, making another bond to give bicyclobutane raises the energy per bond by about the same amount, 26 kJ $\mathrm{mol^{-1}}$, but making a third bond to give tetrahedrane raises the strain energy per bond by 44 kJ $\mathrm{mol^{-1}}$. We could thus say that the tricycle is excessively strained compared to cyclobutane and to bicyclobutane.

Tetrahedrane has been said to be “the most highly strained...of the formally saturated hydrocarbons” [22], but it has competition. In an imaginative look at some C_5 molecules, Balaji and Michl (see Chapter 13) suggested that the bicyclobutane derivative **20**, C_5H_2, may be “possibly perfectly stable once isolated in a matrix”, although they conceded that it “will not be an easy target” [66]. The strain energy of **20**, calculated in the same way as was done above for tetrahedrane (reducing **20** to pentane with ten moles of ethane, B3LYP/6-31G*), is 902 $\mathrm{kJ^{-1}}$ (using the HF/6-31G* level and group equivalents, Balaji and Michl obtained 954 $\mathrm{kJ^{-1}}$, which they described as “awesome”). This gives for **20** a strain energy per bond of 902/9 kJ $\mathrm{mol^{-1}}$ = 100 kJ $\mathrm{mol^{-1}}$, compared to the value of above of 97.6 kJ $\mathrm{mol^{-1}}$ for tetrahedrane. The structure **21** obtained by removing two hydrogens from **20** to make another bond is probably even more strained than **20**. It was not a stationary point at the HF/6-31G* level [66], but is at the B3LYP/6-31G* level (author's observation). This structure however is not a hydrocarbon but rather a carbon cluster.



20

C_5H_2 C_{2v}



21

C_5 D_{3h}

(2) *Ionization energy (IE) (or ionization potential)*. This is the energy needed to remove an electron from a molecule and away to infinity. There are two kinds of IE: the vertical IE, the energy difference between the neutral molecule and the ionized molecule at the geometry of the neutral, and the adiabatic IE, the energy difference between the neutral molecule and the ion at the equilibrium geometry (the relaxed geometry) of the ion. Here we will consider only the vertical IE, because this does not require consideration of the equilibrium geometry of the ion, which may be quite different from that of the neutral precursor, and because it is more of an intrinsic property of the molecule – indeed, the IE is approximately the negative of the energy of the highest-occupied molecular orbital (HOMO; Koopmans' theorem) [69, 70, 71]. The vertical IE can be calculated simply as the calculated energy of the ion at the geometry of the neutral minus the calculated energy of the neutral. Comparing the vertical IE of tetrahedrane, from the energy difference method and from Koopmans' theorem, using the MP2/6-31G* geometry (use of a B3LYP geometry for Koopmans' theorem would raise the problem of the meaning of the Kohn-Sham orbitals used in current DFT calculations) [72]; we ignore ZPE as this is not applicable to a nonstationary point on the potential energy surface, like the cation at the neutral geometry:

neutral tetrahedrane	– 154.10772 hartrees
cation at neutral geometry	– 153.79324 hartrees
HOMO energy of neutral	– 8.99 eV

From the cation/neutral energy difference, IE = 0.31448 hartrees = 8.56 eV.
From the HOMO of the neutral (Koopmans' theorem), IE = 8.99eV.

At the MP2/6-31G* level, energy difference calculations tend to underestimate IEs by 0.1–0.7 eV [73] and Koopmans' theorem to overestimate them by 1–1.5 eV, and to be fairly approximate [74]. Thus the IE of tetrahedrane is likely ca. 8.6 eV. Typical IEs of strained cycloalkanes are ca. 8.6 eV (for cubane, cf. 9.9 eV for cyclohexane) [75], so like another exotic cycloalkane, pyramidane (Chapter 2), tetrahedrane

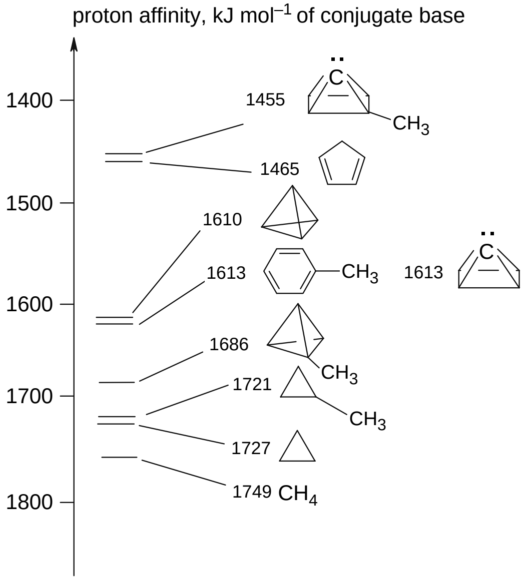


Fig. 6.3 Acidities of some hydrocarbons, calculated by the CBS-4 M method. These are 0 K enthalpy differences between the hydrocarbon and its conjugate base. CBS-4 calculations (CBS-4 M in Gaussian 03). For molecules with methyl groups, the proton loss is from the methyl group. Methane is of extremely low acidity, cyclopentadiene is fairly acidic for a hydrocarbon

appears to have about the IE expected for a strained alkane. The molecular orbitals of tetrahedrane and tetra-*t*-butyltetrahedrane have been analyzed [76].

(3) *Acidity*. By this we mean here the ability of a molecule to donate a proton to a base. We can compare acidities simply by taking the difference in enthalpy of products and reactants for $MH \rightarrow M^- + H^+$. For perspective, some calculated hydrocarbon acidities are given in Fig. 6.3. These are 0 K enthalpy changes, calculated by the CBS-4 method [77], using the CBS-4 M implementation in Gaussian 03.[13] Tetrahedrane (enthalpy change 1610 kJ mol^{-1}) is calculated to be moderately acidic: less acidic than cyclopentadiene (1465 kJ mol^{-1}) but more so than toluene (1613 kJ mol^{-1}), and much more acidic than cyclopropane (1727 kJ mol^{-1}). A calculated (B3LYP/6-311++G**) value of 1621 kJ mol^{-1} has been reported [78]. The somewhat high acidity is readily rationalized as a consequence of the high s character of the exocyclic carbon orbitals (used to bond hydrogen): in the parent tetrahedrane these were calculated to be sp$^{1.46}$ (41% s-character), and the experimental (from NMR coupling) hybridization of the exocyclic orbitals in the tetra-*t*-butyl and tetrakis(trimethylsilyl) derivatives is ca. sp (about 50%) and sp$^{1.16}$ (46%), respectively [33], compared to a canonical tetracoordinate carbon which is sp^3 (25% s character). The exocyclic cyclopropane orbitals have 33% s character [79].

(4) *Basicity*. Computational studies indicate that protonation of tetrahedrane would lead to the homocyclopropenyl cation, the stability of which, taken with the release of the great strain in tetrahedrane, results in a big enthalpy drop. This was calculated (B3LYP) to correspond to a proton affinity of 1053 kJ mol^{-1} (298 K enthalpy of reaction) [80]. A CBS-4 M (cf. Tetrahedrane Acidity above) calculation by the author gave a value of 1004 kJ mol^{-1}. The gas-phase basicity

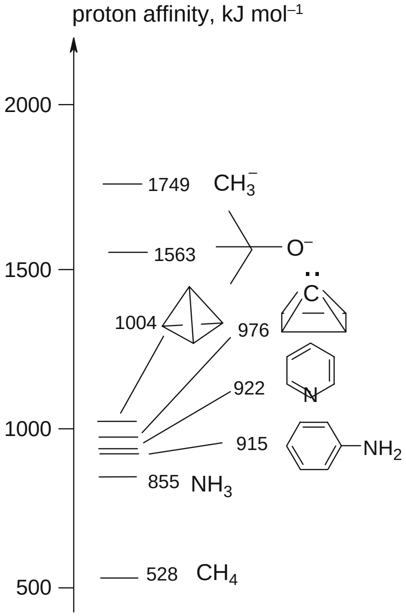
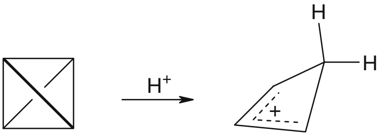


Fig. 6.4 Basicities of some compounds, calculated by the CBS-4 M method. These are 0 K enthalpy differences between the hydrocarbon and its conjugate base. CBS-4 calculations (CBS-4 M in Gaussian 03). Methane is of extremely low basicity, the methyl anion is of extremely high basicity



of tetra-*t*-butyltetrahedrane, measured by Fourier-transform mass spectrometry, is 1035 kJ mol^{-1} [81]. Some basicities are shown in Fig. 6.4. With an enthalpy change of 1004 kJ mol^{-1}, tetrahedrane is calculated to be somewhat more basic than pyridine; this is quite basic for a hydrocarbon.

Synthesis

The synthesis of the parent tetrahedrane must be considered an enormous challenge, in view of the tremendous but thwarted effort expended by the Maier group to this end, but their great success in obtaining several substituted tetrahedranes indicates the quest is by no means hopeless (e.g. Note 4). It is the kinetic stability of tetrahedrane that concerns us here, for no one would expect it to be the global minimum on the C_4H_4 potential energy surface. The indication from computational studies (presented above, *The Parent Tetrahedrane*, *Calculations*) is that the critical step in what is probably the most facile isomerization route for the molecule, conversion to cyclobutadiene, is inversion of the *exo/exo* diradical to the *endo/endo* one (Fig. 6.2), or possibly the direct conversion of tetrahedrane to the *endo/endo* diradical. If this calculated potential energy surface is even roughly correct, then tetrahedrane should be isolable, possibly at room temperature. The problem with synthesizing it, then, may have nothing to do with its instability, but rather simply (!) with finding the right route to it. At present the most promising approach seems to be via tetrakis(trimethylsilyl)tetrahedrane [32, 33]. The theoretical possibility of replacing the electropositive trimethylsilyl groups by hydrogen was recognized by Maier et al. [32] and partially realized in practice by Sekiguchi and Tanaka in their preparation of the monolithium derivative and its protonation to give tris(trimethylsilyl)tetrahedrane [41]. The synthesis of this compound and its stability are of good augur for a successful denouement to the tetrahedrane odyssey.

Notes

1. The platonic solids (the regular solids, regular polyhedra) are the only convex polyhedra with equivalent convex regular polygons as faces. They are the building blocks of the universe in Plato's theory of five elements (in the *Timaeus*), and are examined in Euclid's *Elements*.
2. Octahedrane does not seem to be a stationary point (minimum, transition state, or higher-order saddle point) at the HF/6-31G*, MP2/6-31G* or 3LYP/6-31G* levels.
3. The syntheses [4, 5] and [6] above are discussed and variations and improvements on them are referenced in H. Hopf, "Classics in Hydrocarbon Chemistry", Wiley-VCH, Weinheim, New York, 2000; pp. 60–63.
4. Ref. [33], refs. 20–23.
5. Ref. [22], ref. 19.
6. Ref. [41], ref. 4.
7. See Note 4.
8. C. Lautz, Ph.D. thesis, Department of Chemistry, Justus-Liebig University, Giessen, Germany. The calculations reported in [33] are from this thesis; see Footnote 29 in [33].
9. See Note 8.
10. The borderline barrier for being isolable at room temperature is ca. 100 kJ mol^{-1} for unimolecular reactions: some barriers/room temperature halflives: (a) Decomposition of pentazole and its conjugate base (estimated): 75 kJ mol^{-1}/10 minutes and 106 kJ mol^{-1}/2 days, respectively. V. Benin, P. Kaszynski, J. G. Radziszki, J. Org. Chem., 2002, *67*, 1354. (b) Decomposition of $(CF_3CO)OOO(COCF_3)$: 86.5 kJ mol^{-1}/1 minute. S. v. Ahsen, P. Garciá, H. Willner, M. B. Paci, G. Argüello, Chem. Eur. J., 2003, *9*, 5135.
11. See Note 8.
12. Other examples of using UMP2 calculations in cases where singlet diradicals may be involved are: (a) T. Ströter, G. Szeimies, J. Am. Chem. Soc., 1999, *121*, 7476. (b) T. Ströter, O. Jarosch, G. Szeimies, Chem. Eur. J., 1999, *5*, 1422.
13. Gaussian 03, Revision B.05, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Lyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth,

P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, 2003.

References

1. K. C. Thompson, D. L. Crittenden, M. J. T. Jordan, J. Am. Chem. Soc., 2005, *127*, 4954.
2. P. M. Esteves, G. G. P. Alberto, A. Ramírez-Solís, C. J. A. Mota, J. Am. Chem. Soc., 1999, *121*, 7345.
3. R. N. Grimes, “Advanced Inorganic Chemistry”, F. A. Cotton, G. Wilkinson, C. A. Murillo, M. Bochmann, eds., Wiley, New York, 1999; Chapter 5.
4. P. E. Eaton, T. W. Cole, Jr., J. Am. Chem. Soc., 1964, *86*, 962.
5. P. E. Eaton, T. W. Cole, Jr., J. Am. Chem. Soc., 1964, *86*, 3157.
6. J. C. Barborak, L. Watts, R. Pettit, J. Am. Chem. Soc., 1966, *88*, 1328.
7. R. J. Ternansky, D. W. Balogh, L. A. Paquette, J. Am. Chem. Soc., 1982, *104*, 4503.
8. L. A. Paquette, R. J. Ternansky, D. W. Balogh, G. Kentgen, J. Am. Chem. Soc., 1983, *105*, 5446.
9. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; pp. 63–75.
10. W. Grahn, Chemie in unserer Zeit, 1981, *15*, 52.
11. A. v. Baeyer, Chem. Ber., 1885, *18*, 2269.
12. R. M. Beesley, J. F. Thorpe, Proc. Chem. Soc., 1913, *29*, 346.
13. R. M. Beesley, J. F. Thorpe, J. Chem. Soc., 1920, *117*, 591.
14. K. B. Wiberg, Acc. Chem. Res., 1996, *29*, 229.
15. H. O. Larson, R. B. Woodward, Chem. Ind., 1959, 193.
16. H. O. Larson, Ph.D. Thesis, “Part I: A reinvestigation of Thorpe’s synthesis of bicyclobutane derivatives. Part II: The synthesis of 3′,8-dimethyl-1,2-cyclopentenophenanthrene.” Harvard, 1950.
17. M. B. Goren, E. A. Sokoloski, H. M. Fales, J. Org. Chem., 2005, *70*, 7429.
18. G. Maier, S. Pfriem, U. Schäfer, R. Matusch, Ang. Chem. Int. Ed., 1978, *17*, 520.
19. G. Maier, S. Pfriem, U. Schäfer, K.-D. Malsch, R. Matusch, Chem. Ber., 1981, *114*, 3965.
20. H. Irngartinger, M. Riegler, K.-D. Malsch, K.-A. Schneider, G. Maier, Angew. Chem. Int. Ed. Engl., 1980, *19*, 211.
21. E. Heilbronner, T. B. Jones, A. Krebs, G. Maier, K.-D. Malsch, J. Rocklington, R. Schmelzer, J. Am. Chem. Soc., 1980, *102*, 564.
22. G. Maier, Angew. Chem. Int. Ed. Engl., 1988, *27*, 309.
23. H. Irngartinger, A. Goldmann, R. Jahn, M. Nixdorf, H. Rodewald, G. Maier, K.-D. Malsch, R. Emrich, Angew. Chem. Int. Ed. Engl., 1984, *23*, 993.
24. M. Balci, M. L. McKee, P. v. R. Schleyer, J. Phys. Chem. A, 2000, *104*, 1246.
25. G. Maier, H. Rang, R. Emrich, Liebigs Ann. Chem., 1995, (1), 153.
26. G. Maier, F. Fleischer, Liebigs Ann. Chem., 1995, (1), 169.
27. G. Maier, F. Fleischer, Tetrahedron Lett., 1991, *32*, 57.
28. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; pp. 54–60.
29. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; p. 76, ref. 12.
30. N. C. Baird, M. J. S. Dewar, J. Am. Chem. Soc., 1967, *89*, 3966.
31. N. C. Baird, Tetrahedron, 1970, *26*, 2185.

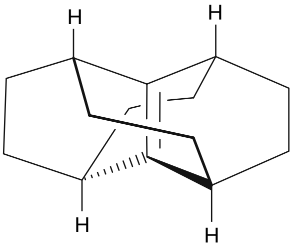
32. G. Maier, J. Neudert, O. Wolf, Angew. Chem. Int. Ed. Engl., 2001, *40*, 1674.
33. G. Maier, J. Neudert, O. Wolf, D. Pappusch, A. Sekiguchi, M. Tanaka, T. Matsuo, J. Am. Chem. Soc., 2002, *124*, 13819.
34. A. Sekiguchi, M. Tanaka, T. Matsuo, H. Watanabe, Angew. Chem. Int. Ed. Engl., 2001, *40*, 1675.
35. J. D. Dill, A. Greenberg, J. F. Liebman, J. Am. Chem. Soc., 1979, *101*, 6814.
36. T. Clark, G. W. Spitznagel, R. Klose, P. v. R. Schleyer, J. Am. Chem. Soc., 1984, *106*, 4412.
37. D. Cremer, E. Kraka, J. Am. Chem. Soc., 1985, *107*, 3811.
38. G. Maier, D. Born, Angew. Chem. Int. Ed. Engl., 1989, *28*, 1050.
39. D. A. Ponomarev, V. V. Takhistov, J. Chem. Ed., 1997, *74*, 201.
40. M. K. Cyranski, Chem. Rev., 2005, *105*, 3773.
41. A. Sekiguchi, M. Tanaka, J. Am. Chem. Soc., 2003, *125*, 12684.
42. M. Tanaka, A. Sekiguchi, Angew. Chem. Int. Ed. Engl., 2005, *44*, 5821.
43. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; section 7.3.1.
44. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 2.
45. G. Vacek, J. M. Galbraith, Y. Yamaguchi, H. F. Schaefer, R. H. Nobes, A. P. Scott, L. Radom, J. Phys. Chem., 1994, *98*, 8660.
46. G. Vacek, B. T. Colegrove, H. F. Schaefer, Chem. Phys. Lett., 1991, *177*, 468.
47. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapters 5 and 7.
48. A. I. Boldyrev, P. v. R. Schleyer, D. Higgins, C. Thomson, S. S. Kramarenk, J. Comp. Chem., 1992, *9*, 1066.
49. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; section 5.5.2.3a.
50. R. S. Sheridan, Org. Photochem., 1987, *8*, 159.
51. J. M. Martell, P. T. Beaton, B. E. Holmes, J. Phys. Chem. A, 2002, *106*, 8471.
52. M. P. McGrath, F. S. Rowland, J. Phys. Chem. A, 2002, *106*, 8191.
53. R. Engelke, J. Am. Chem. Soc., 1993, *115*, 2961.
54. R. Engelke, J. Org. Chem., 1992, *57*, 4841.
55. R. Engelke, J. Phys. Chem., 1992, *96*, 10789.
56. R. Engelke, J. R. Stine, J. Phys. Chem., 1990, *94*, 5689.
57. R. Engelke, J. Phys. Chem., 1989, *93*, 5772.
58. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; Chapter 3.
59. H. Kollmar, J. Am. Chem. Soc., 1980, *102*, 2617.
60. J. B. Foresman, A. Frisch, “Exploring Chemistry with Electronic Structure Methods”, Second Edn., Gaussian Inc., Pittsburgh, 1996; Chapter 8.
61. J. B. Foresman, A. Frisch, “Exploring Chemistry with Electronic Structure Methods”, Second Edn., Gaussian Inc., Pittsburgh, 1996; Chapter 9.
62. A. Nemirowski, H. P. Reisenauer, P. R. Schreiner, Chem. Eur. J., 2006, *12*, 7411.
63. A. Baeyer, Ber., 1885, *18*, 2269.
64. M. B. Smith, K. March, “March’s Advanced Organic Chemistry”, Wiley, New York, 2001; pp. 180–191.
65. E. Lewars, J. Mol. Struct. (Theochem), 2000, *507*, 165.
66. V. Balaji, J. Michl, Pure Appl. Chem., 1988, *60*, 189.
67. K. B. Wiberg, R. F. W. Bader, C. D. H. Lau, J. Am. Chem. Soc., 1987, *109*, 985.
68. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; p. 76, Ref. 9.
69. T. Koopmans, Physica, 1934, *1*, 104.
70. Z. B. Maksic, R. Vianello, J. Phys. Chem., 2002, *106*, 6515.
71. C. Angeli, J. Chem. Educ., 1998, *75*, 1494.
72. R. Stowasser, R. Hoffmann, J. Am. Chem. Soc., 1999, *121*, 3414.
73. J. E. Lyons, D. R. Rasmussen, M. P. McGrath, R. H. Nobes, L. Radom, Ang. Chem. Int. Ed. Engl., 1994, *33*, 1667.
74. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; p. 313.

75. NIST website:http://webbook.nist.gov/chemistry/
76. P. Rademacher, Chem. Rev., 2003, *103*, 933.
77. J. W. Ochterski, G. A. Petersson, J. A. Montgomery, J. Chem. Phys., 1996, *104*, 2598.
78. I. Alkorta, J. Elguero, Tetrahedron, 1997, *53*, 9741.
79. F. J. Weigert, J. D. Roberts, J. Am. Chem. Soc., 1967, *89*, 5962, and refs. therein.
80. R. Notario, J. Elguero, J. Chem. Soc. Chem. Commun., 1995, (15), 1543.
81. R. Notario, O. Castaño, J. L. Andrés, J. Elguero, G. Maier, C. Hermann, Chem. Eur. J., 2001, *7*, 342.

Chapter 7
Orthogonene

Introduction

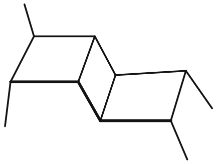
We have examined planar carbon, pyramidal carbon, and strained tetracoordinate carbon (Chapters 1, 2, and 6, respectively). In this chapter we look at "twisted carbon"; more precisely, at highly twisted double bonds. We focus here on the orthogonene molecule **1**:



1

Ideally, this should have a (formal?) double bond twisted through 90° by the rigid scaffolding and exhibit D_{2d} symmetry. The molecule was conceived by Maier and Jeffrey, who examined it theoretically [1] and actually tried to synthesize it, a somewhat rare act of daring in this field [2]. Orthogonene has, in principle, the stereoisomers **1**–**6**, which are shown in Fig. 7.1 using a schematic representation. In isomer **1** all the bridgehead C–H bonds point outward (away) from the molecule, which can be labeled (Fig. 7.1) *oo,oo* (or all-out). In **2** one of these bonds points inward (toward) the molecule, which we can label *io,oo*, and so on. In this notation the stereochemistry at the two ends of the double bond is separated by a comma, and *i* precedes *o*, alphabetically. To be systematic, the structures are drawn with any *in* C–H bonds preferentially at the top left and bottom front (above the plane of the paper), see e.g. *io,io*. The stereochemical situation is somewhat akin to that in the ladderane **7** [3, 4] (an *io,oo* isomer is shown).

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_7,



7

For consistency, for all the structures in Fig. 7.1 the symmetry shown is based on molecular mechanics (MM) and AM1 calculations (for **6** the two methods gave different symmetries) on actual orthogonene structures, and as a very rough indication of relative stability the AM1 heats of formation are given. Interestingly, by this criterion the stabilities appear to decrease monotonically with increasing numbers of *in* C–H bonds. The attempt to compute the *ii,io* isomer **5** led to rearrangement and loss of the orthogonene structure. Higher-level calculations (below) indicate that **1** [5] has at most the D_2 symmetry given by the MM and AM1 calculations rather than the ideal D_{2d} one, and that **4** [6] has C_2 rather than the C_{2v} symmetry given in Fig. 7.1, because of departures of the twist angle from 90°. The chemical and physical properties that a very large twist angle may engender are fascinating to contemplate. We shall examine here isomer **1**, because it is very likely the stablest

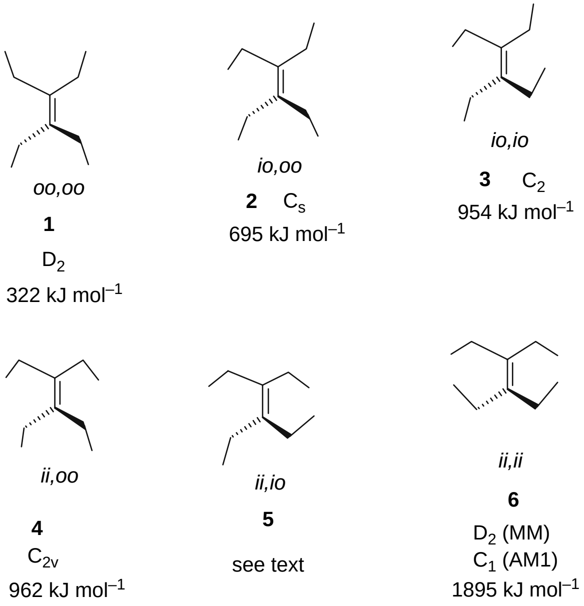
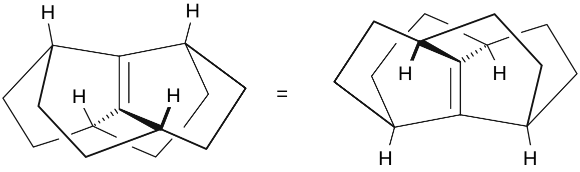


Fig. 7.1 Schematic drawings of the possible (in principle) orthogonenes (ignoring enantiomers). The symmetries are based on molecular mechanics and AM1 calculations and the heats of formation on AM1 calculations. Isomer **5** rearranged on attempted optimization by molecular mechanics and by AM1. See text for *oo,oo* etc

one, and, peripherally, isomer **4**, because it was the first orthogonene to be studied by reasonably high-level methods.



4

Orthogonenes 1 and 4

The standard ab initio or DFT methods [7] used to treat most novel molecules (semiempirical methods [8], because of their extensive parameterization, based on conventional molecules, cannot reliably handle exotic molecules) utilize the assumption that each occupied molecular orbital (MO) contains two paired electrons (restricted HF, MP2, etc. for closed-shell species) or that (usually one) MO holds a single electron (unrestricted HF, MP2, etc. for radicals). These calculations can usually be done in an essentially algorithmic way, using as input a guess structure with standard keywords, optimizing to a stationary point, and examining the result with regard to geometry, frequencies, and other parameters. This is of course an oversimplification, as a reasonably comprehensive study would require judicious selection of one or more levels of calculation, and some exploration of the potential energy surface [9] to probe the relative stabilities of isomers and possible reaction pathways. Nevertheless, the calculations usually execute relatively straightforward "off-the-shelf" algorithms, and in this spirit were called *model chemistries* by that pioneer of practical ab initio calculations, John Pople [10]. A relatively small but by no means unimportant class of molecules possesses a pair of occupied orbitals each with one electron, the spins being mutually opposite. These are *open-shell singlets*, with two unfilled orbitals and singlet multiplicity. Standard model chemistry methods calculate a wavefunction represented by a single determinant composed of spin orbitals derived from doubly-occupied spatial orbitals (for radicals, from doubly-occupied and a singly-occupied spatial orbital, or from two sets of spatial orbitals, one for spin alpha and one for spin beta electrons) [11, 12]. Such methods cannot treat open-shell singlets properly. Recently, attempts have been made to develop DFT-based model chemistries for open-shell singlets, but these are still in a nascent state [13, 14, 15, 16, 17, 18]. In fact, with orthogonene some of these gave unrealistic results, namely a barrier to rearrangement (below) of about 1000 kJ mol^{-1}. For these reasons, **1** was studied with the standard method for open shell singlets, the CASSCF (complete active space self-consistent field) method.

In CASSCF, one chooses a set of electrons contained in a set of occupied and unoccupied orbitals which are called the active space [19, 20]. By promoting electrons from the occupied to the unoccupied MOs of the active space a limited form of configuration interaction (CI) is attained (full CI with a big enough basis set would essentially solve the Schrödinger equation for any molecule[1]). Orthogonene **1** was examined by CASSCF, focusing on the rearrangement in Fig. 7.2. Here a bond migrates relieving strain in the twisted double bond and converts the alkene into a carbene. For a CASSCF calculation on this reaction, the minimum number of electrons is the two pairs in the migrating bond C1C5 bond and the two pairs in the double bond, which become a lone pair in the carbene. The minimum active space is composed of the C1C5σ orbital, the C1C2π orbital, and, to excite the electrons into, the corresponding σ* and π* orbitals. This combination of four electrons and four orbitals corresponds to CASCF(4,4) calculation. A (4,4) calculation is not *mandated*, however, because we might have chosen another active space, particularly in less clear-cut cases. Furthermore, the construction and identification of

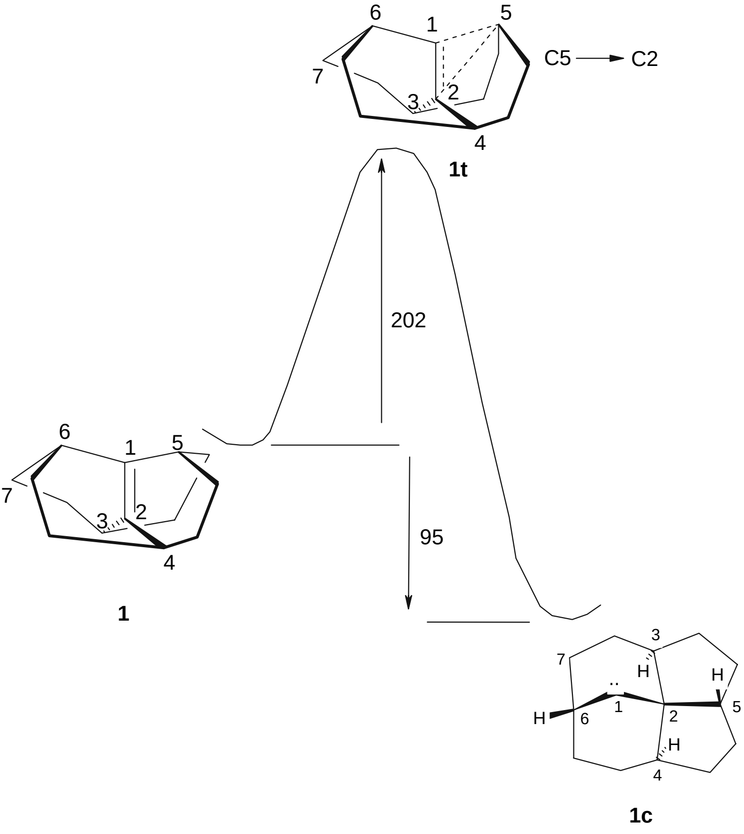


Fig. 7.2 Postulated rearrangement of orthogonene **1** to a carbene. Migration of bond C1–C5 from C1 to C2 through transition state **1t** gives carbene **1c**. The reaction profile, showing activation and reaction energies in kJ mol^{-1}, was calculated by CASMP2/6–31G*//CASSCF(4,4)/6–31G* (see text)

localized orbitals from the delocalized MOs of a molecular orbital calculation can be tricky. Because of these ambiguities a CASSCF calculation is not automatic and straightforward, and thus CASSCF is not a model chemistry. In fact, those who would venture into this field have been warned that “designing and completing these calculations successfully will require considerable care and patience”[2] One might better regard this caveat as a challenge rather than a deterrent.

The result of CASMP2/6–31G*//CASSCF(4,4)/6–31G* calculations on **1** is shown in Fig. 7.2 [5]. These calculations used CASSCF(4,4)/6–31G* geometries to calculate CASMP2/6–31G* energies. The CASMP2 calculations takes into account *dynamic* electron correlation, which is somewhat neglected in the CASSCF(4,4)/6–31G* geometry optimization, which treats the *static* electron correlation of singlet diradicals[3] Orthogonene **1** is predicted to isomerize to a carbene **1c** through a transition state **1t**, with an activation enthalpy of 202 kJ mol^{-1} and a reaction enthalpy of 95 kJ mol^{-1}. This reaction was chosen for study because by analogy with other twisted alkenes (which were not isolated) [21, 22] it is probably the lowest unimolecular reaction pathway available for orthogonene. If the calculated barrier is even roughly correct, this is a remarkable prediction, because the threshold barrier for being isolable at room temperature is, from experience, about 100 kJ mol^{-1}.[4] These calculations thus suggest that **1** cannot only be synthesized, but that it may even be isolable at room temperature!

We can get an idea of the predicted stability of **1** compared to that of isomer **4**, although **4** has not been studied with the CASSCF method. First, that DFT (B3LYP/6–31G*) calculations place **4** 480 kJ mol^{-1} above **1** indicates that **4** is a high-energy species compared to **1**: although this method may not be able to handle well species with singlet diradical character, a *comparative* assessment is probably not far off (note too that the AM1 energies of Fig. 7.1 place **4** 640 kJ mol^{-1} above **1**). Second, these DFT calculations predict for **4** a barrier for rearrangement to a carbene (cf. Fig. 7.2) of about 1 kJ mol^{-1}, but for **1** a barrier of about 120 kJ mol^{-1}, which is considerably lower than, but not wildly different from, the CASSCF result [6]. From now on we will consider only isomer **1**.

The CASSCF calculations [5] indicate some interesting structural features and properties for **1.** The molecule appears to have only C_1 symmetry (Fig. 7.3), but it is not clear if the uneven bond lengths are really uneven due to a Jahn-teller type distortion [23, 24, 25, 26, 27] or if this is just an artifact of the optimization method. The compound is predicted to have a twist angle of 88°, and consonant with this the calculated CC double bond length is 1.453 Å, only a little shorter than the central CC bond length of 1,3-butadiene (1.48 Å), which has little or no π character [28], and the CC bond has CASSCF stretching frequencies of 1499–1519 cm^{-1} (coupled in various ways to CH bending modes). By comparison, tetramethylethylene was calculated at the same level to have a double bond length of 1.350 Å and a stretching frequency of 1815 cm^{-1}. Tetraalkyl alkenes absorb in the IR near 1650 cm^{-1}, so a stretching frequency of ca. 1650/1815(1510) cm^{-1} = 1374 cm^{-1} is expected for **1**; this may be hard to detect in the IR because of the symmetry of the molecule, but it should be visible in the Raman spectrum. The calculations indicate that **1** has only a formal double bond: the strong twist has essentially uncoupled the p atomic orbitals

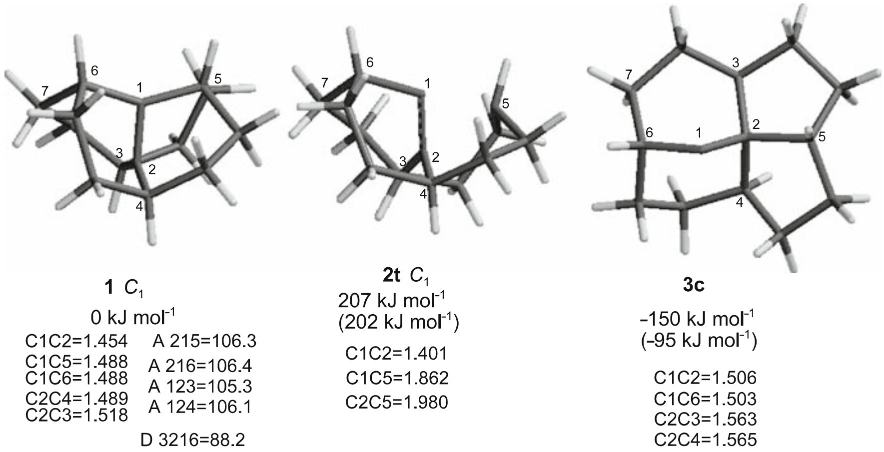


Fig. 7.3 The CASSCF(4,4)/6–31G*-calculated geometries of orthogonene (**1**), the transition state leading to the carbene (**2**), and the carbene (**3**). Bond lengths are in Å and angles in degrees

of the adjacent carbons. In this light the high predicted barrier to rearrangement is surprising. The vertical ionization energy of **1** is calculated (by comparing the energies of 1 and its radical cation at the same geometry) to be only 5.3 eV. This is extraordinarily low for a hydrocarbon (typically alkenes have an IE of 8.3–8.8 eV [29]), and resembles rather the IEs of alkali metals like lithium and sodium. This is consistent with the presence of uncoupled p electrons which should be more weakly bound than bonding electrons, and is similar, for the same reason, to the low IE calculated for the hypothetical planar carbon molecules of Chapter 1.

Synthesis

The route shown here (Fig. 7.4) was recently suggested (private communication) by professor David Jeffrey of the department of chemistry and biochemistry of Kennesaw State University (Georgia, USA), as a possibly more successful alternative to the Jeffrey-Maier route [1] of 1985. The reactions, concepts and potential reagents involved in this discussion are familiar to synthetic organic chemists and will not be referenced here. In the scheme outlined, one starts with 1,5-cyclooctadiene, **1s**, and effects transannular functionalization to **2s** which is converted to **3s**, a cyclooctane ring bearing 1,5- a protected alcohol and an organometallic functionality. Nucleophilic attack of the carbanionic center on a suitable C6 synthon and oxidation of the latent alcohol to a ketone gives **4s**, which has all the carbons needed for **1** and falls short of its connectivity by only three CC "clicks". Successive nucleophilic attack by α-carbons of **4s** on the bromine-bearing carbons gives **5s** and then **6s** (the numbering is simply to show the relationship of **6s** to **1**). Joining C1 and C14 of **6s** by a (formal) double bond yields **1.** Jeffrey's clever proposal has the advantages that it starts with the inexpensive 1,5-cyclooctadiene, the C_6 sidechain

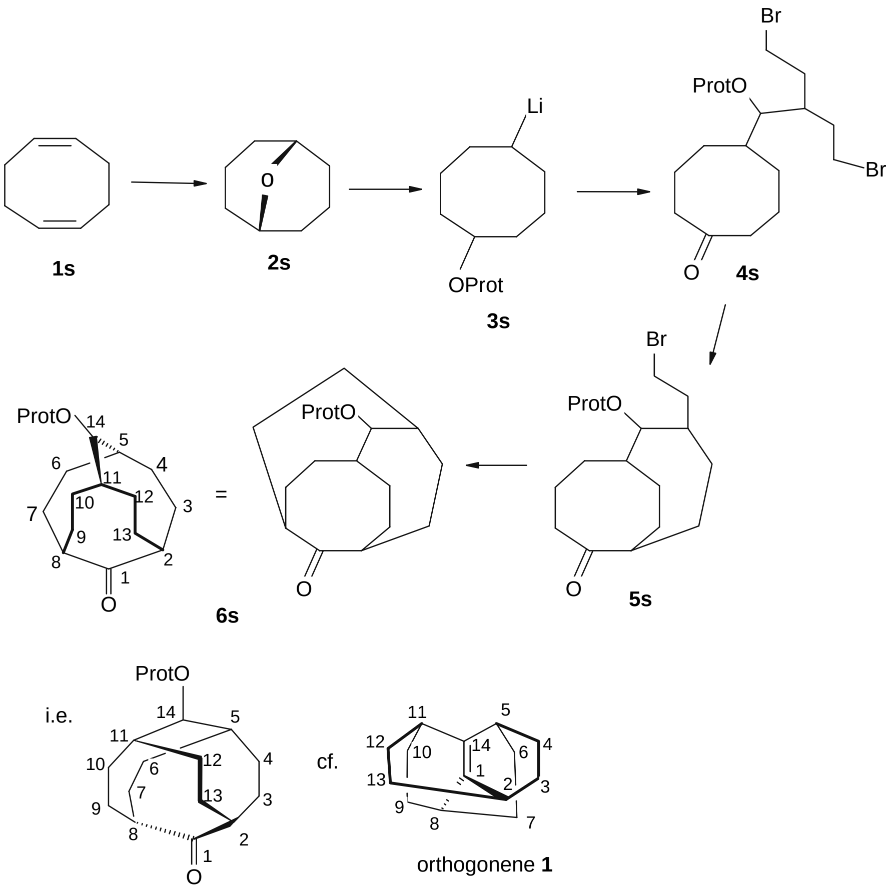
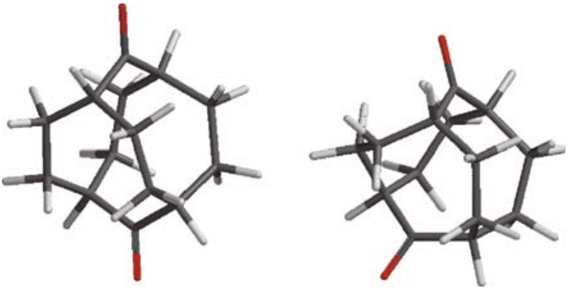


Fig. 7.4 A proposed synthesis of orthogonene **1**. Connecting C1 and C14 is addressed in connection with Fig. 7.5

of **4s** is likely not to demand anything exotic for its fabrication, and all but one of the steps calls on known kinds of reactions. All but one: uniting C1 and C14 to give orthogonene appears challenging, because of the separation of the centers and the strain that seems likely to be incurred in connecting them. Let us consider the possibility of converting the alcohol **7** (not shown) from the protected alcohol **6s** to a diketone and joining C1 and C14; reactions are known which couple two ketone groups to create an alkene. Figure 7.5 shows the structure of two conformations of the diketone; **8a** has D_{2d} symmetry and **8b** C_2 symmetry; AM1 calculations place **8b** 42 kJ mol^{-1} below **8a**. In **8b** the carbonyl carbons are closer than in **8a** (4.264 Å cf. 3.756 Å), but a space-filling representation (with obscuring atoms removed) shows the van der Waals surfaces only barely touching. No doubt they could be squeezed closer, but at the expense of increased strain. Of course there are potential routes from **6s** to **1** which do not go through diketone **8**, but these appear to involve the



8a **8b**

Fig. 7.5 Two conformations of a potential diketone precursor of orthogonene **1**; see discussion in *Synthesis* section

kinds of problems just alluded to, and may also encounter other difficulties. For example, C14 of **6s** might be convertible to a phosphorane carbon C=PR_3, and from thence an intramolecular Wittig reaction with C1 attempted, but the framework flanking C1 and C14 would prevent formation of an oxaphosphacyclobutane which normally collapses to an alkene and a phosphine oxide. Maybe the best route would be via the diketone **8**, possibly through a bis(diazo) compound which on photolysis could afford **1** perhaps, but not necesarily, by way of a dicarbene. The possibility of circumventing the strain problem by generating a high-energy photoexcited intermediate state in this approach renders it attractive, on paper at least, if not at the bench.

Conclusions

Various calculations suggest that the orthogonene stereoisomer with the four bridgehead CH bonds pointing “outward” from the molecule is probably the stablest one. CASSCF calculations indicate that what is likely its lowest-energy isomerization pathway, isomerization to a carbene by CC bond migration, must surmount a barrier of ca. 200 kJ mol^{-1}, which corresponds to a substantial halflife, perhaps days or more, at room temperature. A potentially practical synthesis of orthogonene was suggested (by D. Jeffrey).

Notes

1. See e.g. Ref. [11, p. 8].
2. Ref. [20, p. 229].
3. All molecules with more than one electron experience *dynamic electron correlation*; the choice of the term is self-evident: each electron sees each other electron as a moving particle to be avoided. Some molecules have highest-occupied MOs of equal or nearly equal energy, each with one electron, and so require a computational approach in which the electrons are not taken to be paired in spatial MOs; these molecules experience *static electron correlation*, so-called possibly

because like dynamic correlation it requires going beyond the simplest ab initio method, the Hartree-Fock method, with static being used to contrast the cause of the phenomenon with the case of simple electron avoidance. See C. J. Cramer, "Essentials of Computational Chemistry", Wiley, New York, 2002; Chapter 7.

4. Some barriers/room temperature halflives for unimolecular reactions: (a) Decomposition of pentazole and its conjugate base: 75 kJ mol^{-1}/10 minutes and 106 kJ mol^{-1}/$\frac{1}{2}$ days, respectively. V. Benin, P. Kaszynski, J. G. Radziszki, J. Org. Chem., 2002, *67*, 1354. (b) Decomposition of $CF_3CO)OOO(COCF_3)$: 86.5 kJ mol^{-1}/1 min. S. v. Ahsen, P. Garciá, H. Willner, M. B. Paci, G. Argüello, Chem. Eur. J., 2003, *9*, 5135.

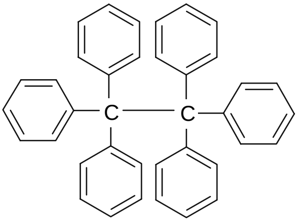
References

1. D. A. Jeffrey, *Synthetic Approaches Toward Orthogonene. II. Calculational Studies of Simple Fulvenes and Fulvalenes.* Ph.D. Dissertation. University of California, Berkeley, 1985. Univ. Microfilms Int., order No. DA8524999. Dist. Abstr. Int. B, **1986**, *46*(9), 3054.
2. D. A. Jeffrey, W. F. Maier, Tetrahedron, 1984, 40, 2799.
3. X. Gao, T. Friščić, L. R. MacGillivray, Angew. Chem. Int. Ed. Engl., 2003, *43*, 232.
4. W. Li, M. A. Fox, J. Am. Chem. Soc., 1996, *118*, 11752.
5. E. G. Lewars, J. Phys. Chem., 2005, *109*, 9827.
6. E. Lewars, Can. J. Chem., 2003, *81*, 1119.
7. E. Lewars, "Computational Chemistry", Kluwer, Boston, 2003; Chapters 5 and 7.
8. E. Lewars, "Computational Chemistry", Kluwer, Boston, 2003; Chapter 6.
9. E. Lewars, "Computational Chemistry", Kluwer, Boston, 2003; Chapter 2.
10. J. A. Pople, Acc. Chem. Res., 1970, *3*, 217.
11. W. J. Hehre, L. Radom, P. v. R. Schleyer, J. A. Pople, "Ab Initio Molecular Orbital Theory", Wiley, New York, 1986; Chapter 2.
12. J. A. Pople, D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, 1970; Chapter 1.
13. Y. Shao, M. Head-Gordon, A. Krylov, J. Chem. Phys., 2003, *118*, 4807.
14. J. Gräfenstein, E. Kraka, M. Filatov, D. Cremer, Int. J. Mol. Sci., 2002, *3*, 360.
15. D. Cremer, M. Filatov, V. Polo, E. Kraka, S. Shaik, Int. J. Mol. Sci., 2002, *3*, 604.
16. D. Cremer, Mol. Phys., 2001, *99*, 1899.
17. J. Gräfenstein, D. Cremer, Mol. Phys., 2001, *99*, 981.
18. J. Gräfenstein, A. M. Hjerpe, E. Kraka, D. Cremer, J. Phys. Chem. A 2000, *104*, 1748.
19. I. N. Levine, "Quantum Chemistry", Fifth Edn., Prentice Hall, Engelwood Cliffs, 2000; pp. 448–453.
20. J. B. Foresman, A. Frisch, "Exploring Chemistry with Electronic Structure Methods", Second Edn., Gaussian Inc., Pittsburgh, 1996; pp. 228–236.
21. T. Ströter, O. Jarosch, G. Szeimies, Chem. Eur. J., 1999, *5*, 1422.
22. T. Ströter, G. Szeimies, J. Am. Chem. Soc., 1999, *121*, 7476.
23. A. Toyota, S. Koseki, H. Umeda, K. Suzuki, K. Fujimoto, J. Phys. Chem. A, 2003, *107*, 2749.
24. I. B. Bersuker, Chem. Rev., 2001, *101*, 1067.
25. M. Hargittai, B. Réffy, M. Kolonits, C. J. Marsden, J.-L. Heully, J. Am. Chem. Soc., 1997, *119*, 9042.
26. T. A. Miller, Angew. Chem. Int. Ed. Engl., 1994, *33*, 962.
27. D. W. Kohn, P. Chen, J. Am. Chem. Soc., 1993, *115*, 2844.
28. M. B. Smith, J. March, "March's Advanced Organic Chemistry", Wiley, New York, 2001; p. 37 and references therein.
29. S. G. Lias, J. E. Bartmess, J. F. Liebman, J. L. Holmes, R. D. Levin, W. G. Mallar, J. Phys. Chem. Ref. Data Suppl., 1988, *17(S1)*, 315, 316, 360, 361.

Chapter 8
Hexaphenylethane

Introduction

Hexaphenylethane, **1**, is interesting because all attempts to make it have failed, and its synthesis would represent the denouement to a historical saga and shed light on certain questions of theoretical interest.



1

Hexaphenylethane: The Classical Period

The first attempt to make hexaphenylethane seems to have been by Gomberg [1, 2]. His stated reason for this seems now quite prosaic; it was ancillary to another problem, namely to compare its behavior with that of tetraphenylmethane toward a color test, thus checking the reliability of this test as evidence for the tetraphenylmethane structure.* Interestingly, the tetraphenylmethane work, the motive force for the attempted hexaphenylethane synthesis, evidently found its justification in the desire to probe the limits to the crowding of groups around a carbon atom, a matter clearly closely connected to the structure and properties of hexaphenylethane.

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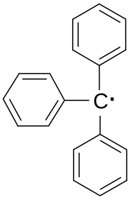
*The test involved nitrating the hydrocarbon and adding a crystal of the nitro compound to ethanolic KOH. Tetranitrotetraphenylmethane gave no color, unlike trinitrotriphenylmethane, which has a relatively acidic aliphatic hydrogen.

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_8,

The history of the hexaphenylethane problem is a counterpoint of experiments and their interpretations: experiments in which a principal performer was Moses Gomberg, and interpretations of these by him and others. The tale has been ably chronicled ^{1,2,3} and will be only briefly recounted here, where the emphasis is rather on the significance of hexaphenylethane for structural theory.

In 1900 Gomberg published the results of his attempt to make hexaphenylethane, in the *Journal of the American Chemical Society* and in the then more-prestigious *Berichte* (in those days journals tolerated this kind of simultaneous publication) [1, 2]. He reported that the reaction of chlorotriphenylmethane with certain metals, preferably zinc, in benzene with careful exclusion of oxygen gave a hydrocarbon. This was not obtained pure, but its reactions with oxygen and halogens led Gomberg to conclude that it was "extremely unsaturated". These reactions (principally the very ready formation of what was identified as triphenylmethyl peroxide) led him to the conclusion that the solid (impure) hydrocarbon was the triphenylmethyl radical (**2**). For about a decade after its initial synthesis, there was considerable debate about the structure of the hydrocarbon; besides Gomberg's triphenylmethyl radical proposal, other suggestions were hexaphenylethane (**1**), and the "quinoid" (methylenecyclohexadiene) structures **3** and **4**.^{4,5} Structure **3** was proposed by Jacobsen in 1905 [3]; it will turn out to be of some special interest.



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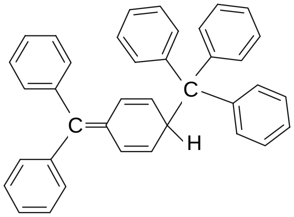

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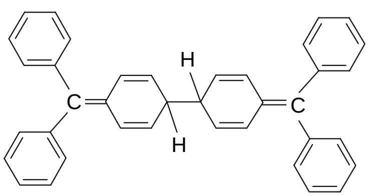
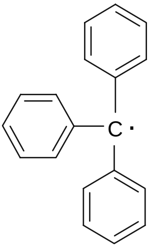


4

Gomberg soon realized that his chlorotriphenylmethane-zinc reaction led to *two* substances, a colorless crystalline one and a yellow solution-phase one [4, 5], and in 1908 Schmidlin showed that the two substances are in equilibrium in solution [6]. In a 1914 review [7] Gomberg accommodated this very important result by proposing an equilibrium of **1**, **2**, and **3** ([7], p. 1162), his scheme being somewhat complicated by the inclusion of complexed (associated) radicals **2** and the understandable failure to distinguish, in those pre-quantum chemistry days, between tautomerism and resonance. The yellow solution color was ascribed to **2** in equilibrium (we now see this as resonance) with **2**′, while the structure of the colorless solid was recognized to be still undecided (([7], p. 1162): "Whether we assign to the dimolecular triphenylmethyl the constitution of an associated molecule, or of hexaphenylethene [*sic*], or of a quinol"...). Gomberg is here conceding that the colorless substance could be associated triphenylmethyl radicals, hexaphenylethane, or the Jacobsen methylenecyclohexadiene structure **3**; indeed, in the same paper he says of the colorless substance “Triphenylmethyl melts at 145°” (p. 1147). As McBride put it, “he left no base untouched”.[6]



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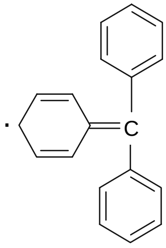
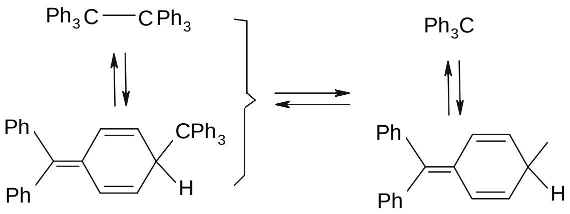
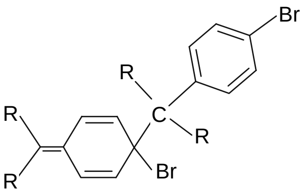


2′

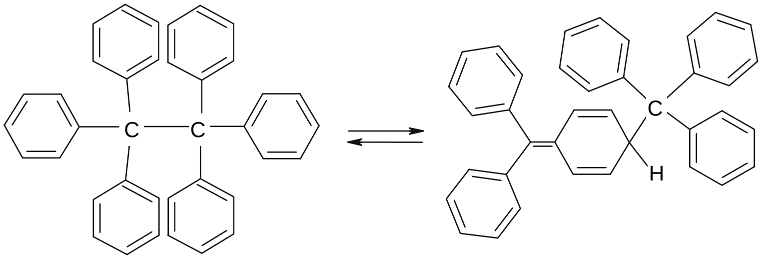
In the same year as Gomberg’s review, a monograph by Schmidlin interpreted the situation more succinctly: the main process was said to be probably an equilibrium between triphenylmethane radicals and hexaphenylethane [8]. This became the standard interpretation until 1968, but was apparently never fully accepted by Gomberg, and in particular, the “quinoid” Jacobsen structure **3** was by no means excluded as late as 1919, when the equilibrium below (with Ph generalized to R) is said to have been “fairly well established” (the structure with the dangling bond we would now consider to be a resonance form of the radical) [9]:



In a 1923 paper the possibility was considered of a dibromo molecule related to **3** reacting with silver [10]:



This was apparently the last approvingly speculative mention in a research publication of a methylenecyclohexadiene type structure as an alternative to a hexaphenylethane. Gomberg’s 1925 review [11] of organic radicals mentions (p. 118) Schmiedlin’s suggestion that the color of “hexaphenylethane” solutions is due to tautomerism between colorless hexaphenylethane and a yellow “quinoid” species (to modern eyes this is peculiar-looking, as it posits facile migration of a triphenylmethyl group between a benzylic and a *p*-benzene position) but points out that unlike a dissociation reaction, where the rate of dimerization decreases with dilution, tautomerism is inconsistent with the fact that the color of the solution intensifies on dilution:



1 **3**

The simple hexaphenylethane-triphenylmethane equilibrium was, however, considered “inadequate” ([12], p. 102) and, in general, a process of dissociation of hexaarylethanes into triarylmethyl radicals with tautomerism (resonance to us) to a quinonoid form ([12], p. 123) was postulated.

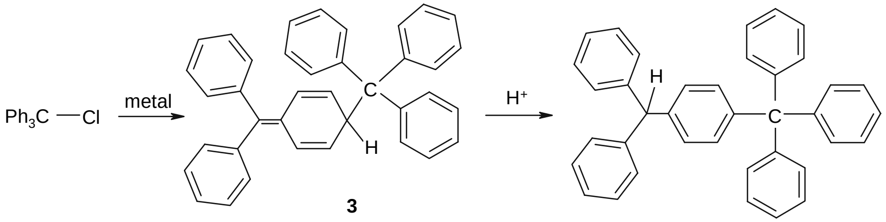
By about 1925, then, there seems to have been general agreement that Gomberg had prepared hexaphenylethane, and that in solution this was in equilibrium with (essentially) the triphenylmethyl radical. In subsequent decades, mainly in the 1930 s, there appeared several publications on experiments with the alleged hexaphenylethane [13, 14, 15].

Hexaphenylethane: The Modern Period

There are three aspects to what we can call the modern hexaphenylethane period: the demonstration in 1968 that hexaphenylethane did not exist, the preparation in 1978 of the first genuine (unbridged) hexaphenylethane derivative, and the interplay at about this time of reliable computational and experimental methods of probing the structure of hexaphenylethane and related compounds.

The demonstration in 1968 that hexaphenylethane did not exist. In 1968 Lankamp, Nauta and MacLean showed that the Gomberg dimer is not hexaphenylethane, but rather the methylenecyclohexadiene **3** [16]. This was shown for **3** and some methyl- and *t*-butyl-substituted analogs by examination of their UV and proton NMR spectra (the proton NMR of **3** was also discussed by Smith [17]). In retrospect, it is perhaps surprising that for at least about four decades chemists were comfortable with the hexaphenylethane structure, because there were anomalies with the dimerization of triphenylmethyl-type radicals [16] and, going back almost to 1900, with the properties of “hexaphenylethane”.[8] The dimerization anomalies stem from the fact that the dimerization of some triarylmethyl and diarylmethyl radicals is inhibited by substituents in ways that seemed odd if the products were ethanes; for example, a *t*-butyl group at the *p*-position of each phenyl group of triphenylmethyl prevents dimerization of the radical [18]. Note that **3** is formed in preference to **1** although it entails loss of the aromaticity of a benzene ring.

Anomalies with the supposed hexaphenylethane structure were evident by 1906, namely acid-catalyzed aromatization and *p*-halogen lability; these are discussed in great historical detail by McBride. Gomberg found (1902) that treatment of his "triphenylmethyl" (soon to be regarded as hexaphenylethane) with hydrochloric acid gave a hydrocarbon soon assigned (correctly) the structure *p*-benzhydryltetraphenylmethane (**5**) [19, 20]. Regarding *p*-halogen lability, Gomberg and Cone found (1906) that halotriphenylmethanes with a *p*-halogen reacted quickly with silver to form unsaturated compounds which readily form peroxides. These unsaturated compounds slowly react further with silver (or possibly silver ion) losing the ring halogen (when *para*, but not when *ortho* or *meta*) [21]. These facts are now seen to be readily accommodated (by analogy in the case of the *p*-halogen compounds) by Jacobsen's "quinoid" structure **3** [3] for the colorless compound from the chlorotriphenylmethane-metal reaction:



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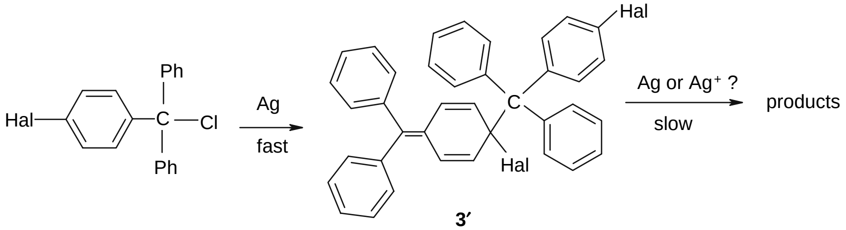


3′

At the time too (ca. 1906) it was well-known that methylenecyclohexadiene ("quinoid") systems aromatize readily, and that allylic halogens, as in **3**′, are very reactive, in contrast to aromatic halogen. Nevertheless, the Jacobsen structure **3** was to disappear into obscurity until 1968 [16].

The preparation in 1978 of the first genuine (unbridged) hexaphenylethane. With the revelation in 1968 that the dimer in equilibrium with triphenylmethyl was the methylenecyclohexadiene **3**, the hexaphenylethane problem, believed for decades to have been solved , arose again in a sharply focused form: synthesis. Around the time of the structure disproof of the "traditional" hexaphenylethane, derivatives of this compound were known, but in all of these steric *ortho*-type repulsions (Fig. 8.1) were reduced or eliminated by *ortho* bonding, as in for example **6** [22] and

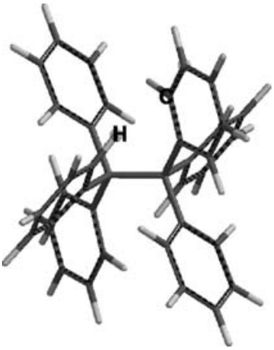
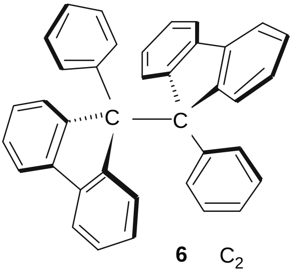
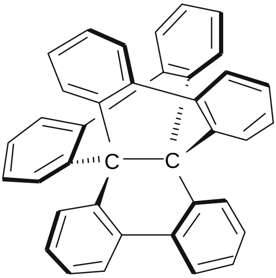


Fig. 8.1 Hexaphenylethane (S_6 conformation), calculated by AM1. The HC distances shown are calculated at 2.36 Å; the sum of these *ortho* H and C van der Waals radii are 1.11 + 1.68 Å = 2.79 Å, and a space-filling representation shows these atoms to be in contact. There are three such interactions

7 [23]. In these molecules nonbonded interactions across the central CC bond have been reduced by removing H atoms and pinning back aryl groups with zero-carbon bridges.



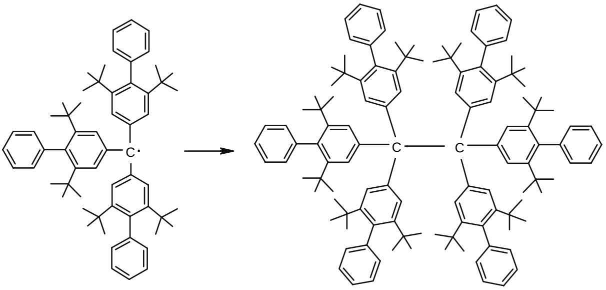
6 C_2



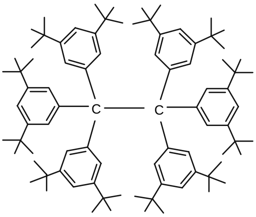
7 C_3

The preparation of the first genuine (unbridged) hexaphenylethane was reported in 1978, when Stein, Winter and Rieker revealed that when a benzene solution of the colored radical *tris*(3,5-di-*t*-butyl-4-phenyl)phenylmethyl (**8**) was concentrated (over 7 months!) there were obtained colorless crystals which in solution dissociated slowly to **8** [24]. Definitive evidence for the hexaphenylethane structure **9** for the colorless material came from X-ray crystallography. Definitive, with one caveat: the ethane central CC bond was reported to be 147 pm (1.47 Å) long. This is an astonishingly short length for an sp^3–sp^3 CC bond, and an absurdly short one for such a bond between carbons loaded with bulky substituents like those in **9**, but to be fair the authors pointed out that "Due to the poor quality of the crystals, the bond lengths quoted in the text are to be regarded as preliminary values". The apparent bond length anomaly brings us to the computational aspect of the modern phase of hexaphenylethane chemistry.

The interplay of reliable computational and experimental methods of probing the structure of hexaphenylethane and related compounds. The anomalously short bond length of 1.47 Å reported for the first "genuine" hexaphenylethane, the



8 **9**



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hexakis(biphenyl) compound (**9**) of Stein et al. (1978) was challenged proleptically (1977) and then after the claim (1981, 1986, 1988), by Mislow's research group [25, 26, 27, 28]. Perhaps the first reliable calculations of the structure of hexaphenylethanes were reported in 1977 [25]. Molecular mechanics (MM) revealed two low-lying minima, with S_6 and (lowest) D_3 symmetry, and a central CC length of 1.64 Å. Prompted by the publication of an X-ray structure for **9**, these calculations were revisited with "a thorough investigation along computational lines" [26]. Several MM forcefields, as well as semiempirical quantum mechanical (MNDO) calculations agreed with the earlier work [25] that the D_3 conformer of hexaphenylethane is the stablest (8–20 kJ mol^{-1} lower than the S_6), and that the critical CC bond length is ca. 1.64 Å (1.60–1.64 by MM, 1.68 by MNDO). Directing their attention specifically to the hexaphenylethane derivative of Stein et al. [24], Osawa et al. [26] calculated the geometry of **9** (this, $C_{122}H_{150}$, was at the time, 1981, perhaps the biggest molecule subjected to geometry optimization by MM – and thus by any method). A central CC length of ca. 1.60 Å (depending on the forcefield and the conformer) was found; **9** was calculated to be entirely analogous to hexaphenylethane, for which a CC length of 1.69 Å was found using the forcefield used in this paper. The authors concluded that the X-ray structure reported [24] was in error, unless there were some novel shrinkage effect in **9** that was not handled by these MM or MNDO methods. They pointed out that the importance of such an effect warranted a reinvestigation of the structure of **9**.

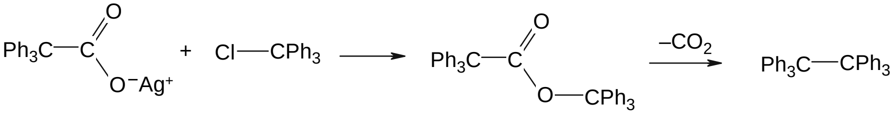
Definitive reinvestigations relevant to the structure of **9** were reported in 1986 and 1988. Kahr et al. were able to grow X-ray-quality crystals of hexakis(3,5-di-*t*-butylphenyl)ethane (**10**) (by letting a cyclohexane solution of the triarylmethyl radical stand at room temperature for 2 months) [27]. Stein et al. had not been able to obtain crystals of this simpler (cf. **9**) hexaarylethane of X-ray-quality. X-ray analysis proved the hexaarylethane structure **10** and gave a central CC length of 1.67 Å (cf. 1.65 Å calculated by MM). The authors concluded that "the claim for bond shortening [in **9**] may now be safely dismissed." Despite these words, the remote possibility remained that **9** was somehow indeed special in sporting an abnormally short key CC bond. This remoteness receded with the report of an NMR study of **9** and **10** [28]. Yannoni et al. obtained crystals of **9** and **10** (in a mere week, from cyclohexane solutions "by carefully controlling the solvent volume") enriched in

^{13}C in the critical CC moiety (these compounds were synthesized with the aid of ^{13}C $(COCl)_2$). The crystals of **9** were unsuitable for X-ray work (significantly, Stein et al. reported that their pioneering X-ray crystals were of poor quality [24]). Compound **9**, and the compound **10** which had earlier been X-ray-analyzed [27], were examined by ^{13}C nutation NMR spectroscopy, a procedure in which spectral data were compared with calculations for varied CC bond lengths. Comparing experimental and calculated data gave a CC bond length of 1.64–1.65 Å for both **9** and **10**. From nutation NMR work on other molecules for which CC bond lengths are known from other experiments, the method is considered to be accurate, and the conclusion was drawn that "these results remove any last doubt that [the initially reported CC length of **9**] is grossly in error". The good agreement between the calculated, X-ray, and NMR results for the central CC bond of hexaarylethanes is reassuring. Noteworthy is the fact that NMR measures internuclear distance averaged over vibrational motion, while X-ray diffraction measures a kind of electron-density-centroids separation.

Our survey of the history of the modern period of the chemistry of hexaphenylethane concludes with a study which, while not strictly combining experiment and calculations, fits here conveniently. This is a state-of-the-art (ca. 2002) computational investigation of hexaphenylethane by Vreven and Morokuma [29]. They used a somewhat involved application of Morokuma's ONIOM procedure, in which the critical part of a molecule is studied at a high computational level and surrounding regions deemed less important are treated at a lower level. These workers obtained for the central C–C bond a length of 1.72 Å and a dissociation energy of 69.5 kJ mol^{-1} (16.6 kcal mol^{-1}). They noted that this calculated length for the parent compound is significantly longer than the experimental X-ray diffraction length of 1.67 Å for a derivative [27], and suggested that crystal packing, or even small substituents effects, may shorten the bond, because it is so soft toward stretching, as indicated by the calculated vibrational frequency of 230 cm^{-1}, cf. 1011 cm^{-1} for ethane at the same computational level. Their "calculations predict HPE to be stable, i.e. the BDE [bond dissociation energy] is positive, although this C–C bond is indeed very weak. Therefore synthesis of this compound might be feasible." The ethane C–C BDE is 377 kJ mol^{-1} (90.1 kcal mol^{-1}) [30], so the hexaphenylethane bond is indeed predicted to be exceedingly weak. This calculated bond length/bond energy pair conform well to an excellent, simple empirical correlation between the two kinds of parameters discovered by Zavitsas [31]. Although this cannot be called a *prediction* of one from the other for hexaphenylethane, since the calculated values of [29] were used for one of Zavitsas's data points, the compatibility with the correlation for the other 40 molecules used in the study strongly suggests that the ONIOM values are reasonably accurate. The problem with making hexaphenylethane likely lies not with the instability of this molecule, but rather with the preference of the triphenylmethyl radical to dimerize faster to the methylenecyclohexadiene **3** than to the hexaarylethane. This is a kinetic effect probably arising from less steric hindrance in the transition state for formation of the methylenecyclohexadiene: this dimerization mode is less disfavored by nonbonded (steric) interactions than is the "end-on" dimerization of $Ph_3C^{\cdot}$ + $^{\cdot}$CPh3.

Synthesis

Apart from Gomberg's halotriphenylmethane-metal reaction, there have been a couple other approaches to hexaphenylethane. In 1908 Anschütz reported an attempt based on heating the silver salt of triphenylacetic acid with chlorotriphenylmethane [32]. He envisaged:



Evidently, the triphenylmethyl ester of triphenylacetic acid was indeed obtained; furthermore, this was reported to lose CO_2 on heating, giving "an unidentified product", $C_{38}H_{30}$, melting at about 210°C. This is intriguing, assuming the $C_{38}H_{30}$ molecular formula is correct, which seems likely, since the $C_{19}H_{15}$ moieties would probably be conserved in atom content, if not in structure (cf. the Jacobsen structure **3** where a benzene ring is converted to a cyclohexadiene). It seems likely that Anschütz's product was **5**, (mp 227°, e.g. [33]), formed via **3** from triphenylmethyl radicals (the melting point of **3** is 153° [34]).

A more recent attempt to make hexaphenylethane, by Arkin et al., was based on the apparently favorable juxtaposition of iodotriphenylmethane molecules in the crystal [35]. The solid was heated and variously monitored by ^{13}C NMR, ESR, and differential scanning calorimetry. However, hexaphenylethane was not obtained (the main product was triphenylmethane).

These three unsuccessful approaches to hexaphenylethane – coupling with a metal, decarboxylation, and thermolysis in the solid state – depend on generating triphenylmethyl radicals. Yet the synthesis of **9** and **10** (above) shows that some triarylmethyl radicals, at any rate, can indeed lead to hexaarylethanes. Why does a solution of the triphenylmethyl radical normally yield the methylenecyclohexadiene **3** rather than hexaphenylethane **1**, while with care the corresponding triarylmethyl radicals can be made to deposit crystals of **9** or **10**? Thermodynamics assures us that **1**, **2**, and **3** should be in equilibrium in solution, because we know that **3** dissociates in solution, and from the properties of **9** and **10** we expect **1** to behave likewise. There do not seem to have been any experiments specifically designed to measure the concentration of **1** in solution, and it may of course be undetectably low. Assuming the radical to be in equilibrium just with the methylenecyclohexadiene **3**, the equilibrium constant for dissociation of **3** was measured to be 3.09×10^{-4}, from the UV absorption at 516 nm, where **3** (and presumably **1** too, from general considerations of structure and UV properties) does not absorb significantly, showing a very low relative concentration of the radical [34]. It seems likely that in solution the main species is **3** rather than **1**, e.g. because routine concentration of solutions gives **3** (if the solution contains mostly **3** we expect concentration to deposit **3**). However, if the dimer **1** packs better into a crystal lattice than the dimer **3**, i.e. if the molar free energy of crystalline **1** is lower than that of crystalline **3**, then slow

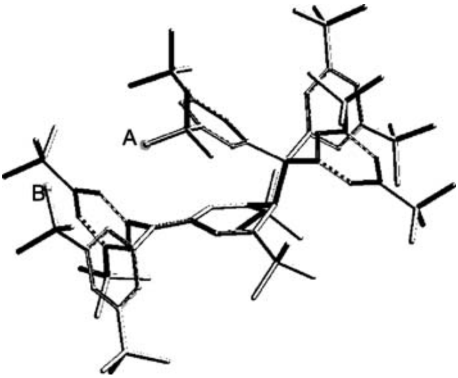
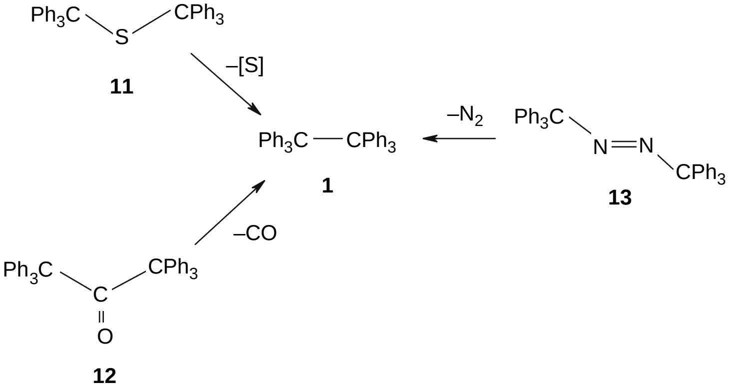


Fig. 8.2 Analogue of the methylenecyclohexadiene dimer **3** (the Jacobsen "quinoid" structure), formed from triphenylmethyl radical with *t*-butyl groups on all *m*-positions; Cs symmetry, calculated by AM1. Hydrogens have been removed for clarity. The distance between a hydrogen on carbon A and a hydrogen on carbon B is calculated to be 2.83 Å; the sum of the van der Waals radii is 2.79, and a space-filling representation shows these hydrogens to be in contact. Here are two such interactions

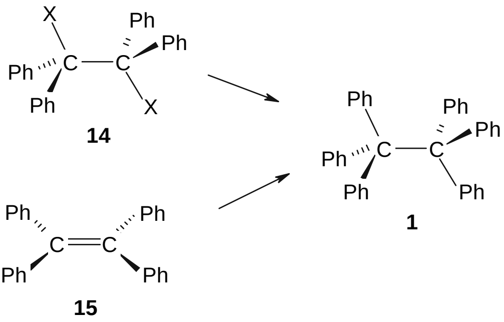
concentration of a solution may yield crystalline **1**, even if **1** is a minor component in solution. This appears to be the reason why crystalline **9** and **10** can be obtained from careful control of the concentration of solutions of the corresponding triarylmethyl radicals, although the solutions contain at equilibrium mainly the radicals, and on routine concentration deposit as solids these very stable radicals. Inspection of a model indicates that **9** and **10** have over **1**, with regard to formation of a crystalline hexaarylethane, the advantage that the *m*-*t*-butyl groups discourage formation of a methylenecyclohexadiene structure by steric interactions (Fig. 8.2). Nevertheless, some hope that the strategy may work for **1** is given by the fact that the high symmetry of **1** (probably S_6 [29]) may allow it to fit better into a lattice than can **3** (essentially Cs symmetry [36]).

Another putative approach to hexaphenylethane is to remove a "spacer" from between two triphenylmethyl groups, e.g.

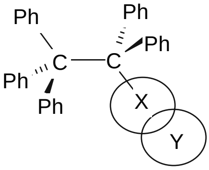


The main problem with these approaches is that there is no guarantee that compounds like **11**, **12**, and **13**[9] would, upon ejection of the spacer, lead to the elusive hydrocarbon: if coupling of triphenylmethyl radicals occurred, this would probably form the methylenecyclohexadiene **3**, rather than **1**. The situation is not hopeless: in a matrix, loss of CO or N_2 from **12** or **13** might leave the radicals so positionally constrained as to unite to form **1**. Anticipating the result of attempted excision of sulfur from **11** is problematic [37, 38].

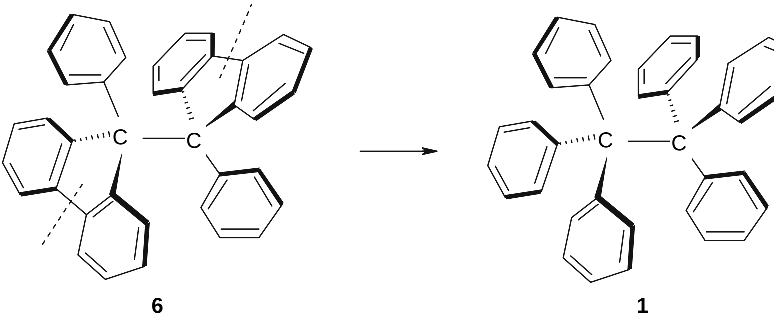
Finally, one might attempt to construct on, or introduce into, a less heavily-laden ethane **14** or ethene **15** the final phenyl groups, i.e.:



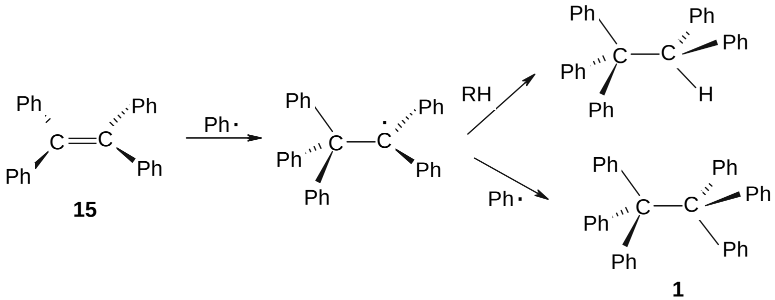
An obvious problem with the process **14** → **1** is that the reagent Y needed to convert the presumably relatively sterically undemanding X into the bulkier phenyl group could engender a very hindered transition state:



A variation of this concept which, however, is not free of this problem, is the possibility of reductively cleaving the ortho–ortho bond in a known bridged hexaarylethane, e.g.



The process **15** → **1** may (naively perhaps) be envisaged as occurring by effectively immersing **15** in a sea of phenyl radicals: a high radical concentration seems desirable to avoid a sterically much more favorable hydrogen abstraction in the second step:



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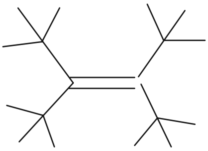
Both phenyl-addition steps appear to have favorable enthalpies: B3LYP/6-31G* single-point energies on AM1 geometries indicate the first and second steps to be exothermic by 82 and 237 kJ mol^{-1}, respectively, but a problem is posed here by the well-known fact that in radical reactions encounters between two radicals tend to be rare.

A Related Compound

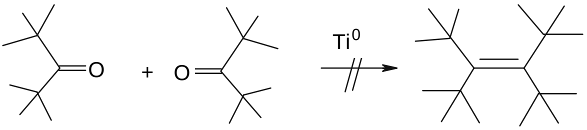
Perhaps the best-known rival to hexaphenylethane as a sterically crowded, unknown compound, is tetra-*t*-butylethene:



16

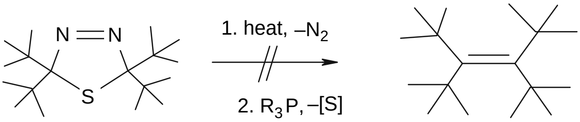
This molecule is briefly discussed here because the approaches to it that have been tried are somewhat analogous to those that have been suggested here for making hexaphenylethane. The situation with regard to **16** has been nicely summarized by Hopf, ca. 2000 [39] and Lenoir et al. 2006 [40], and there appear to have been no significant advances in our knowledge of this compound, experimental or theoretical, from then till now (mid 2007). The methods that have been explored are: (1) joining two halves directly, (2) removing a spacer from between two halves, (3) converting a less sterically demanding group to the *t*-butyl group, and (4) adding the final *t*-butyl group to a moiety with masked *t*-butyl groups. Here I give one example of each of the four approaches.

(1) *Joining two halves directly.* McMurray coupling of ketones with zero-valent titanium is a straightforward way (when it works) of converting ketones to alkenes; it did not work for **17**.



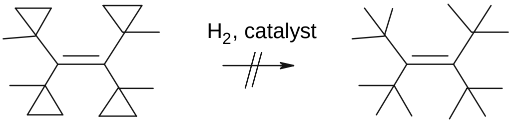
17 **17** **16**

(2) *Removing a spacer from between two halves.* The Barton-Kellogg alkene synthesis has been used to prepare several crowded alkenes. Here 1-thia-3,4-diazacyclopent-3-enes (Δ^3-1,3,4-thiodiazolines) are relieved of N_2 and S (the selenium analogs have also been used) to give an alkene. The method did not work when applied to **18**.



18 **16**

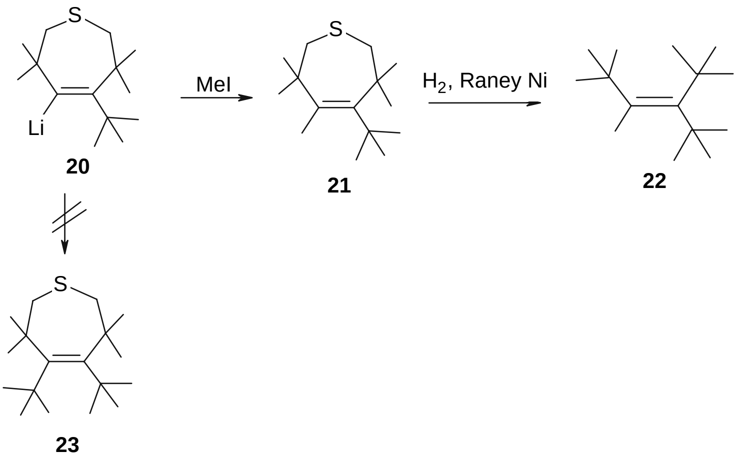
(3) *Converting a less sterically demanding group to the t-butyl group.* The alkene **19** tetrasubstituted with the methylcyclopropyl group (which is evidently smaller than *t*-butyl) could be made by the above thiadiazacyclopentene route, but the methylcyclopropyl groups could not be hydrogenolytically converted to *t*-butyl groups:



19 **16**

(4) *Adding the final t-butyl group to a moiety with masked t-butyl groups.* The vinyllithium derivative **20** could be methylated to give the masked tri-*t*-butylmethylethene **21**, which was converted to tri-*t*-butylmethylethene(**22**), but the masked tetra-*t*-butylethene **23** could not be prepared.

The litany of failures might make one pessimistic about the possibility of synthesizing tetra-*t*-butylethene were it not for the fact that there is good reason to think that the compound should be essentially a normal, albeit strained, singlet alkene, capable of existence: DFT calculations predict a singlet ground state with a 45° twist and 389 kJ mol^{-1} of strain [41]. The formation of **16** from two di-*t*-butylcarbene molecules should be exothermic by 310 kJ mol^{-1} with a barrier of 105 kJ mol^{-1}, but a much more favorable process, with a 21 kJ mol^{-1} barrier, is the



intramolecular insertion of carbene carbon into a CH bond to form 1,1-dimethyl-2-*t*-butylcyclopropane [41]. Another putative route to **16** thus seems to be domed to failure.

Conclusions

In the light of all these calculations and experiments, what can we say about hexaphenylethane? The synthesis of the substituted hexaphenylethanes **9** and **10** and the calculations of Vreven and Morokuma (above) indicate that hexaphenylethane can exist. As was exhorted for tetra-*t*-butylethene, the search for it “must and will continue” [39].

Notes

1. (a) A human and chemical biography of Gomberg: C. Rüchardt, Nachrichten aus der Chemie, 2000, *48*, 904. (b) A very brief account of Gomberg’s achievement and its recognition: K. MacDermott, Chem. Eng. News, 2000, *78*, 47.
2. A very detailed account of the historical saga: J. M. McBride, Tetrahedron, 1974, *30,* 2009.
3. A historical account oriented to the failure of Gomberg to be awarded the Nobel prize: L. Eberson, Adv. Phys. Org. Chem., 2001, *36*, 59.
4. See Note 2.
5. See Note 3.
6. See Note 2, p. 2016.
7. See Note 2.
8. See Note 2.
9. (a) The sulfide: R. G. R. Bacon, J. Köchling, J. Chem. Soc., 1964, *Suppl.*, 5594; D. Vorlander, E. Mittag, Berichte, 1919, 52B, 413. The disulfide: C. R. Williams, J. F. Britten, D. N. Harpp, J. Org. Chem., 1994, *59*, 806.(b) the ketone: R. E. Bruns, P. M. Kuznesof, J. Organomet. Chem., 1973, *56*, 131. (c) the azo compound: S. Sugimori, Nippon Kagaku Zasshi, 1971, *92*, 426.

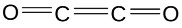
References

1. M. Gomberg, J. Am. Chem. Soc., 1900, *22*, 757.
2. M. Gomberg, Ber. Dtsch. Chem. Ges., 1900, *33*, 3150.
3. P. Jacobsen, Ber. Dtsch. Chem. Ges., 1905, *38*, 196.
4. M. Gomberg, Ber. Dtsch. Chem. Ges., 1901, *34*, 2726.
5. M. Gomberg, Ber. Dtsch. Chem. Ges., 1902, *35*, 1822, 2397.
6. J. Schmidlin, Ber. Dtsch. Chem. Ges., 1901, *41*, 2471.
7. M. Gomberg, J. Am. Chem. Soc., 1914, *36*, 1144.
8. J. Schmidlin, "Das Triphenylmethyl", Ferdinand Enke, Stuttgart, 1914; pp. 64, 213.
9. M. Gomberg, C. S. Schoepfle, J. Am. Chem. Soc., 1919, *41*, 1655.
10. M. Gomberg, F. F. Blicke, J. Am. Chem. Soc., 1923, *45*, 1765, 1767.
11. M. Gomberg, Chem. Rev., 1925, *1*, 91.
12. J. Schmidlin, "Das Triphenylmethyl", Ferdinand Enke, Stuttgart, 1914; p. 233.
13. R. C. Mithoff, G. E. K. Branch, "Kinetics of the Reaction of Hexaphenylethane with Oxygen", J. Am. Chem. Soc., 1930, *52*, 255.
14. H. E. Bent, G. R. Cuthbertson, M. Dorfman, R. E. Leary, "Single Bond Energies. I. The C–C Bond in Hexaphenylethane", J. Am. Chem. Soc., 1936, *58*, 165.
15. H. E. Bent, E. S. Ebers, "Vapor Density of Hexaphenylethane", J. Am. Chem. Soc., 1936, *58*, 2073.
16. H. Lankamp, W. Th. Nauta, C. MacLean, Tetrahedron Lett., 1968, (2), 249.
17. W. B. Smith, J. Chem. Educ., 1970, *47*, 535.
18. P. W. Selwood, R. M. Dobres, J. Am. Chem. Soc., 1950, *72*, 3860.
19. M. Gomberg, Ber. Dtsch. Chem. Ges., 1902, *35*, 3914.
20. M. Gomberg, Ber. Dtsch. Chem. Ges., 1903, *36*, 376.
21. M. Gomberg, L. H. Cone, Ber. Dtsch. Chem. Ges., 1906, *39*, 3274.
22. H. A. Staab, H. Brettschneider, H. Brunner, Chem. Ber., 1970, *103*, 1101.
23. G. Wittig, W. Schoch, Liebigs Ann. Chem., 1971, *749*, 38.
24. M. Stein, W. Winter, A. Rieker, Angew. Chem. Int. Ed. Engl., 1978, *17*, 692.
25. W. D. Hounshell, D. A. Dougherty, J. P. Hummel, K. Mislow, J. Am. Chem. Soc., 1977, *99*, 1916.
26. E. Osawa, Y. Onuki, K. Mislow, J. Am. Chem. Soc., 1981, *103*, 7475.
27. B. Kahr, D. Van Engen, K. Mislow, J. Am. Chem. Soc., 1986, *108*, 8305.
28. N. Yannoni, B. Kahr, K. Mislow, J. Am. Chem. Soc., 1988, *110*, 6670.
29. T. Vreven, K. Morokuma, J. Phys. Chem. A, 2002, *106*, 6167.
30. E. V. Anslyn, D. A. Dougherty, "Modern Physical Organic Chemistry", University Science Books, Sausalito, CA, 2006; p. 72.
31. A. A. Zavitsas, J. Phys. Chem. A, 2003, *107*, 897.
32. R. Anschütz, Liebigs Ann. Chem., 1908, *359*, 196.
33. A. E. Tshitshibabin, Ber. Dtsch. Chem. Ges., 1908, *41*, 2421.
34. T. H. Colle, P. S. Glaspie, E. S. Lewis, J. Org. chem., 1978, *43*, 2722.
35. C. R. Arkin, B. Cowans, B. Kahr, Chem. Mater., 1996, *8*, 1500.
36. N. S. Blom, G. Roelofsen, J. A. Kanters, Cryst. Struct. Commun., 1982, *11*, 297.
37. J. L. Dye, K. D. Cram, S. A. Urbin, M. Y. Redko, J. E. Jackson, M. Lefenfeld, J. Am. Chem. Soc., 2005, *127*, 9338.
38. R. B. Woodward, Pure Appl. Chem., 1973, *33*, 145, 159.
39. H. Hopf, "Classics in Hydrocarbon Chemistry", Wiley-VCH, Weinheim, New York, 2000; pp. 138–142.
40. D. Lenoir, C. Wattenbach, J. F. Liebman, Struct. Chem., 2006, *17*, 419.
41. H. M. Sulzbach, E. Bolton, D. Lenoir, P. v. R. Schleyer, H. F. Schaefer, J. Am. Chem. Soc., 1996, *118*, 9908.

Chapter 9
Ethenedione, C_2O_2

Introduction

Ethenedione (ethylenedione, carbon monoxide dimer, C_2O_2), **1**, is an interesting molecule for at least three reasons: (1) it is a small, simple-looking molecule with no immediately obvious reason why it should not be able to exist, yet it has defied decades of attempts to prepare it [1, 2, 3, 4], (2) it is a dimer of the well-known carbon monoxide, and unknown dimers, oligomers and polymers of well-known stable molecules have been of interest for some time [5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15], (3) theory indicates that the ground state should be a triplet [1, 2, 16, 17, 18, 19], a characteristic which would put it in the small class of simple molecules like O_2 which are ground state triplets despite the fact that a straightforward closed-shell Kekulé structure (with all electrons represented as bonds or as lone pairs) can be written for them.



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There are surprisingly many papers which, directly or somewhat adventitiously, address the ethenedione problem, and only those which seem to bear directly on our discussion will be given here; these should provide entry to the relatively few others.

Electronic Structure and Stability of Ethenedione

The structure **1** is somewhat misleading, in that taken literally it implies a closed-shell molecule with the orbital pattern

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 3\sigma_u^2\ 4\sigma_g^2\ 4\sigma_u^2\ 5\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4\ 5\sigma_u^2$$

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_9,

However, theoretical considerations indicate that the orbitals are arrayed energetically so that the two uppermost electrons must be placed in degenerate π molecular orbitals [19]:

$$1\sigma_g^2\ 1\sigma_u^2\ 2\sigma_g^2\ 2\sigma_u^2\ 3\sigma_g^2\ 3\sigma_u^2\ 4\sigma_g^2\ 4\sigma_u^2\ 5\sigma_g^2\ 1\pi_u^4\ 1\pi_g^4\ 2\pi_u^2$$

Figure 9.1 shows a pictorial representation of the valence orbitals, calculated by the AM1 method (the assignment of σ- and π-type orbitals depend somewhat on the level of calculation, but the two uppermost occupied orbitals remain singly-occupied π-type molecular orbitals). The expected triplet ground state of ethenedione would seem to be good news for its stability, because the dissociation of triplet C_2O_2 to two ground-state (i.e. singlet) CO molecules, while exergonic[1], is spin-forbidden [20, 21], and although dissociation to one triplet and one singlet CO molecule is

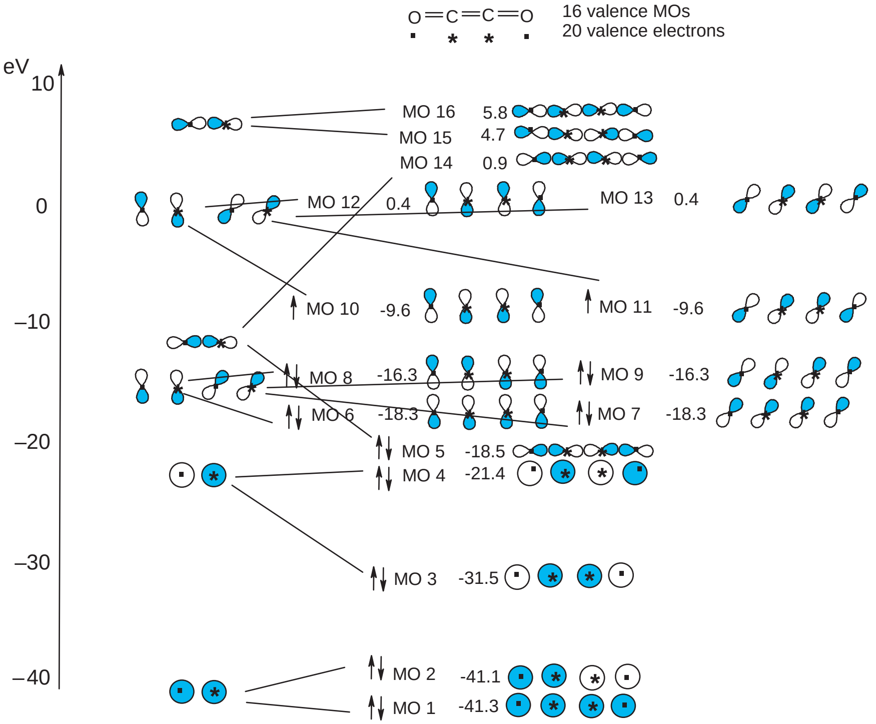


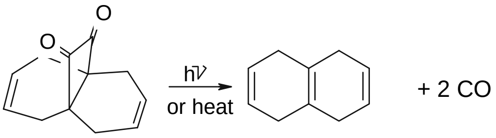
Fig. 9.1 The (valence) molecular orbitals of ethenedione. For the correlations with the MOs of carbon monoxide only one set of CO orbitals is shown; thus for example MO1 actually results from [O(2s)+C(2s)] + [O(2s)+C(2s)], and MO2 results from [O(2s)+C(2s)] – [O(2s)+C(2s)]. These AM1 MO energies are very approximate. For the construction of such MO diagrams see [55] Unlike the case of 2 CO, bringing two CH_2 groups together does not lead to a triplet because CH_2 lacks degenerate orbitals and thus so does ethene [55]

allowed, these products lie at much higher energy than C_2O_2[2], so triplet C_2O_2 should be a bound species (in contrast to earlier calculations, Talbi and Chandler also predicted linear singlet C_2O_2 to be bound, albeit with a possible low-energy distortion leading to dissociation [2]). There is however, a potential problem: if the singlet potential energy surface of C_2O_2 crosses the triplet surface at a geometry which allows the triplet facile access to the singlet surface, intersystem crossing [17, 20] can occur leading to the singlet state, which may be unbound (not a relative minimum on a potential energy surface)[2, 19][3], unlike the triplet[4]. The failure of their neutralization-reionization (NR) experiments to detect any sign of C_2O_2 led Schröder et al. to examine the intersystem crossing situation here [16] (earlier NR experiments by Chen and Holmes had given a tantalizing hint of the formation of this molecule [3]). Their sophisticated analysis of the potential energy surfaces led to the conclusion that triplet ethenedione would indeed rapidly cross to the singlet, unbound (?) state, dissociating to CO with a calculated lifetime of about 0.5 ns. This was a striking finding, because for some years triplet ethenedione had been regarded as a bound, reasonably stable molecule by virtue of its inability to dissociate directly to two ground state (singlet) carbon monoxide molecules. The intersystem crossing finding can be viewed as a depressing conclusion or as a call to arms. Depressing because it appears to rule out the possibility of observing ethenedione not only under ordinary laboratory conditions, but even by matrix isolation near absolute zero, a versatile technique that has proved very successful for taming highly reactive molecules [22]. A call to arms because recent experiments have shown that species with lifetimes of less than a nanosecond can be spectroscopically observed [23, 24, 25, 26]. The matter is briefly discussed in the *Synthesis* section.

Attempts to make Ethenedione

Ethenedione made its literature debut in 1913, when Staudinger and Anthes reported that oxalyl chloride and bromide reacted with metals, e.g. zinc, to form carbon monoxide [27]. For the reaction of BrCOCOBr with Hg they drew the interesting (but perhaps puzzling) inference that “Since Hg_2Br_2 does not decompose it into $COBr_2$ and CO, the reaction with Hg must consist in the formation of OC:CO which, however, is not capable of existence at room temperature and at once decomposes further into CO”. This is a clear statement of their belief that they had generated ethenedione. The next publications of direct relevance to ethenedione seem to have appeared in 1968, when the 1,2-diketones **2** and **3** were found to suffer thermal and photochemical (**2**) [28] or photochemical (**3**) [29] decarbonylation. No evidence was given for the extrusion of C_2O_2 rather than stepwise loss of CO.

Strating et al. reported that similar reactions of dibenzobicyclo[2.2.2]diones (cf. **3**) also gave loss of CO and aromatization [30]. Although for photolysis of one dibenzobicyclo[2.2.2]dione attempts to trap C_2O_2 failed, the mass spectrometric detection of C_2O_2 by NR mass spectrometry was claimed for irradiation of dibenzobicyclo[2.2.2]octadiene-2,3-dione. This appears to be at odds with the findings of Schröder et al. (above), but this work, and that of Chen and Holmes



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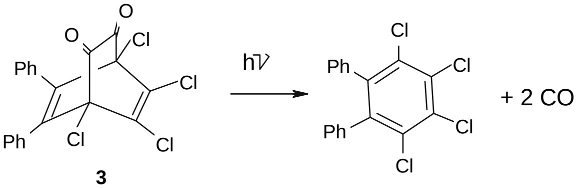

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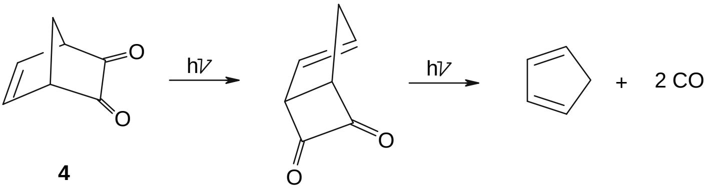
[1c, above], appears to warrant repetition. Sülze et al. also failed to detect C_2O_2 by NR mass spectrometry [31]. Rubin et al. found that bicyclo[2.2.1]heptene-2,3-dione (**4**) and related compounds underwent a 1,3-carbon shift and then loss of CO from the cyclobutanedione, but no specific search for C_2O_2 seems to have been done [32]:



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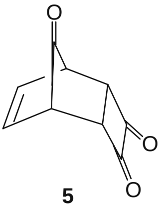
Matrix isolation photolysis experiments near absolute zero would appear to offer a good chance of preparing ethenedione (with the reservation that such aspirations may be negated by the molecule's being inherently subject to rapid dissociation [16]). In the event, photolysis of **5** and of **6** and **7** [33] in an argon matrix gave no sign of the formation of ethenedione. These results are in accord with earlier theoretical work by Haddon which suggested that bicyclic diones are unlikely to serve as precursors of ethenedione [34].



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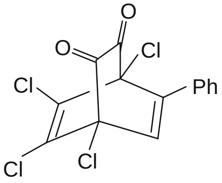

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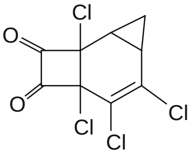

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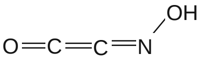
After all these negative findings one might be forgiven being heartened by the synthesis of the oxime of ethenedione, **8**, which Maier and coworkers were able to prepare by matrix isolation photolysis at 10 K of **9**, **10**, and **11** [35].



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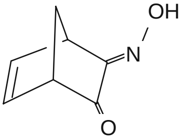

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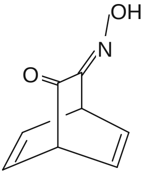

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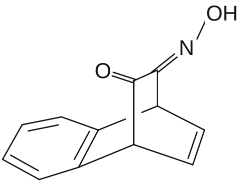

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In conventional, wet, chemistry, an oxime is merely a masked ketone, and said ketone can usually be liberated by hydrolysis of the oxime. However, such an approach to ethenedione appears to be quixotic: under conventional solution conditions not only would the (probable) ultrashort lifetime of the ketone be an impediment to its spectroscopic observation, but even the generation of this molecule seems unlikely here, because of the sensitivity of the required intermediates along the hydrolysis pathway, e.g. O=C=C(OH)NHOH. The synthesis of ethenedione oxime, while clearly interesting, probably lies off the path to the elusive diketone.

Species Related to Ethenedione

To help put ethenedione in perspective, a quick look is warranted at the state of our knowledge of these related species: isomers of ethenedione, the cation and anion of neutral ethenedione, the sulfur analogues OCCS and SCCS, and the imines OCCNH and HNCCNH.

Isomers of ethenedione were considered by Korkin et al., who examined **12–16** [19]. They were able to locate as stationary points within 400 kJ mol^{-1} of linear triplet ethenedione (found to be the stablest of the C_2O_2 species considered), at the Hartree-Fock level, only **12** and **13**, and **13** dissociated on attempted optimization at a correlated (MBPT(2), essentially MP2) level; singlet, slightly nonplanar C_{2v} **12** lay 291 kJ mol^{-1} above triplet ethenedione. Surprisingly, in a study of potential high-energy clusters Evangelisti found an alternative minimum somewhat similar to **12**, namely the tetrahedral structure **18** (Fig. 9.2) [36]. This can be viewed as **12** squeezed so nonplanar that the oxygens have somehow bonded (the convention to depict trivalent C and O is to put a formal negative charge on C and a positive charge on O). Although they lie much higher than triplet ethenedione at the MP2/6-31G* level, **12** and **18** may actually be the most realistic C_2O_2 targets for synthesis; this is briefly discussed in the *synthesis* section. The isomer **17** was also studied theoretically as a ligand bound to nickel [37].

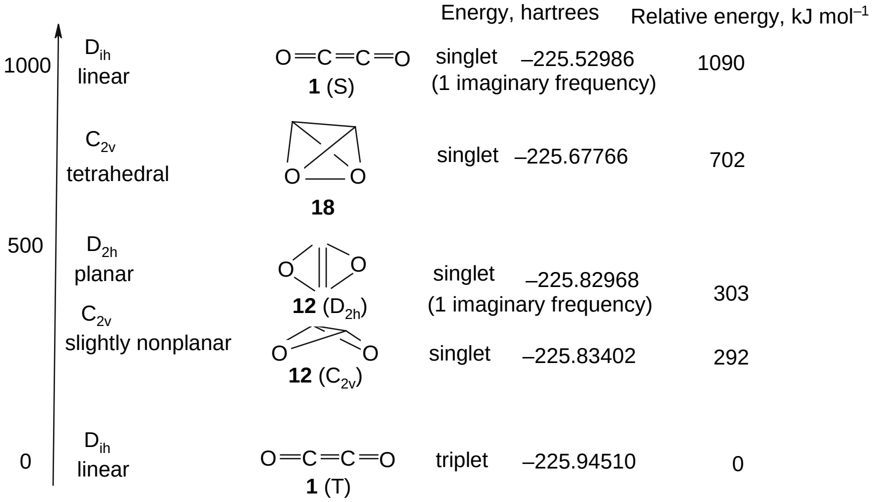
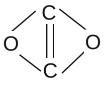


Fig. 9.2 Results of MP2/6-31G* calculations on some C_2O_2 molecules. The energies do not include the ZPEs (which are all 33±5 kJ mol^{-1}). Singlet ethenedione and D_{2h} (planar) C_2O_2 had an imaginary frequency and are thus (at least at this calculational level) transition states rather than relative minima. Author's calculations



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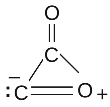

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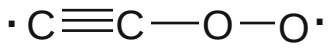

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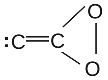

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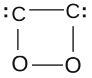

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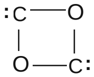

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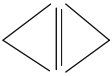
The cation and anion of neutral ethenedione are well-known. The radical cation, $OCCO^{\bullet+}$, was prepared by the reaction of $CO^{\bullet+}$ with CO, isolated in a neon matrix and studied by ESR supplemented by ab initio calculations [38], and it has also been generated by mass spectrometry [39, 40]. The dication is known too [41, 42]. The radical anion was been reported and subjected to extensive theoretical analysis [43][6].

The sulfur analogues OCCS and SCCS are known. Ethenonethione (thioxoethenedione), OCCS, has been observed by neutralization-reionization mass spectroscopy [44], isolated in a cryogenic matrix [45], and has been studied by ab initio computations [2]. Ethenonedithione (dithioxoethenedione), SCCS, has also been studied in the same three ways as OCCS [2, 46]. The three species OCCO, OCCS, and SCCS are calculated to be linear ground state triplets, but the $^1\Delta_g$ singlets are also predicted to be potential energy surface relative minima; only SCCS is predicted to lie below its ground state dissociation product, CS [2].

The imines OCCNH and HNCCNH are apparently unknown. For OCCNH (ethenonimine, iminoethenone), Trindle [1] and Wentrup and coworkers [47] in studies of OCCNH and many related structures calculated that the ground state should be a singlet. Using the G2(MP2) method, an activation energy for decomposition into HNC + CO of 14 kJ mol^{-1} and a reaction energy of 125 kJ mol^{-1} were calculated, and it was concluded that it is “unlikely to be an observable species”, in accord with the failure to detect it by neutralization-reionization mass spectroscopy [47]. For HNCCNH (ethenonediimine, diiminoethenone) the singlet state of this molecule and several isomers were studied computationally (but not barriers to decomposition) and a potential energy surface relative minimum was found [48]. Both OCCNH and HNCCNH are predicted to be nonlinear [47, 48]. Using MP2/6-31G* calculations the author found: OCCNH, for exothermic decomposition to CO + HNC, barrier 14 kJ mol^{-1}, reaction energy -128.5 mol^{-1}; HNCCNH, for exothermic decomposition to 2 HNC, barrier 81 kJ mol^{-1}, reaction energy -34 mol^{-1}. These calculations indicate that both OCCNH and HNCCNH should be observable by matrix isolation near 10 K, and that HNCCNH may even be isolable (although probably not persistent) at or not much below room temperature[7].

Synthesis

Before considering possible approaches to ethenedione, let us consider the bicyclic alkene **12** (above) and the tetrahedral ether **18** (Fig. 2). They are dioxa derivatives of, respectively, bicyclo[1.1.0]but-1(3)-ene (**19**) and tetrahedrane (**20**).



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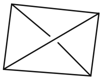

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Alkene **19** is very strained, but probably has a singlet ground state and may be stable in a cryogenic matrix [49, 50]. The anion of **19** has been generated in the gas phase and the heat of hydrogenation of the neutral has been calculated by a thermodynamic cycle [51]. There is good evidence for the generation of a (highly reactive) derivative of **19** [52]. Tetrahedrane, **20**, has not been made but several derivatives are known (Chapter 6). The spontaneous dissociation and singlet-triplet crossing problems that bedevil ethenedione probably do not arise for **19** and **20**, and there is experimental suggestiveness, from the preparation of derivatives, that these two molecules can be made: the barrier to the their synthesis is probably posed by recalcitrance to synthetic methodology rather than by nature. The likely ability of the these hydrocarbons to exist suggests that **12** and **18** may be more realistic synthesis goals than ethenedione.

Conclusions

As noted above, although Talbi and Chandler predicted linear singlet ethenedione to be bound, in contrast to earlier conclusions, they conceded that distortive motions away from linearity could lead to rapid dissociation [2], and Schröder et al. [16], accepting earlier work by Korkin et al. [19] on the inherent instability of singlet ethenedione, concluded that the (bound) triplet would cross to the singlet in about 0.5 ns and immediately dissociate. Even if the singlet does not immediately dissociate, it does appear to be rather fragile, and any residual hope for a reasonably stable ethenedione would seem to almost perish with the prediction of the facile “singletization” of the (hitherto considered stable) triplet. If one accepts the calculations, the only currently known method that offers hope of observing ethenedione is some form of nanosecond or femtosecond spectroscopy. Recent experiments in which molecular beams are coupled to the creation and observation of transients by laser beams have shown that species with lifetimes of about 100 fs (10^{-13}s) can be spectroscopically observed [23]. Since this is 10^4 times as long as the predicted ca. 0.5 ns lifetime of ethenedione, this molecule is, to the femtochemist, long-lived! To implement such an experiment, a precursor is needed from which the elusive molecule could be generated by laser photolysis. Possibilities are photoexcitation of the known van der Waals dimer of CO [53], or photocleavage of one of the diones above, or of the known cyclobutenedione [54] (rather than 1,2-cyclobutanedione, to obviate cleavage to ketene), or of the (unknown) 1,2-diaza-3,4-cyclobutenedione, a formal ethenedione-dinitrogen adduct. Whether the exceedingly coy molecule will yield to such superficially seductive approaches remains to be seen.

Notes

1. MP2/6-31G* calculations yield these energies (ignoring ZPE): triplet C_2O_2, −225.94510 a.u., triplet CO, −112.78584 a.u., singlet CO, −113.02122 a.u. So at this level CO (triplet) + CO (singlet) lie 0.13804 a.u. = 363 kJ mol^{-1} above triplet C_2O_2 and 2 CO (singlet) lie 0.09734 a.u. = 226 kJ mol^{-1} below triplet C_2O_2. At this level linear (D_{ih}) C_2O_2 had one imaginary frequency, leading to bending to a transoid (C_{2h}) structure, and the C_{2h} structure dissociated to 2 CO on attempted optimization. For a detailed examination of the energies and structures of several electronic states of C_2O_2 and C_2S_2 see refs. [1, 2].
2. See Note 1.
3. See Note 1.
4. See Note 1.
5. (a) Matrix isolation: D. M. Birney, J. A. Berson, J. Am. Chem. Soc., 1985, *107,* 4553. (b) Kinetics and thermodynamics of the decabonylation: D. M. Birney, J. A. Berson, Tetrahedron, 1986, *42,* 1561.
6. The work in ref. [43] is discussed in C. J. Cramer, “Essentials of Computational Chemistry”, Wiley. New York, 2002; p. 228.
7. Experience shows that the threshold barrier for isolability at room temperature for a unimolecular process is about 100 kJ mol^{-1}. Some barriers/room temperature halflives for unimolecular reactions: (a) Decomposition of pentazole and its conjugate base: 75 kJ mol^{-1}/10 minutes and 106 kJ mol^{-1}/2 days, respectively. V. Benin, P. Kaszynski, J. G. Radziszki, J. Org. Chem. 2002,

67, 1354. (b) Decomposition of $CF_3CO)OOO(COCF_3)$: 86.5 kJ mol^{-1}/1 minute. S. v. Ahsen, P. Garciá, H. Willner, M. B. Paci, G. Argüello, Chem. Eur. J., 2003, *9*, 5135.

References

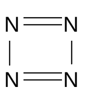
1. C. Trindle, Int. J. Quantum Chem., 2003, *93*, 286.
2. D. Talbi, G. S. Chandler, J. Phys. Chem. A, 2000, *104*, 5872, refs. 3–23.
3. H. Chen, J. L. Holmes, J. Mass Spectrom. Ion Processes, 1994, *133*, 111, 112.
4. J. A. Berson, D. M. Birney, W. P. Dailey III, J. F. Liebman, Chem., Molecular Structure and Energetics (1988), 6 (Mod. Models Bonding Delocalization), 391, 445.
5. A. Gambi, A. G. Gimanini, P. Strazzolini, J. Mol. Struct. (Theochem), 2001, *536*, 9.
6. G. Frapper, J.-Y. Saillard, J. Am. Chem. Soc., 2000, *122*, 5367.
7. N. Boder, P. Buchwald, Chem. Phys. Lett., 2000, *319*, 645.
8. P. Pekka, Chem. Commun., 1999, 495.
9. E. Lewars, J. Mol. Struct. (Theochem), 1996, *363*, 1.
10. E. Lewars, J. Mol. Struct. (Theochem), 2000, *530*, 265.
11. K. A. Nguyen, M. S. Gordon, J. A. Montgomery, Jr., H. H. Michaels, J. Phys. Chem., 1994, *98*, 10072.
12. W. H. Jones, J. Phys. Chem., 1992, *96*, 594.
13. W. H. Jones, J. Phys. Chem., 1991, *95*, 2588.
14. L. Wang, P. G. Mezey, J. Phys. Chem. A, 2005, *109*, 3241.
15. T. M. Klapötke, Angew. Chem. Int. Ed. Engl., 1999, *38*, 2536.
16. D. Schröder, C. Heinemann, H. Schwarz, J. N. Harvey, S. Dua, S. J. Blanksby, J. H. Bowie, Chem. Eur. J., 1998, *4*, 2550.
17. G. Trinquier, G.-P. Malrieu, J. Am. Chem. Soc., 1987, *109*, 5303; see p. 5309 and refs. 32.
18. G. P. Raine, H. F. Schaefer, R. C. Haddon, J. Am. Chem. Soc., 1983, *105*, 194.
19. A. A. Korkin, A. Balkova, R. J. Bartlett, R. J. Boyd, P. v. R. Schleyer, J. Phys. Chem., 1996, *100*, 5702.
20. N. J. Turro, “Modern Molecular Photochemistry”, University Science Books, Sausalito, CA, 1991; Chapter 6.
21. J. P. Lowe, “Quantum Chemistry”, second edn., Academic Press, New York, 1993; p. 419.
22. R. S. Sheridan, Org. Photochem., 1987, *8*, 159.
23. Y. Sato, H. Kono, S. Koseki, Y. Fujimura, J. Am. Chem. Soc., 2003, *125*, 8019.
24. A. J. Alexander, R. N. Zare, Acc. Chem. Res., 2000, *33*, 199.
25. R. L. Rawls, Chem. Eng. News, 2000, *May 22*, 35.
26. R. Dagani, Chem. Eng. News, 1999, *Oct. 18*, 12.
27. H. Staudinger, E. Anthes, Ber. Dtsch. Chem. Ges, 1913, *46*, 1426.
28. J. J. Bloomfield, J. R. Irelan, A. P. Marchand, Tetrahedron Lett., 1968, *54*, 5647.
29. D. Bryce-Smith, A. Gilbert, Chem. Commun., 1968, *21*, 1319.
30. J. Strating, B. Zwanenburg, A. Wagenaar, A. C. Udding, Tetrahedron Lett., 1969, 125.
31. D. Sülzle, T. Weiske, H. Schwarz, Int. J. Mass Spectrom. Ion Processes, 1993, *125*, 75.
32. M. B. Rubin, M. Weiner, H. D. Scharf, J. Am. Chem. Soc., 1976, *98*, 5699.
33. M. B. Rubin, A. Patyk, W. Sander, Tetrahedron Lett., 1988, 6641.
34. R. C. Haddon, Tetrahedron Lett., 1972, 3897–3900.
35. G. Maier, H. P. Reisenauer, B. Roether, J. Eckwert, Liebigs Ann. Chem., 1996, 303–306.
36. S. Evangelisti, Chem. Phys., 1997, *218*, 21.
37. Q. S. Li, J. Guan, J. Phys. Chem. A, 2003, *107*, 8584.
38. L. B. Knight, J. Steadman, K. P. Miller, D. E. Bourman, E. R. Davidson, D. Feller, J. Chem. Phys., 1984, *80*, 4593.
39. J. Mähnert, H. Baumgärtel, K.-M. Weitzel, J. Chem. Phys., 1995, *103*, 7016.
40. K. Hiroaka, T. Mori, S. Yamabe, J. Chem. Phys., 1991, *94*, 2697.

41. M. W. Wong, J. Mass Spectrom., 1995, *30*, 1144.
42. M. Adelhelm, Angew. Chem. Int. Ed. Engl., 1969, *8*, 516.
43. J. R. Thomas, B. DeLeew, P. O'Leary, H. F. Schaefer, B. J. Duke, B. O'Leary, J. Chem. Phys., 1995, *102*, 6525, and refs. therein.
44. D. Sülzle, J. K. Terlouw, H. Schwarz, J. Am. Chem. Soc., 1990, *112*, 628.
45. G. Maier, H. P. Reisenauer, R. Ruppel, Angew. Chem. Int. Ed. Engl., 1997, *36*, 1862.
46. R. G. A. R. Maclagan, J. Mol. Struct. (Theochem), 2005, *713*(1–3), 107, and refs. therein.
47. R. Flammang, Y. Van Haverbeke, S. Laurent, M. Barbieux-Flammang, M. W. Wong, C. Wentrup, J. Phys. Chem., 1994, *98*, 5801.
48. R. A. Evans, P. Lorencak, K. Tae, C. Wentrup, J. Am. Chem. Soc., 1991, *113*, 7261.
49. B. A. Hess, W. D. Allen, D. Michalska, L. J. Schaad, H. F. Schaefer, J. Am. Chem. Soc., 1987, *109*, 1615.
50. B. A. Hess, W. D. Allen, D. Michalska, L. J. Schaad, J. Am. Chem. Soc., 1987, *109*, 7546.
51. P. K. Chou, S. R. Kass, J. Am. Chem. Soc., 1991, *113*, 697.
52. G. Szeimies, J. Harnisch, O. Baumgärtel, J. Am. Chem. Soc., 1977, *99*, 5183.
53. L. A. Surin, D. N. Fourzikov, F. Lewen, B. S. Dumesh, G. Winnewisser, A. R. W. McKellar, J. Mol. Spectrosc., 2003, *222*, 93.
54. J. C. Hinshaw, J. Chem. Soc., Chem. Commun., 1971, 630.
55. E. V. Anslyn, D. A. Dougherty, "Modern Physical Organic Chemistry", University Science Books, Sausalito, CA, 2006; sections 1.2 and 1.3.

Chapter 10
Nitrogen Oligomers and Polymers: Superfuels or Chimeras?

Introduction

In Chapter 9 we considered a dimer of the small, stable molecule carbon monoxide. Here we examine a class of molecules which represents the concatenation of two or more small, stable molecules, namely dinitrogen (actually, we shall also examine some species with an odd number of nitrogen atoms); examples are **1**–**4**:



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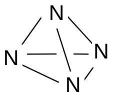

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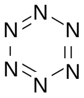

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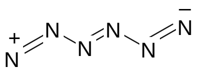


4

We saw that C_2O_2 is likely to be at best very short-lived, for fundamental theoretical reasons; what is the situation with regard to nitrogen oligomers and polymers? For perhaps no other class of compounds of theoretical and potential practical interest is there so little experimental and so much computational information available: there have been hundreds of publications on calculations of nitrogen oligomers and polymers, but relatively few experimental papers. In this chapter no attempt will be made to discuss all the computational work that has appeared on these compounds; rather, the experimental situation (what we know) will be reviewed, and an indication will be given of our theoretical knowledge (what we think we know). These compounds are interesting because of their structural novelty, their experimental coyness, and their supposed potential applications as high-energy-density materials (powerful propellants and/or explosives). This latter possibility arises from the fact that the triple bond of dinitrogen, the expected decomposition product of these higher allotropes, is much stronger than the nitrogen-nitrogen double or single bond, the standard bond energies being 946, 418, and 160 kJ mol^{-1}, respectively. The decomposition would thus be accompanied by a large drop in enthalpy; of course it would also be favored by a large entropy increase. We will refer to species beyond N_2 as polynitrogens.

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_10,

Experimental Results

The experimental aspect will be presented first, to emphasize the dearth of such results. We can put polynitrogens into four classes: neutral molecules, extended-molecular allotropes, isolable ions, and ephemeral ions mainly of mass-spectrometric interest. This fourth class will not be discussed.

Neutral molecules are the polynitrogen species of main interest because they represent pure polymerized nitrogen without the esthetic distraction of a counterion, because they have been the most difficult to realize experimentally, and because being pure nitrogen they are in principle the best candidates for high-energy-density materials. Closed-shell species would seem to be of particular interest, because most stable molecules fall into this class, but radicals and even-electron open-shell molecules will also be mentioned where appropriate. We will consider N_3, N_4, N_5, N_6, N_7, N_8, and "larger molecules".

The simplest neutral polynitrogen, the N_3 radical (azide radical), has been generated as a fleeting molecule by flash photolysis of HN_3 (hydrazoic acid) [1] and by reaction of HN_3 with fluorine atoms [2]. Being a simple free radical, there appears to be no question of its isolation as a stable substance.

The neutral even-electron N_4 (tetranitrogen; specific name depending on the structure) represents a richer and continuing saga. In 2000 Zheng et al. reported evidence for an N_4 molecule which they suggested to be tetraazatetrahedrane, **2**, generated from N_2 in a microwave or electric discharge plasma, trapped by matrix isolation, and tentatively identified by a (weak) IR absorption which was probed by an isotopic $^{14}N/^{15}N$ shift [3]. However, Lee, and Martin showed by their calculations of the vibrational frequencies of **2** that this shift could not be due to this molecule [4] (see too refs. 50, 53, 55, and 56 in [5]). In 2002 Cacace et al. reported the detection of an N_4 molecule, generated by neutralization-reionization of the N_4 radical cation, for which they suggested an openchain C_s triplet structure $NN\cdots NN$ with weakly bound NN moieties [6, 7]. This work was reinvestigated by Nguyen et al. in an experimental study augmented by a very thorough computational investigation of the N_4 potential energy surface and reported with an abundance of references to the work on these species [5]. They were unable to reproduce the neutralization-reionization results of Cacace et al., and concluded that only a very small amount of neutral N_4 is formed in such experiments; the calculations suggested that such mass spectrometry experiments generate as the N_4 species triplet azidonitrene, N_3–N. Rennie and Mayer, however, subsequently reported the detection of N_4 by neutralization-reionization mass spectrometry, and their extensive computations on ionization/neutralization reactions of various species led them to conclude that the N_4 molecule was most likely triplet azidonitrene [8]. In recent studies by Barber et al. isotopic scrambling was observed when molecules in a $^{14}N_2/^{15}N_2$ mixture were excited by energy transfer from electronically excited xenon [9]. This was considered to arise most probably from an "excited complex"; no structure was assigned to this, but there were said to be "ongoing efforts to synthesize tetrahedral nitrogen" and experiments were said to be "underway in an effort to quench some portion of the N_4 complex to either the theoretically stable tetrahedral or rectangular species." An attempt to detect **2**, of T_d or D_{2h} symmetry, by seeking the calculated Raman lines (the Raman spectra of such symmetric molecules should have more observable lines than the IR spectra) in laser-irradiated liquid or solid nitrogen was unsuccessful [10].

Neutral N_5 is perforce a radical and so one immediately suspects that it will not be a reasonably stable species, and in fact there do not appear to be any reports of attempts to synthesize or detect this molecule.

Neutral N_6 is rather interesting (as will be seen more clearly in the discussion of its examination by computational methods). In pulse radiolysis experiments on solutions containing azide ion, kinetic evidence was presented for an N_6 species formed by dimerization of azide radicals, with a UV absorption maximum at 242 nm and a room temperature halflife for decomposition to N_2 of ca. 200 μs [11]. On the basis of the similarity of the UV spectrum to that of benzene, and the earlier reported pattern of isotopic scrambling on electrolysis of labeled azide, it was suggested that this species might be hexaazabenzene (hexazine), **3**, or, on the basis of the UV, an analogue of 1,3,5-hexatriene. In a study of the electrolytic oxidation of azide ion the rate constant for azide radical dimerization was studied, but no structure was suggested for this (supposed?) dimer [12]. The photolysis (in an organic glass at 77 K, or by flash photolysis) of an azide-platinum complex, *cis*-diazidobis(triphenylphosphine)platinum(II), *cis*-$Pt(N_3)_2(PPh_3)_3$, was said to generate N_6, for which the hexaazabenzene (**3**) structure was favored [13]. The N_6 assignment rests, in the 77 K experiments, on a yellow color and on a UV absorption at 380 nm, both of which on warming disappeared with evolution of N_2, and in the flash photolysis experiments on a 380 nm transient which decomposed with first-order rate constant $1.66 \times 10^2\ s^{-1}$. No evidence for the hexaazabenzene structure was given beyond the reference to early calculations [14, 15] which suggested that **3** is slightly stabilized, from which the authors concluded that it "therefore can certainly be stable at low temperatures." This question of the stability of **3** is examined in the section on computational work.

Neutral N_7 is (like N_5) a radical and so is likewise not expected to be reasonably stable. In an experiment of some relevance to N_7, laser-ablated scandium atoms were codeposited with argon/nitrogen at 10 K (the purpose was to study scandium nitride species) [16]. The reported IR spectra gave no indication of the presence of a compound with an N_7 ring coordinated to scandium, a compound which has been predicted by computational methods to "have a fair chance of existing" [17].

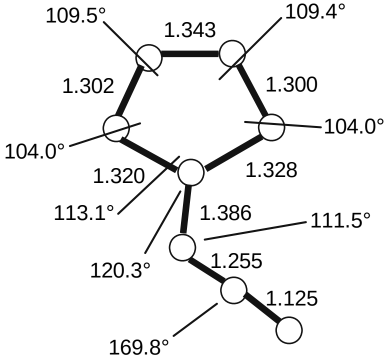
There appear to be no reports of actual attempts to synthesize neutral N_8 compounds, but three computational papers do address the synthesis directly. Fau and Bartlett explored the reaction of the known N_5^+ [18, 19, 20] with azide ion N_3^- in a careful analysis replete with computational caveats and concluded that "isolation of covalently bonded N_8 will be difficult . . . because the most likely product has a decomposition barrier of only 18 kcal mol^{-1} [75 kJ mol^{-1}]. It may not be formed at all because one of the approach pathways has great potential for mutual neutralization and subsequent fragmentation" [21]. The only grounds for some optimism lay in the possibility that in solution at low temperatures acyclic N_8 molecules may be isolable; these were calculated to dissociate with barriers of ca. 67–79 kJ mol^{-1}

into N_2 and N_6 (which latter would not be isolable because it would be destroyed by its great free energy of formation). For isolability at room temperature the threshold barrier is ca. 100 kJ mol^{-1} (see below). A second computational study of the reaction of N_5^+ with N_3^- by Wang et al. examined a sequence of reactions leading to azidopentazole, **5** (Fig. 10.1) (and interconversion of various N_8 isomers) and concluded that this route to **5** may be possible [22]. Azidopentazole was the lowest-energy N_8 compound of many examined computationally by Glukhovtsev et al. (although these workers warn us that "*caution!* [azidopentazole], like other pentazoles should have a low decomposition barrier") [23]. A third study of the N_5^+ N_3^- reaction, by Gagliardi et al. found no viable route to **5** [24].

There do not seem to have been any reports of attempts to synthesize neutral polynitrogens with nine or more atoms.

Extended-molecular allotropes are forms of nitrogen in which the atoms form an extended lattice, analogous to carbon atoms in diamond or graphite. Eremets et al. reported that at very high pressures (240 GPa, ca. 2×10^6 atmospheres) nitrogen forms a "semiconducting non-molecular" phase and, intriguingly, suggest that it "could result in applications at ambient pressures" [25]. This material was made in tiny amounts in a diamond anvil; any such applications would require the procurement of bulk quantities and confirmation that it is indeed kinetically stable at ambient pressures. These workers also reported that above 2000 K (!) and 110 GPa (in a laser-heated diamond anvil cell) another allotrope of nitrogen formed [26]. It remains to be seen if these high-pressure solids can be handled in any quantity under ambient conditions.

Isolable ions, i.e. polynitrogen cations and anions, have met with more synthetic success than have neutral molecules. Although there is experimental evidence (above) for neutral N_4 and N_6 species, none have been isolated; in contrast, the azide ion N_3^- has been known for well over a century, an N_5 cation has been made in macroscopic amounts, and an N_5 anion has been detected.

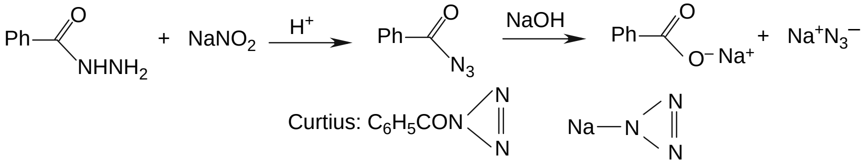


5

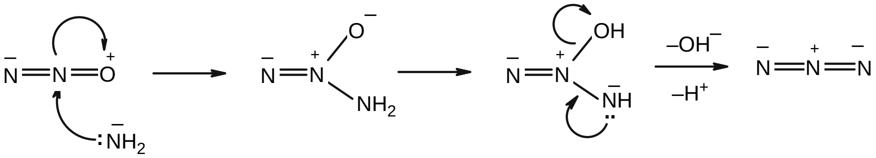
Bond lengths in Å

Fig. 10.1 Azidopentazole, calculated structure (B3LYP/6-311+G*) [23]

Sodium azide, with the azide ion, N_3^-, was first reported in 1890, by Curtius [27]. He called it Stickstoffnatrium (“nitrogen sodium”) and recognized it as a derivative of hydrazoic acid, HN_3, which he also described (“. . . a gas of very peculiar, horribly penetrating smell”) and called Stickstoffwasserstoffsäure (“nitrogen hydrogen acid”) or Azoamid. Curtius made sodium azide by converting benzoylhydrazine to benzoyl azide with nitrous acid and hydrolyzing the azide with sodium hydroxide (cf. the reaction of benzoyl chloride with sodium hydroxide to give sodium chloride):



Of course our concept of ionic compounds did not exist at the time, and in fact Curtius depicted azides as having a three-membered ring (above). The usual route to sodium azide is by reaction of nitrous oxide with sodium amide, which presumably occurs by nucleophilic attack of amide ion on N_2O and elimination of water [28]:



Sodium azide is fairly safe to handle and has many uses, while heavy-metal (e.g. lead) azides are shock-sensitive explosives used as detonators [28, 29]. Perhaps the most widespread use of an azide is that of sodium azide in airbags, where thermally induced ignition releases nitrogen (for current applications of azides, consult the internet). An important use of the azide ion is the preparation of organic azides, which are important in synthesis [30]. The azide ion is linear and centrosymmetric [31].

There have been no reports of the isolation of N_4 ions; these would be radical ions, which suggests heightened reactivity compared to closed-shell species.

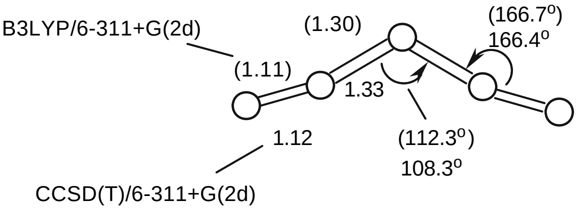
The synthesis of the pentanitrogen cation N_5^+ (**6**) marks a milestone in polynitrogen chemistry [32], because this is only the second polynitrogen to have been actually isolated, as distinct from just spectroscopically detected. Salts of the azide ion were first reported in 1890 [27], and salts of the pentanitrogen cation in 1999 [18]. The hiatus suggests that the synthesis of polynitrogens involves problems. The first N_5^+ salt used the hexafluoroarsenate counterion:

$$N_2F^+AsF6^- \quad + \quad HN_3 \xrightarrow[-78°C]{HF} N_5^+AsF_6^- + HF$$

This salt is fairly stable at room temperature, but a 5 mg sample exploded and destroyed a Raman spectrometer probe; the hexafluoroantimonate anion proved to give a stabler salt [19]. In a determined search for high-energy-density materials salts of N_5^+ with other anions, including azido-containing anions, have been made, e.g. $N_5^+[B(N_3)_4]^-$ [20]. Compounds like these, and others with a high mass ratio of azide to metal, e.g. $Ti(N_3)_4$ [33], are in a sense an approach to “solid nitrogen”: $Ti(N3)_4$ is by mass 78% nitrogen, and $N_5[B(N_3)_4]$ is a whopping 96%. It is almost as if boron were being used as a glue to give us N_{17}. The calculated (Fig. 10.2) [18] and experimental (from X-ray analysis of $N_5^+Sb_2F_{11}^-$, [19]) structures of the cation **6** are the same to within experimental error. The cation can be described as a resonance hybrid of six structures which give all the NN bonds some multiple-bond character [19]. The bonding has also been subjected to an involved theoretical analysis in terms of electron distribution, which led to the conclusion that the geometry can be rationalized by invoking three-center four-electron (3c-4e) bonding [34].

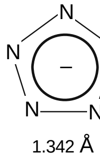
The pentanitrogen anion that has dominated theoretical probing and experimental endeavor is the pentazole anion (pentaazacyclopentadienyl anion) (**7**, Fig. 10.3). This structure has been pursued to the near-exclusion of putative isomeric species because the well-known stability of the hydrocarbon analogue $C_5H_5^-$ suggests that the polynitrogen, too, may possess special stability, and because substituted pentazoles ($N_5{-}R$) have long been known [35, 36] and offer an obvious potential route to pentazole anion, either by some analogous synthesis, leading to N_5H (i.e. R = H) and then to N_5^-, or by removal of an R group with deposition of an electron pair on the ring. In the event, the anion has recently been made by the second of these approaches, using as the precursor $N_5{-}R$ with an electron-donating R group; three variations on this theme have been reported. The first detection of the pentazole anion was reported by the Christe group in 2002 [37]. They generated the ion in a mass spectrometer by accelerating the conjugate base of *p*-hydroxyphenylpentazole (made in CH_3CN solution from *p*-hydroxyphenylpentazole and a base like pyridine) through a high voltage and allowing it to collide

Fig. 10.2 The N_5^+ cation. This calculated structure [18] is essentially the same as the experimental (X-ray crystallographic) one [19]



6

N_5^+ Bond lengths in Å



7

Fig. 10.3 The pentazole anion, calculated structure (C_{5h} symmetry) [37]

with nitrogen or argon molecules (Fig. 10.4). The second report of the detection of **7** used laser detachment ionization on solid *p*-N,N-dimethylaminophenylpentazole to generate **7**, which was detected by mass spectrometry (Fig. 10.4) [38]. The authors say that unlike the mass spectrometric collision method laser detachment in principle allows matrix isolation of **7** and thus its study by IR and UV spectroscopy. These two approaches have been analyzed theoretically, with the conclusion that electronically excited states are involved [39]. A third reported route to **7** was the oxidation of *p*-methoxyphenylpentazole with ceric ammonium nitrate in solution (Fig. 10.4) [40]. The pentazole anion was said to have been generated in the presence of zinc ion and identified by ^{15}N NMR spectroscopy of the zinc salt in solution

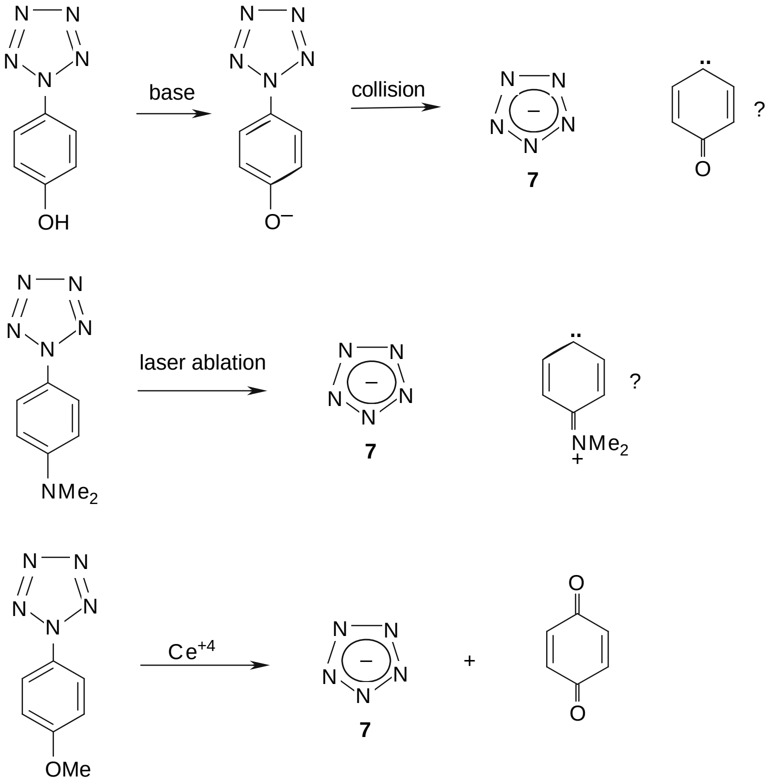


Fig. 10.4 Two synthesis of pentazole anion [37, 38] and an attempted synthesis [40]

at −40°C. However, repetition of this experiment by the Christe group and examination of the products by ^{15}N NMR and Raman spectroscopy gave no evidence for the generation of **7**, indicating that the isolation of the anion remains elusive [41]. (but see note 1 added in proof).

The halflife of **7** in methanol solution at 0°C has been inferred (by a combination of calculations, and measurements on other reactions) to be an encouraging 2.2 days (barrier 106 kJ mol^{-1}); this procedure also indicated a halflife of only 10 minutes (barrier 75 kJ mol^{-1}) for N_5H, which does not bode well for the use of azidopentazole, N_5N_3 as a high-energy-density material [42]. The availability of N_5^+ and the possibility that N_5^- may become available in a synthetically useful form suggests the exciting possibility of the synthesis of the salts $N_5^+N_3^-$ and $N_5^+N_5^-$. Unfortunately, this seems not to be possible: calculations using estimated lattice energies and calculated adiabatic ionization energies and electron affinities indicate that for $N_5^+N_3^-$ electron transfer should cause spontaneous decomposition to the N_3 radical and molecular nitrogen. This received strong support when $N_5^+SbF_6^-$ and alkali metal azides were mixed in solution, whereupon a "violent" reaction occurred with nitrogen evolution [43]. Calculations by other workers indicated a barrier of about 67 kJ mol^{-1} (16 kcal mol^{-1}) for decomposition of solid $N_5^+N_5^-$, despite which low value they asserted that "If a crystalline form of $N_5^+N_5^-$ could be stabilized it would be an ideal monopropellant . . . "; their conclusions for $N_5^+N_3^-$ were less sanguine: they concluded that this entity (best described as a complex with strong electron transfer rather than an ion pair) would decompose with a barrier of only 50 kJ mol^{-1} (12 kcal mol^{-1}) [44]. A study of the potential energy surface for the N_5^+ + HN3 reaction suggested that N_8H^+ may be an accessible high-energy-density species [45].

The reaction of N_3^- with photoexcited triplet ketones has been reported to give a transient $N_6^{\bullet}$ radical anion for which a structure with two N_3 units held together by one or two long bonds was suggested [46].

Theoretical Results

In contrast to the few reports of attempts to synthesize polynitrogens, there are hundreds of computational papers on these species. Fortunately, a fraction of these will suffice to give a fair perspective on our theoretical understanding of these (almost all experimentally unknown) compounds. We will first report on some surveys of a variety of polynitrogens, then look in some detail at a few of those of particular interest, considering cyclic and then acyclic molecules.

Cyclic N_8 Molecules

Glukhovtsev et al. examined molecules with 4, 6, 8, 10, 12, and 20 atoms, seeking to identify the stablest of these polynitrogens [23]. They optimized the geometries of 32 molecules, cyclic and acyclic, and estimated the energies of another eight acyclics by an increment method. For the cyclic molecules, aromaticity was probed by a magnetic criterion and strain energies were estimated by comparison of energies with those of a set of standard group values. The salient conclusion of this study was that pentazoles (five-membered nitrogen rings) are the thermodynamically stablest nitrogen compounds. Azidopentazole (Fig. 10.1, **5**) was identified as a reasonable target for synthesis, and the reaction between LiN_5 (an as-yet unprepared derivative of the pentazole anion **7**) and the known N_3–Halide was suggested as a possible route to it. Nguyen and Ha, too, found azidopentazole to be the thermodynamically stablest of three N_8 isomers, octaazapentalene **8** and diazidodiazene **9** (Fig. 10.5), and azidopentazole, **5** (Fig. 10.1; conventional bonding is left unspecified in the representations of **8** and **9**) but did not calculate decomposition barriers [47]. They suggested that **5** may be preparable by somehow replacing the X group on a substituted pentazole X–N_5 by N_3.

One should note that in seeking a high-energy-density material, what we really want (synthesis problems aside) is a substance that is kinetically stable and thermodynamically *un*stable (high-energy compared to dinitrogen), and these calculations, since barriers to decomposition were not evaluated, did not address directly kinetic stability. If the energy-releasing decomposition reaction is well-defined, the thermodynamic aspect is relatively easy to calculate reliably, since it does not require one to locate a transition state and, what is more challenging, to calculate for this a good relative energy [48]. The standard heat of formation of azidopentazole, calculated by the author using the reliable atomization method at the G3 level (G3 calculations: [49, 50, 51]; cf. G2 heats of formation by the atomization method [52]) is 940 kJ mol^{-1}. Clean decomposition to dinitrogen would thus liberate 940 kJ of heat energy for each 112 g (the molecular weight) of **5**, i.e. we can assign it in this sense an energy density of (1000/112)940 = ca. 8400 kJ kg^{-1}. Compare this with the all- single-bond octaazacubane (**10**), with a calculated heat of formation of 1854 kJ mol^{-1} (443 kcal mol^{-1}) [53]; this translates to ca. 16600 kJ kg^{-1}. We can compare azidopentazole with a more familiar energy-rich material, a stoichiometric hydrogen-oxygen mixture (this is used in the space shuttle, mixed in situ in the rocket motor). The molar heat of formation of water is −242 kJ, and standard

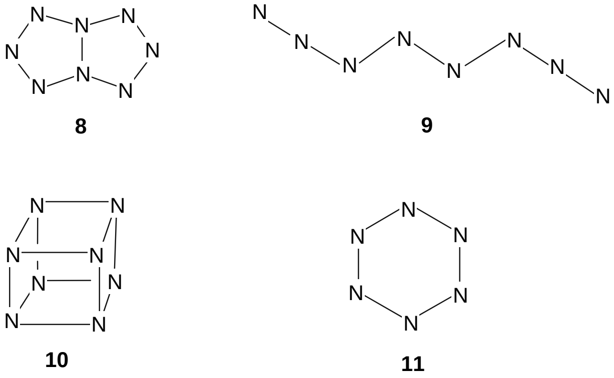

8 **9** **10** **11**

Fig. 10.5 Some polynitrogens discussed in the text. Bond order (single, double, etc.) is not specified corrections for the heat capacity and latent heat of vaporization of water give H_2/O_2 (gas, stoichiometric, for the formation of gaseous H_2O) an energy density of ca. 11000 kJ kg^{-1}. Kinetic stability aside, azidopentazole is fairly impressive as a potential high-energy-density material, although it is interesting that the prosaic but practical hydrogen-oxygen propellant combination seems better, on a mass-basis, than this exotic (and still putative) chemical explosives/propellant. Of course the utility of a chemical explosive or propellant depends on other things in addition to this simple energy content; several of these more sophisticated criteria are treated by Engelke in a paper on nitrogen cubanoids [53].

That azidopentazole is probably the lowest-energy (thermodynamically stablest) N_8 isomer seems to have led to the tacit assumption that it is likely to be the kinetically stablest, an assumption that is not at all necesarily true. The kinetic aspect of the stability of **5** has been examined with the conclusion that the barrier is at most about 84–105 kJ mol^{-1}: Gagliardi et al. calculated a barrier of 79 kJ mol^{-1} (19 kcal mol^{-1}) [54], Chung et al. 46 kJ mol^{-1} (13 kcal mol^{-1}) [55], and Goldberg et al. 92–105 kJ mol^{-1} (22–25 kcal mol^{-1}) [56]. All conclude that this low a barrier is unpromising for the application of this compound as a high-energy-density material: the threshold for room-temperature stability toward unimolecular decomposition is about 100 kJ mol^{-1}: see [42] above, also note 2. Azidopentazole thus seems to be only a borderline possibility as a practical high-energy-density material.

Octaazacubane, **10** (Fig. 10.5), mentioned above, is another interesting N_8 polynitrogen that was surveyed by Glukhovtsev et al. [23] and was the subject of pioneering work by Engelke [53, 57, 58], who also investigated ten [53] and all 22 [57] azacubanes, formal derivatives of the known cubane, $(CH)_8$ [59]. In a detailed examination of ten azacubanes, Engelke calculated (above) that **10** would be a much more powerful explosive/propellant than the powerful explosive HMX [53]. Glukhovtsev et al. also found **10** to be a very high-energy molecule, lying about 1020 kJ mol^{-1} above **5**, by comparison of their B3LYP/6-311+G* energies [23]. Engelke [53, 57] and Engelke and Stine [58] concluded from the absence of very low-frequency vibrations that these molecules likely reside in reasonably deep potential wells, and decomposition to dinitrogen along a symmetric pathway indicated a barrier of ca. 420–670 kJ mol^{-1} (100–160 kcal mol^{-1}) [58]. Symmetry arguments led Lauderdale et al. to conclude that “One would . . . expect that N_8 . . . would be relatively stable” [60]. However, more detailed studies of the potential energy surface for the decomposition of octaazacubane led to a different conclusion: Schmidt et al. calculated a rate-determining barrier of ca. 63 kJ mol^{-1} (15 kcal mol^{-1}) on the “rather complicated” dissociation pathway, and concluded that its stability was “too modest to allow hope for its handling in bulk quantity” [61]. Gagliardi et al. also concluded that the dissociation would likely be a complex multistep process, and found a barrier of 92 kJ mol^{-1} (22 kcal mol^{-1}) for a critical step, indicating that it is “unlikely that N_8 will exist for a long time at room temperature” [62]. This evident fragility is disappointing, particularly in view of the fact that cubane itself is quite stable kinetically, although highly strained. Apropos of this, the high energy content of octaazacubane was ascribed by Engelke not to strain, but rather to the great strength of the NN triple compared to single bond [53]; however this was disputed by Gagliardi et al. [63].

Cyclic N_6 Molecules

Besides the N_8 molecules azidopentazole and octaazocubane, the N_6 hexaazabenzene (**11**) is of special interest. Interestingly, there do not seem to have been any serious early expectations that hexaazabenzene would be analogous to benzene in being kinetically stable. Perhaps the first reference to a computation on **11** is by Roberts, where he points out that a simple Hückel calculation on this molecule would be exactly analogous to one on benzene, provided the nitrogen lone pairs were assumed to be in-plane and nitrogen rather than carbon *p*-orbital parameters were used [64]. Such a calculation would be performed on an assumed fixed geometry and provide at best only suggestive information, like the HOMO–LUMO gap, and the Hückel resonance energy, which could be compared to the values for benzene and might indicate the effect of replacing carbon by the more electronegative nitrogen. The first quantitatively useful computations on **11** were evidently done by Mortimer [65] and by Dewar and Gleicher [66]. Hückel-type calculations allowed an estimate of the heat of atomization from overlap populations [65], and in a paper on the development of the simple Hückel method into an approach which gave reliable bond lengths and heats of formation for conjugated molecules, it was reported that "The calculated heat of formation of hexazine suggests that its preparation may prove somewhat difficult . . . " [66]; subsequent work indicates that this may be an understatement.

Following these earliest (in the 1960s) references to hexaazabenene, the molecule appeared in the 1970s as part of examinations of polynitrogens in a modest number of studies with perforce (in view of the limited capabilities of the methods then available) modest results: further semiempirical calculations by Dewar [67] and early ab initio calculations by Wright [14, 15] and Palmer et al. [68, 69] gave no definitive results. The next decade, however, saw calculations which dealt directly with the key questions about hexazine: is it a relative minimum on the potential energy surface, and if so, how stable might it be kinetically (that this species is unstable thermodynamically compared to dinitrogen can scarcely have been in doubt)? These are of course the key questions about all these unknown polynitrogens. Ha et al. concluded that planar hexazine (of D_{6h} or D_{3h} symmetry) should decompose without a barrier to dinitrogen, but suggested that it might be stabilized by solvent or matrix effects [70]. They calculated for D_{6h} **11** (planar, hexagonally symmetric) that it would (assuming it could somehow exist) absorb at 391 nm, and suggested that it might be the species responsible for the 380 nm absorption in the 77 K diazidoplatinum photolysis experiments of Vogler et al. [13]. The agreement with the experimental absorption is good, especially in view of the somewhat rudimentary method that had to be used at the time (CIS, configuration interaction, singles). The author calculated the UV spectrum of **11** with D_{6h} (**12**) and with D_2 (**18**, nonplanar, like twist cyclohexane; below) symmetry, using the probably more reliable time-dependent DFT (TDDFT) method [71] and obtained the results shown in Table 10.1 (the acyclic species **17** is discussed below). The calculated absorptions could certainly be regarded as supporting the formation of D_2 **11** (376 nm cf. a reported 380 nm). However, subsequent work strongly indicated that hexaazabenzene would not persist at 77 K.

Table 10.1 UV absorptions of polynitrogens calculated with Gaussian 03 by TDDFT, using B3P86/6-311++G** TD=(Singlets, NStates=6) [71]. The numbers refer to idealized absorption maxima (nm) and (in parentheses) oscillator strengths, a measure of absorption intensity; bands of theoretical oscillator strength zero can in fact give rise to weak absorption

Hexaazabenzene (**12**), D_{6h} MP2/6-31 G* geom	Hexaazabenzene (**18**), D_2 MP2/6-31 G* geom	Acyclic N_6, C_2 (**17a**) MP2/6-31 G* geom	Acyclic N_6, C_{2h} (**17b**) B3LYP/6-31 G* geom
505 (0.0000)	423 (0.0000)	431 (0.0004)	439 (0.0005)
480 (0.0000)	405 (0.0035)	338 (0.0020)	344 (0.0000)
480 (0.0000)	376 (0.0037)	267 (0.0003)	253 (0.0119)
475 (0.0131)	338 (0.0000)	233 (0.0629)	216 (0.0000)
423 (0.0000)	251 (0.0000)	227 (0.0002)	213 (0.0000)
236 (0.0000)	243 (0.0086)	204 (0.0034)	189 (0.0004)

Indications that D_{6h} **11** may be rather fragile came in 1981 [70] and 1982 [72] (above). Soon after, the problem was met head-on by Saxe and Schaefer [73] who examined the hexaazabenzene potential energy surface and calculated the frequencies of **11**-type species.[3] Calculation of the frequencies of a species permits determination of the curvature of the potential energy surface at that point, i.e. assignment of the species as a minimum, transition state of hilltop [74]. They concluded that the N_6 potential energy surface in the region of D_{6h} **11** is very flat: significant geometry changes result in only small energy changes. This meant that to confidently characterize (as minima, transition states or hilltops) species with the gross hexaazabenzene structure but of various symmetry classes required a computational level higher than was available to these workers, in particular, optimizations at a correlated level (correlated energies were single-point, i.e. calculated on SCF-level geometries). Although their other conclusions were quite tentative, the study predicted D_{6h} hexaazabenzene to be a relative minimum (about 960 kJ [about 230 kcal] above three moles of dinitrogen molecules – “a dimple on top of a mountain”), in contrast to three then-recent studies which found it to decompose without a barrier [67, 70, 72]. A corollary of the flatness of the potential energy surface is the susceptibility of **11** to geometric deformation, which suggested the possibility that it could be stabilized by solvent or matrix effects and might possibly have been the species responsible for the 380 nm absorption in the photolysis experiment [13]. Another study of hexaazabenzene at the SCF level with calculations of frequencies and single-point correlated energies was reported by Engelke in 1989 [75]. This work involved the N_6 analogues of the five $(CH)_6$ isomers [76, 77] that have been of particular interest to chemists: structures **12–16** (Fig. 10.6) are analogues (replace N by CH) of, respectively, benzene, Dewar benzene, benzvalene, prismane (or triprismane), and bicyclopropenyl. Note that all of these benzene valence isomers have been synthesized while none of the nitrogen compounds are known! Calculations at the SCF level with a 4-31 G* basis found all five N_6 isomers to be “stable”, meaning that they were relative minima at this level. However, for D_{6h} hexaazabenzene (**12**), unlike the case of **13–16**, the lowest-energy vibration (208 cm^{-1}) would in the limit lead to dissociation into three molecules of dinitrogen. That **12** had a low-frequency

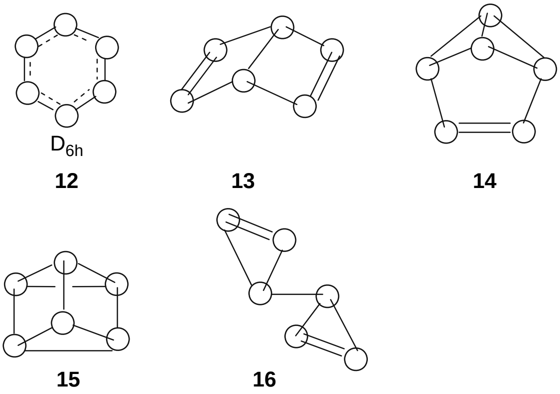


Fig. 10.6 Nitrogen analogues of the five benzene valence isomers [75]

dissociative-type mode but the other structures did not, suggested that this species was less “rigidly defined” (less stable?).

As indicated above, one problem with this work of Saxe and Schaefer [73] and Engelke [75] was that calculations with electron correlation [78], which were done with configuration interaction, CI, had to be performed on structures optimized at the SCF, rather than a correlated, level, which obviated the possibility of checking the curvature of the potential energy surface at the correlated level. The 1990s saw the widespread use of calculations in which electron-correlated potential energy surfaces were calculated by the convenient Møller-Plesset (specifically MP2) or density functional theory (DFT) methods [78]. Let us consider calculations on hexaazabenzene by four groups, in the 1990s and in 2001 and 2004. At the SCF level Engelke had found all five N_6 analogues of the benzene valence isomers (Fig. 10.6) to be relative minima, with an indication from the vibrational frequencies that **12** was less “rigidly defined” than the others [75]. Reexamination of these five isomers (diazide, **17**, was also examined and the C_2 structure **17a**, as well as the quite similar C_i structure, were found to be relative minima: Fig. 10.7) on the MP2-correlated (MP2/6-31 G*) potential energy surface found only **13** (hexaazadewar benzene), **14** (hexaazabenzvalene), and **15** (hexaazaprismane) to be relative minima at that level; in particular, hexaazabenzene, **12**, was

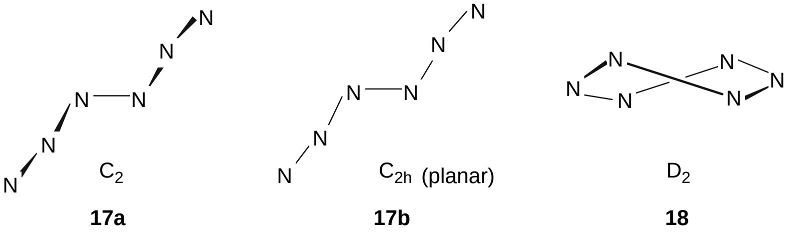


Fig. 10.7 Stable isomers of N_6 at the MP2/6-31 G* level [80, 23]. Bond order (single, double, etc.) is not specified

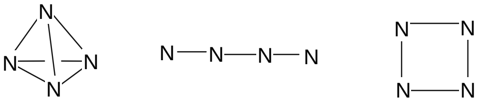
a hilltop with two imaginary frequencies [79].[4] Glukhovtsev et al. surveyed N_6 isomers with MP2/6-31 G* optimizations [80], and molecules with 4, 6, 8, 10, 12, and 20 nitrogens with MP2/6-31 G* and DFT optimizations [23]. D_{6h} **12** was a hilltop on the MP2/6-31 G* potential energy surface, in agreement with Engelke's result [79], but a relative minimum was found for the D_2 geometry **18** (Fig. 10.7) [80]. Using higher-level correlated (MP4SDTQ/6-31 G*) single-point calculations on the MP2/6-31 G* geometries the acyclic molecule diazide, **17a** (C_2), was lower in energy than **18** by about 109 kJ mol^{-1} (26 kcal mol^{-1}) (**17a** was in fact the lowest of all the N_6 isomers examined), and **18** was 895 kJ mol^{-1} (214 kcal mol^{-1}) above three dinitrogen molecules. Glukhovtsev et al. pointed out that the D_{6h} MP2/6-31 G* geometry which had been considered a transition state by Ha and Nguyen [81] is in fact a hilltop. These molecules were revisited in a broader survey of polynitrogens in which DFT as well as MP2 methods were used [23]. The DFT (B3LYP/6-311+G*) calculations were in general agreement with the earlier, MP-type [80], results: with D_{6h} symmetry hexaazabenzene was a hilltop with two imaginary frequencies, but with D_2 symmetry (**18**) it was a relative minimum; diazide (**17b**, planar unlike the twisted MP2 structure **17a**) was also a relative minimum, 134 kJ mol^{-1} (32.1 kcal mol^{-1}) below **18**.

Using DFT and coupled-cluster[5] methods, Tobita and Bartlett (2001) executed a comprehensive search of the N_6 potential energy surface [82]. They examined the benzene valence isomers **11**, **13**, **15**, and **16**, and the acyclic **17**. DFT agreed with earlier studies that for hexaazabenzene the D_{6h} structure **12** is not a relative minimum [cf. 75, 80], but that the D_2 structure **18**, is [cf. 80]. The geometry of the D_2 structure varied significantly with the computational method; with the PW91 functional a structure resembling two well-bound N_3 units was obtained, and at the CCSD(T) method and the aug-cc-pVDZ basis a van der Waals $(N_3)_2$ structure was obtained (cf. Ha and Nguyen [81]). A CCSD(T)/cc-pVDZ optimization gave a properly bound D_2 minimum, but the dissociation mode vibration was only 74 cm^{-1}; these results all suggest that D_2 hexaazabenzene is, at best, a molecule that would dissociate with a low barrier. In fair agreement with Glukhovtsev et al. [80] the acyclic diazide was a relative minimum (the C_{2h} **17b**, rather than the C_2 **17a** structure as in [80]), 92 kJ mol^{-1} (from heats of formation: $212-189 = 22$ kcal mol^{-1}) below **18**, and 791 kJ mol^{-1} (189 kcal mol^{-1}) above three dinitrogen molecules; the values in [80] are quite similar, 109 and 895 kJ mol^{-1}.

Fabian and Lewars studied the structures and the kinetic and thermodynamic stabilities of benzene and the azabenzenes with one to six nitrogens [83]. Again, the relative-minimum structure for hexaazabenzene was found to have D_2 symmetry (**18**). The barrier to decomposition to three dinitrogen molecules was calculated to be very low: 2 kJ mol^{-1} by MP2/6-31 G*, -1 kJ mol^{-1} by B3LYP/6-31 G*, and -9 kJ mol^{-1} from CCSD(T)/6-31G* single-point energies on MP2 geometries (the negative barriers are probably just due to the errors in zero-point energies, possibly combined with errors in the single-point method itself [84]; this suggests that **18**, ca. 800-900 kJ mol^{-1} above three dinitrogens, has a barrier to fragmentation of at most 10-20 kJ mol^{-1}. Despite the evident great fragility of **18**, it seems to be aromatic, in the sense of sustaining a diatropic ring current and having a quite even cyclic electron distribution; the aromaticity of N_6 rings has been noted by others [85, 86, 87, 88]. However, from the viewpoint of thermodynamic stability compared to an open-chain analogue (e.g. benzene cf. hexatriene) hexaazabenzene is not aromatic [83]. From all these studies one can conclude that hexaazabenzene may be capable of marginal existence (with a very low barrier for fragmentation to dinitrogen) as a nonplanar D_2 molecule. Hexaazabenzene is unlikely to endure at 77 K, so it is probably not the species seen in the azide-platinum photolysis experiments [13], despite the fact that the TDDFT UV spectra (above) seem to agree better with D_2 hexaazabenzene than with acyclic N_6.

Cyclic N_4 Molecules

Although several cyclic N_4 structures can be drawn, the tetrahedral, acyclic, and rectangular structures seem the most realistic for synthesis (**19**, **20**, and **21** Fig. 10.8). We looked at reports of the preparation of **19** [3] and evidence against this [4, 8], and the report of the preparation of **20** (as weakly-bound N_2 moieties) [6, 7] and counterevidence [5], as well as other so-far unsuccessful attempts to characterize an N_4 species [9, 10]. We will look at some theoretical treatments of **19**, **20**, and **21**. Schleyer and coworkers found all three structures to be relative minima (B3LYP/6-31 G*) with the triplet state of the acyclic C_{2h} **20** being the lowest-energy N_4 species [23, 89, 90]. Nguyen et al. reviewed the status, experimental and theoretical, of N_4 species and reported their extensive computational studies of cationic, and neutral triplet and singlet N_4 molecules [5]. They concluded that triplet acyclic **20** with an azidonitrene structure, NNN–N (essentially a compact azide unit bonded to a nitrogen atom) was the lowest-energy N_4 species and most likely the species detected by Cacace et al. [6,7], and calculated that it should lie 56 kJ mol^{-1} below tetrahedral N_4 **19**, 69 kJ mol^{-1} below singlet azidonitrene, and 714 kJ mol^{-1} above dinitrogen, with this decomposition barrier being about 40 kJ mol^{-1}. Tetrahedral N_4, **19**, while being more energetic than azidonitrene, had a calculated barrier to decomposition of 250 kJ mol^{-1}, in agreement with work by Lee and Rice (barrier ca. 255 kJ mol^{-1}, **19** ca. 780 kJ mol^{-1} above dinitrogen [91]) and Dunn and Morokuma (barrier ca. 250 kJ mol^{-1} [92]). Tetraazacyclobutadiene, rectangular **21** (D_{2h}), is about as energetic as **19** or slightly higher (e.g. ca. 750 cf. 740 kJ^{-1} [23]) but seems to be much less stable kinetically: the barrier for its dissociation has been calculated at from 13 to 138 kJ mol^{-1} (3–33 kcal mol^{-1}) depending on the method [93] and 27 kJ mol^{-1} (6.5 kcal mol^{-1}) [94]. This can be compared with ca. 40 kJ mol^{-1}



19 **20** **21**

Fig. 10.8 Some N_4 isomers. Bond order (single, double, etc.) is not specified for acyclic azidonitrene and ca. 250 kJ mol^{-1} for tetraazatetrahedrane (above). If the barrier for **19** is even approximately correct, tetraazatetrahedrane should be a kinetically stable very high-energy substance, with one caveat: Yarkony pointed out the possibility that spin-orbit coupling might cause the molecule to cross over to an excited state potential energy surface from which facile dissociation could occur [95]. With this reservation, **19** is an important synthesis target.

Cyclic Polynitrogens with Several Rings

We finish our survey of theoretical work on polycyclic polynitrogens with ribbons [96] and cage-type polycyclic molecules [97, 98, 99, 100]. Wang and Mezey examined nitrogen and nitrogen-rich (N/H) molecules composed of fused rings forming helical ribbons. An N_{26} molecule was found to have a dissociation barrier of only 4.85 kJ mol^{-1}, hopelessly low for practical applications [96]. Zhou et al. studied "multilayer" structures reminiscent of carbon nanotubes and found structures with pentagons to be favored [97]. Strout probed factors affecting the thermodynamic stability of various N_{14} and N_{16} [98] and Strout and coworkers similarly examined N_{18} polyhedra [99] and N/O cage compounds [100]. Manaa calculated optical properties for the potentially useful fullerene derivative $C_{48}N_{12}$ [101] and considered N_{60} itself, suggesting that a bis(pentazole) N_{10} molecule might be used to elaborate the azafullerene [102]. As imaginative as the structures are, these studies suffer from the dearth of direct calculations of decomposition barriers (that such species lie thermodynamically far above dinitrogen or small N/H or N/O molecules is not surprising) and from the fact that the synthesis of detectable, not to mention technically useful, amounts of the compounds is a truly daunting task.

Acyclic Molecules

Acyclic unbranched polynitrogens $N \cdots N$ (somewhat misleadingly called linear) with up to about 20 atoms have been studied computationally. All this work can be simply summarized: they are almost monotonously unpromising as high-energy-density materials by virtue (?) of low barriers for decomposition to, ultimately, dinitrogen; the situation was reviewed by Strout and coworkers [103]. In this paper an optimistic barrier for the decomposition of N_9 [104] was revised downward, from 148 kJ mol^{-1} (35.4 kcal mol^{-1}) to ca. 71 kJ mol^{-1} (ca. 17 kcal mol^{-1}). As indicated above, the threshold barrier for isolation at room temperature is ca. 100 kJ mol^{-1}, and this may bestow a halflife of only minutes to days at room temperature [42].[6] Chung et al. suggested that a barrier of at least 125 kJ mol^{-1} (ca. 30 kcal mol^{-1}) is probably needed for the robust room-temperature stability that a useful high-energy-density material must have [55]. As Strout and coworkers point out, "linear, cyclic and small cage N_x molecules generally do not meet this criterion for stability" and "the accumulation of theoretical data . . . seems sufficient to draw the conclusion that *all* [emphasis in original] acyclic nitrogen molecules will lose N_2 (and possibly other fragments) too easily for any such molecule to be a viable HEDM. A viable all-nitrogen HEDM will have to take some form other than acyclic molecules, perhaps nitrogen cages or other three-dimensional forms" [103]. This pessimism about acyclic and simple cyclic polynitrogens perhaps accounts for the baroque structures considered in the section above (*Cyclic Polynitrogens with Several Rings*).

Because it is an isomer of hexaazabenzene, which has been of special interest (*Cyclic N6 Molecules*, above), this section closes with another look at acyclic N_6 (diazide), which we briefly considered in connection with hexaazabenzene. Gagliardi et al. examined *cis* and *trans* diazide structures and carried out a careful study of the kinetic stability of the lower-energy *trans* C_{2h} structure (**17b**) [105]. This molecule, 96 kJ mol^{-1} (212−189 = 23 kcal mol^{-1}) below D_2 hexaazabenzene and the stablest N_6 isomer [82], was found to decompose to three dinitrogens in a concerted manner with a barrier of 105–126 kJ mol^{-1} (25–30 kcal mol^{-1}). Diazide is a candidate for two roles: it could be the species responsible for the 380 nm absorption in the azide-platinum photolysis experiments of Vogler et al. [13] (it is certainly a better candidate than hexaazabenzene), although it must be admitted that the agreement of the calculated and experimental UV spectrum is not good (Table 10.1); or it just might be, *pace* Strout and coworkers [103], a viable high-energy-density material, its calculated decomposition barrier [105] being, at the high end of the estimate (126 kJ mol^{-1}), about at the threshold for eligibility for this task. The two roles are evidently mutually exclusive, since the transient in the photolysis experiment "immediately disappeared" on warming the 77 K matrix [13]. Whether or not diazide was actually made in this experiment, some such approach seems promising (see the *Synthesis* section).

Some "Conventional" Polynitrogens

The exotic polynitrogens that have been the subject of most of this account are not very promising from the point of view of stability and ease of synthesis, with the possible exception of diazide, above. Somewhat more prosaic are known azido compounds like $N_5^+[B(N_3)_4]^-$ [20] and $Ti(N_3)_4$ [33], mentioned above (*Isolable ions*). There are related compounds that come to mind that, on the basis of their resemblance to known substances, may be expected to be synthetically more accessible, for example the polynitrogen nitrogen triazide, $N(N_3)_3$, and the near-polynitrogen tetraazidomethane (carbon tetraazide), $C(N_3)_4$. These are particularly plausible candidates for synthetic realization because the azide group is a pseudohalogen group and NX_3 and CX_4 (X=halogen) are well-known. The group 15 triazides have been investigated computationally, and bismuth triazide has been prepared, but an attempted synthesis of nitrogen triazide failed [106]. Michels et al. calculated the structures and energetics of $N(N_3)_3$ and the related species $HN(N_3)_2$, $N(N_3)_2^-$, $N(N_3)_4^+$ and calculated a barrier of 39 kJ for the decomposition of $N(N_3)_3$ [107]. Although this indicates that $N(N_3)_3$ would not be useful as a high-energy material, they proposed routes to it:

$$NX_3 + 3\,Me_3SiN_3 \rightarrow N(N_3)_3 + 3\,Me_3SiX$$

or

$$N(SiMe_3) + 3XN3 \rightarrow N(N_3)_3 + 3\,Me_3SiX$$

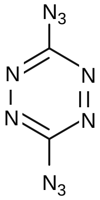
$Si(N_3)_4$ is known; it is said to be violently explosive [108].

Computations on $C(N_3)_4$ have been reported [109]. The salt $[C(N_3)_3{}^+][SbCl_6{}^-]$ was made by the reaction

$$3SbCl_4N_3 + CCl_4 \rightarrow [C(N_3)_3^+][SbCl_6^-] + 2SbCl_5$$

The salt was reported to be sensitive to shock or sudden heating [110]. This cation has been paired with other anions, particularly $N(NO_2)^-$ and $ClO_4{}^-$ to give highly energetic salts [111]. This line of work reached its climax with the preparation, reported in early 2007, of tetraazidomethane [112]. This compound, 93% nitrogen by mass, was made from $[C(N_3)_3{}^+][SbCl_6{}^-]$ and lithium or sodium azide or, more conveniently, by the extraordinarily simple procedure of reacting trichloroacetonitrile with sodium azide in warm acetonitrile solution. Although tetraazidomethane, a colorless liquid with a rich chemistry, can be purified by gas chromatography at 80°C, it is a dangerous substance which can explode for no clear reason.

Other organic molecules with a very high nitrogen content have been synthesized, e.g. 3,6-diazido-1,2,4,5-tetrazine, **22**:



22

This compound, C_2N_{10}, is 85% nitrogen by mass. All these azido compounds suffer from the fact that they are dangerous to handle, being sensitive to shock, static electricity, and friction, or no obvious stimulus [113]. The title of a recent review, “Organic azides. An exploding diversity of a unique class of compounds” could be interpreted in two ways [114]. The long-known hydrazoic acid, HN_3 (98% nitrogen), is a dangerously explosive substance [115, 116]; ammonium azide (93% nitrogen), a well-known salt [117], has been described, surprisingly, as a weak explosive [118].

Synthesis

Of all the pure nitrogen compounds, the one that will prove easiest to synthesize on a preparative scale, in contrast to just detecting it in, say, a mass spectrometer or a matrix, is probably acyclic N_6, diazide, **17**. This is because the azide ion and metal-coordinated azido compounds are well-known. Whether or not it was actually formed in the photolysis experiments of Vogler et al. [13], reductive dimerization of azide ion, perhaps coordinated to a metal ion, is a promising route to **17**. The reduction might be triggered chemically, photochemically, or electrolytically. If diazide is indeed tethered by a barrier of 105–126 kJ mol^{-1} [105], it does not require to be kept at typical matrix isolation temperatures (ca. 10 K or lower), and just might be isolable at room temperature. Another intriguing goal for synthesis is tetraazatetrahedrane, **19**. However its luster is dimmed by the possibility that the high calculated barrier (ca. 250 kJ mol^{-1}, [5, 91, 92]) for decomposition may be evaded by crossing over to a dissociative potential energy surface [95], and by the fact that the conceptual and practical problems of elaborating a tetrahedral arrangement of nitrogen atoms could make the challenges of synthesizing carbocyclic tetrahedrane (Chapter 6) seem trivial. These synthesis problems exist for all cyclic polynitrogens, which moreover, except perhaps for acyclic N_6 (**17**) and tetraazatetrahedrane (**19**), do not hold the promise of a high barrier.

Conclusions

The contrast between the abundance of theoretical work on nitrogen polymers and the sparsity of (published, at any rate) experimental results is noteworthy. This probably testifies to the difficulty of devising and realizing viable syntheses of these compounds; indeed, only for diazide does there seem to be a reasonably straightforward realistic route to obtaining a polynitrogen in some quantity; fortunately, diazide is also one of the few (perhaps the two, along with tetraazatetrahedrane) polynitrogens that hold some promise of being stable at anything but very low temperature. One senses almost a certain desperation in the move from the examination of simple acyclic and cyclic structures to the consideration of baroque polycyclic structures [96, 97, 98, 99, 100, 102]. Should a nitrogen polymer ever be isolated under more or less ambient conditions, one suspects that, although fascinating as a long-sought “stable” allotrope of dinitrogen, it will be a sensitive substance, prone to unpremeditated detonation. But hope is not easily extinguished, and a serious worker in this field might still wonder if nitrogen is “the fuel of the future” [119]. Be that as it may, the chemist who is not overly concerned with technical applications will be encouraged by the fact that there does seem to be an abundance of polynitrogen structures that are potential energy surface minima, and thus which, even if only of theoretical interest, should be observable under cryogenic conditions.

Notes

1. Butler et al. have recently reported that in a revision of their approach, isotopic labeling "proved unequivocally" that HN_5 and/or N_5^- was formed in solution: R. N. Butler, J. M. Hanniffy, J. C. Stephens, L. A. Burke, J. Org. Chem., 2008, *73*, 1354.
2. The barrier /halflife for the decomposition of $CF_3CO)OOO(COCF_3)$: 86.5 kJ mol^{-1}/1 minute. S. v. Ahsen, P. Garciá, H. Willner, M. B. Paci, G. Argüello, Chem. Eur. J. 2003, *9*, 5135.
3. This paper begins with a nice short summary of hexaazabenzene work up to the time.
4. This paper begins with a brief review of N_4, various N_6, and N_8.
5. Coupled cluster CCSD(T) calculations, coupled cluster with singles, doubles and perturbative (i.e. approximate) triples, are the highest-level calculations currently available for routine, practical computations: I. N. Levine, "Quantum Chemistry", Fifth Edn., Prentice Hall, Englewood Cliffs, New Jersey, 2000; pp. 568–573, 590–591, 694, 697.
6. See Note 1.

References

1. A. E. Douglas, W. J. Jones, Can. J. Phys., 1965, *43*, 2216.
2. J. M. Dyke, N. B. H. Jonathan, A. E. Lewis, A. Morris, Mol. Phys., 1982, *47*, 1231.
3. J. P. Zheng, J. Waluk, J. Spanget-Larson, D. M. Blake, J. G. Radziszewski, Chem. Phys. Lett., 2000, *328*, 227.
4. T. J. Lee, J. M. L. Martin, Chem. Phys. Lett, 2002, *357*, 319.
5. M. T. Nguyen, T. L. Nguyen, A. M. Mebel, R. Flammang, J. Phys. Chem. A, 2003, *107*, 5452.
6. F. Cacace, G. de Petris, A. Troiani, Science, 2002, *295*, 480.
7. F. Cacace, Chem. Eur. J., 2002, *8*, 3838.
8. E. E. Rennie, P. M. Mayer, J. Chem. Phys., 2004, *120*, 10561.
9. J. Barber, D. E. Hof, C. A. Meserole, D. J. Funk, J. Phys. Chem. A, 2006, *110*, 3853.
10. H. Ostmark, O. Launila, S. Wallin, R. Tryman, J. Raman, Spec., 2001, *32*, 195.
11. E. Hayon, M. Simic, J. Am. Chem. Soc., 1970, *92*, 7486.
12. V. Plzak, H. Wendt, Ber. Bunsenges. Physik. Chem., 1979, *83*, 481.
13. A. Vogler, R. E. Wright, H. Kunkley, Angew. Chem. Int. Ed. Engl., 1980, *19*, 717.
14. J. S. Wright, J. Am. Chem. Soc., 1974, *96*, 4753.
15. J. S. Wright, Theor. Chim. Acta, 1974, *36*, 37.
16. G. V. Chertihin, L. Andrews, C. W. Bauschlicher, J. Am. Chem. Soc., 1998, *120*, 3205.
17. L. Gagliardi, P. Pyykkö, J. Am. Chem. Soc., 2001, *123*, 9700.
18. K. O. Christe, W. W. Wilson, J. A. Sheehy, J. A. Boatz, Angew. Chem. Int. Ed. Engl., 1999, *38*, 2004.
19. A. Vij, W. W. Wilson, V. Vij, F. S. Tham, J. A. Sheehy, K. O. Christe, J. Am. Chem. Soc., 2001, *123*, 6308.
20. R. Haiges, S. Sneider, T. Schroer, K. O Christe, Angew. Chem. Int. Ed. Engl., 2004, *43*, 4919.
21. S. Fau, R. J. Bartlett, J. Phys. Chem. A, 2001, *105*, 4096.
22. L. J. Wang, S. Li, Q S. Li, J. Comp. Chem., 2001, *22*, 1334.
23. M. N. Glukhovtsev, H. Jiao, P. v. R. Schleyer, Inorg. Chem., 1996, *35*, 7124.
24. L Gagliardi, G. Orlandi, S. Evangelisti, B. O. Roos, J. Chem. Phys., 2001, *114*, 10733.
25. M. I. Eremets, R. J. Hemley, H.-K. Mao, E. Gregoryanz, Nature, 2001, *411*, 170.
26. M. I. Eremets, A. G. Gavriliuk, I. A. Trojan, D. A. Dzivenko, R. Boehler, Nat. Mater., 2004, *3*, 558.
27. T. Curtius, Berichte, 1890, *23*, 3023.
28. J. C. Bailar, H. J. Emeléus, R. Nyholm, A. F. Trotman-Dickenson, eds., "Comprehensive Inorganic Chemistry", Pergamon, New York, 1973; vol. 2, pp. 276–293.

29. W. Zhu, J. Xiao, H. Xiao, J. Phys. Chem. B, 2006, *110*, 9856, and refs. therein.
30. M. B. Smith and K. March, “March’s Advanced Organic Chemistry”, Wiley, New York, 2001; see index.
31. P. Botschwina, J. Chem. Phys., 1986, *85*, 4591, and refs. therein.
32. R. Rawls, C&EN News, 25 January 1999, 7.
33. R. Haiges, J. A. Boatz, S. Schneider, T. Schroer, M. Yousufuddin, Angew. Chem. Int. Ed., 2004, *43*, 3148.
34. R. Ponec, J. Roithová, X. Gironés, J. Jug, J. Mol. Struct. (Theochem), 2001, *545*, 255.
35. R. Huisgen, I. Ugi, Angew. Chem., 1956, *68*, 505.
36. P. Carlqvist, H. Oestmark, T. Brinck, J. Phys. Chem. A, 2004, *108*, 7463.
37. A. Vij, J. G. Pavlovich, W. W. Wilson, v. Vij, k. O. Christe, Angew. Chem. Int. Ed. Engl., 2002, *41*, 3051.
38. H. Östmark, S. Wallin, T. Brinck, P. Carlqvist, A. Claridge, E. Hedlund, L. Yudina, Chem. Phys. Lett., 2003, *379*, 539.
39. L. Belau, Y. Haas, S. Zilberg, J. Phys. Chem. A, 2004, *108*, 11715.
40. R. N. Butler, J. C. Stephens, L. A. Burke, J. Chem. Soc., Chem. Commun., 2003, *8*, 1016.
41. T. Schroer, R. Haiges, S. Schneider, K. O. Christe, J. Chem. Soc., Chem. Commun., 2005, *12*, 1607.
42. V. Benin, P. Kaszynski, J. G. Radziszewski, J. Org. Chem., 2002, *67*, 1354.
43. D. A. Dixon, D. Feller, K. O. Christe, W. W. Wilson, A. Vij, V. Vij, H. D. B. Jenkins, R. M. Olson, M. S. Gordon, J. Am. Chem. Soc., 2004, *126*, 834.
44. S. Fau, K. J. Wilson, R. J. Bartlett, J. Phys. Chem. A, 2002, *106*, 4639.
45. L. J. Wang, Q. S. Li, P. Warburton, P. G. Mezey, J. Phys. Chem. A, 2002, *106*, 1872.
46. M. S. Workentin, B. D. Wagner, F. Negri, M. Z. Zgierski, J. Lusztyk, W. Siebrand, D. D. M. Wayner, J. Phys. Chem., 1995, *99*, 94.
47. M. T. Nguyen, T.-K. Ha, Berichte, 1996, *129*, 1157.
48. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; section 5.5.2.
49. L. A. Curtiss, K. Raghavachari, P. C. Redfern, V. Rassolov, J. A. Pople, J. Phys. Chem. A, 1998, *109*, 7764.
50. L. A. Curtiss, K. P. Redfern, J. Pople, J. Chem. Phys., 2000, *112*, 7374.
51. D. J. Henry, C. J. Parkinson, L. Radom, J. Phys. Chem. A, 2002, *106*, 7927.
52. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; section 5.5.2.3.
53. R. Engelke, J. Am. Chem. Soc., 1993, *115*, 2961, and refs. therein.
54. L. Gagliardi, S. Evangelisti, A. Bernhardssan, R. Lindh, B. O. Roos, Int. J. Quantum Chem., 2000, *77*, 311.
55. G. Chung, M. W. Schmidt, M. S. Gordon, J. Phys. Chem. A, 2000, *104*, 5647.
56. M. Goldberg, S. Hoz, H. Basch, J. Mol. Struct. (Theochem), 2003, *663*, 135.
57. R. Engelke, J. Org. Chem., 1992, *57*, 4841.
58. R. Engelke, J. R. Stine, J. Phys. Chem., 1990, *94*, 5689.
59. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; section 5.2.
60. W. J. Lauderdale, J. F. Stanton, R. J. Bartlett, J. Phys. Chem., 1992, *96*, 1173.
61. M. W. Schmidt, M. D. Gordon, J. A. Boatz, Int. J. Quantum Chem., 2000, *76*, 434.
62. L. Gagliardi, S. Evangelisti, P.-O. Widmark, B. O. Roos, Theor. Chem. Acc., 1997, *97*, 136.
63. L. Gagliardi, S. Evangelisti, B. O. Roos, P.-O. Widmark, J. Mol. Struct. (Theochem), 1998, *428*, 1.
64. J. D. Roberts, “Notes on Molecular Orbital Calculations”, W. A. Benjamin, Inc., New York, 1962; p. 77.
65. F. S. Mortimer, Adv. Chem. Ser., 1965, *54*, 39.
66. M. J. S. Dewar, G. J. Gleicher, J. Chem. Phys., 1966, *44*, 759.
67. M. J. S. Dewar, Pure Appl. Chem., 1975, *44*, 767.
68. M. H. Palmer, A. J. Gaskell, R. H. Findlay, Tetrahedron Lett., 1973, 4659.

69. M. H. Palmer, A. J. Gaskell, R. H. Findley, Chem. Soc., Perkin Trans. 2: Physical Organic Chemistry, 1974, *7*, 778.
70. T. K. Ha, R. Cimiraglia, M. T. Nguyen, Chem. Phys. Lett., 1981, *83*, 317.
71. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 419–421.
72. H. Huber, Angew. Chem. Int. Ed. Engl., 1982, *21*, 64.
73. P. Saxe, H. F. Schaefer, J. Am. Chem. Soc., 1983, *105*, 1760.
74. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 2.
75. R. Engelke J. Phys. Chem., 1989, *93*, 5722.
76. T. C. Dinadayalane, U. D. Priyakumar, G. N. Sastry, J. Phys. Chem. A, 2004, *108*, 11433 and references therein.
77. I. Gutman, J. H. Potgier, J. Chem. Ed., 1994, *71*, 222.
78. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; section 5.4.
79. R. Engelke J. Phys. Chem., 1992, *96*, 10789.
80. M. N. Glukhovtsev, H. Jiao, P. v. R. Schleyer, Chem. Phys. Lett., 1992, *198*, 547; corrections Chem. Phys. Lett., 1993, *204*, 394.
81. T.-K. Ha, M. T. Nguyen, Chem. Phys. Lett., 1992, *195*, 179.
82. M. Tobita, R. J. Bartlett, J. Phys. Chem. A, 2001, *105*, 4107.
83. J. Fabian, E. Lewars, Can. J. Chem., 2004, *82*, 50.
84. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 241–242.
85. M. Gambiagi, M. S. de Gambiagi, C. D. dos Santos Silva, A. P. de Figueiredo, Phys. Chem. Chem. Phys., 2000, *2*, 3381.
86. P. v. R. Schleyer, H. Jiao, N. J. R. van Eikema Hommes, J. R. Nicolaas, V. G. Malkin, O. Malkina, J. Am. Chem. Soc., 1997, *119*, 12669.
87. S. Sakai, J. Phys. Chem. A, 2002, *106*, 10370.
88. J. J. Engelberts, R. W. A. Havenith, J. H. Van Lenthe, L. W. Jenneskens, p. W. Fowler, Inorg. Chem., 2005, *44*, 5266.
89. M. N. Glukhovtsev, P. v. R. Schleyer, Int. J. Quantum Chem., 1993, *46*, 119.
90. A. Kotkin, A. Balkova, R. J. Bartlett, R. J. Boyd, P. v. R. Schleyer, J. Phys. Chem., 1996, *100*, 5702.
91. T. J. Lee, J. E. Rice, J. Chem. Phys., 1991, *94*, 1215.
92. K. M. Dunn, K. Morokuma, J. Chem. Phys., 1995, *102*, 4904.
93. A. Larson, M. Larsson, J. Chem. Soc., Faraday Trans., 1997, *93*, 2963.
94. M. Bitterova, H. Ostmark, T. Brinck, Chem. Phys. Lett., 2001, *347*, 220.
95. D. R. Yarkony, J. Am. Chem. Soc., 1992, *114*, 5406.
96. L. Wang, P. G. Mezey, J. Phys. Chem. A, 2005, *109*, 3241.
97. H. Zhou, N.-B. Wong, G. Zhou, A. Tian, J. Phys. Chem. A, 2006, *110*, 3845.
98. D. L. Strout, J. Phys. Chem. A, 2004, *108*, 10911.
99. S. E. Sturdivant, F. A. Nelson, D. L. Strout, J. Phys. Chem. A, 2004, *108*, 7087.
100. S. E. Sturdivant,, D. L. Strout, J. Phys. Chem. A, 2004, *108*, 4773.
101. M. R. Manaa, Chem. Phys. Lett., 2004, *400*, 23.
102. M. R. Manaa, Chem. Phys. Lett., 2000, *331*, 262.
103. M. D. Thompson, T. M. Bledson, D. L. Strout, J. Phys. Chem. A, 2002, *106*, 6880.
104. Q. S. Li, L. J. Wang, J. Phys. Chem. A, 2002, *105*, 1203.
105. L. Gagliardi, S. Evangelisti, V. Barone, B. O. Roos, Chem. Phys. Lett., 2000, *320*, 518.
106. T. M. Klapotke, A. Schulz, Main Group Met. Chem., 1997, *20*, 325.
107. H. H. Michels, J. A. Montgomery, Jr., K. O. Christe, D. A. Dixon, J. Phys. Chem., 1995, *99*, 187.
108. E. Wiberg, H. Z. Michaud, Z. Naturforsch., 1954, *B9*, 500.
109. Q. S. Li, H. X. Duan, J. Phys. Chem. A, 2005, *109*, 9089.
110. U. Mueller, K. Dehnicke, Angew. Chem. Int. Ed. Engl., 1966, *5*, 841.

111. M. A. Petrie, J. A. Sheehy, J. A. Boatz, G. Rasul, G. K. Sura Prakash, G. A. Olah, k. O. Christe, J. Am. Chem. Soc., 1997, *119*, 8802.
112. K. Banert, Y.-H. Joo, T. Rüffler, B. Walfort, H. Lang, Angew. Chem. Int. Ed. Engl., 2007, *46*, 1168.
113. V. J. Hruby, L. Boteju, G. Li, Chem. Eng. News, 1993, *71*(41), 2.
114. S. Braese, C. Gil, K. Knepper, V. Zimmermann, Angew. Chem. Int. Ed. Engl., 2005, *44*, 5188.
115. T. Curtius, Berichte, 1890, *23*, 3023.
116. L. F. Audrieth, Chem. Rev., 1934, *15*, 169.
117. W. S. Frost, J. C. Cothran, A. W. Browne, J. Am. Chem. Soc., 1933, *55*, 3516.
118. G. S. Yakovleva, R. Kh. Kurbangalina, L. N. Stesik, Fizika Goreniya i Vzryva, 1977, *13*, 473; Chem., Abstr., 87: 154298.
119. R. J. Bartlett, Chem. Ind., 2000, *4*, 140.

Chapter 11
Oligomers and Polymers of Carbon Dioxide and CO_2/N_2

Introduction

In Chapter 10 we considered oligomers and polymers of dinitrogen. Here we finish our look at covalent aggregates of small, stable molecules by examining dimers, trimers etc. of carbon dioxide and of carbon dioxide with dinitrogen. We will consider primarily the molecules shown in Figs. 11.1 and 11.2. These species are interesting in themselves, because of their structural novelty; they are also interesting in comparison with the nitrogen compounds of Chapter 10, with regard to investigating the effect of replacing –N=N– units by –C(=O)O–. Like the N_2 allotropes of Chapter 10, these putative compounds are based wholly or partly on another small, common, stable molecule, CO_2. Unlike the all-nitrogen compounds they do not seem to have been examined explicitly as potential high-energy density materials. Some carbon oxides which are not stoichiometrically CO_2 oligomers will also be peripherally mentioned.

CO_2 Compounds

We focus on molecules which are topologically simply-connected carbon dioxide moieties, i.e. they could in principle decompose to O=C=O without molecular rearrangement. We also relegate to a secondary status molecules with an O–O bond, as it is well-known that this tends to be a destabilizing feature. Molecules **1-CO_2** and **2-CO_2** in Fig. 11.1 are the simplest species that lie within these constraints, and the acyclic species **3-CO_2**, **4-CO_2**, and **5-CO_2** are slight variations on the theme: they are CO_2 chains capped with H and OH, to maintain the oxidation level of $(CO_2)_n$; they may be regarded as hydrated ring-opened forms of a cyclic dimer, trimer and tetramer, respectively. We begin by presenting our recent DFT calculations and recounting our published ab initio results [1] on these molecules.

The five molecules in Fig. 11.1 were studied at the B3LYP/6-31G* level. Their calculated geometries are shown in Figs. 11.1 and 11.3 gives the reaction profiles (geometries and energies) for their decomposition to carbon dioxide of the two cyclic species. Relevant energies are also given in Fig. 11.3: the uncorrected and

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_11,

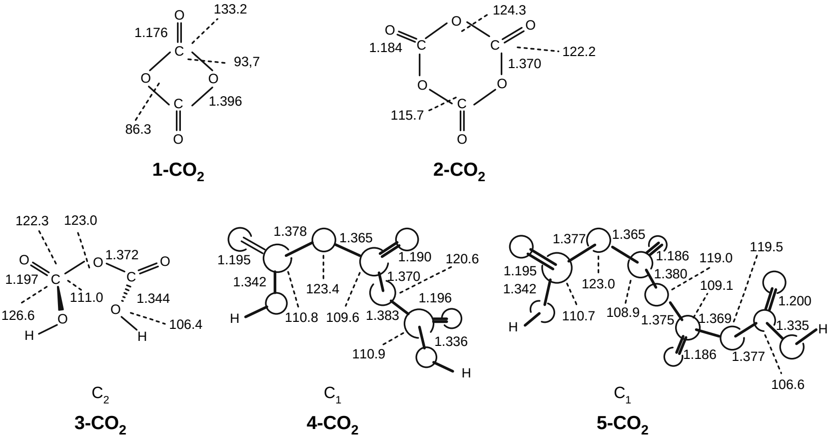


Fig. 11.1 The CO_2 "polymers" considered in this chapter. B3LYP/6-31G* structures are depicted, with symmetry designations and selected bond lengths (Å) and angles (degrees). The three acyclic molecules are CO_2 chains capped with H and OH to maintain the oxidation level of $(CO_2)_n$, and are hydrated ring-opened forms of a cyclic dimer, trimer and tetramer. The structures shown for the acyclics are only plausible conformations, with no imaginary frequencies, and not necessarily the lowest-energy conformations

ZPE (zero point energy)-corrected (the ZPEs have been themselves corrected by multiplication by 0.9806 [2]) B3LYP/6-31G* [3] energy release is 182 kJ mol^{-1} for the dimer and 215 kJ mol^{-1} for the trimer. The results for the high-accuracy CBS-4M [4] and G2(MP2) [5] methods are similar. These reaction energies are not large compared to those calculated by the high-level ab initio G3 method (Chapter 10) for polynitrogens or a stoichiometric H_2/O_2 mixture: for the CO_2 dimer, the reaction energy is E(products) − E(reactants) = −182 kJ mol^{-1}, i.e. 182 kJ mol^{-1} is released on decomposition to CO_2, ca. 2100 kJ kg^{-1}, and for the trimer the energy released is 215 kJ mol^{-1} (ca. 1600 kJ kg^{-1}). By comparison octaazacubane, N_8, is calculated to release 1854 kJ mol^{-1} (ca. 16600 kJ kg^{-1}, and a stoichiometric H_2/O_2 mixture ca. 11000 kJ kg^{-1}. The energy given out by octaazacubane presumably comes partly from release of ring strain, but likely has a large component due to conversion of NN single to triple bonds.

The calculated activation energies for the dimer and trimer (B3LYP/6-31G*, 40.7, and 83.2 kJ mol^{-1}; MP2/6-31G* [1], 40.8, and 79.6 kJ mol^{-1} respectively) are too low to permit handling at room temperature (this is certainly true for the dimer and probably so for the trimer), which experience shows demands a barrier of at least about 100 kJ mol^{-1}.[1] Both compounds should, however, be quite stable under matrix isolation conditions [6].

The acyclic molecules **3-CO₂**, **4-CO₂**, and **5-CO₂** could in principle decompose by base- or acid-catalyzed reactions, indicated for the "dimer", or through the cyclic transition states **3-CO₂-T**, **4-CO₂-T**, and **5-CO₂-T** (Fig. 11.4). Of these reactions only the cyclic transition state decomposition of the "dimer" (**3-CO₂-T**) was

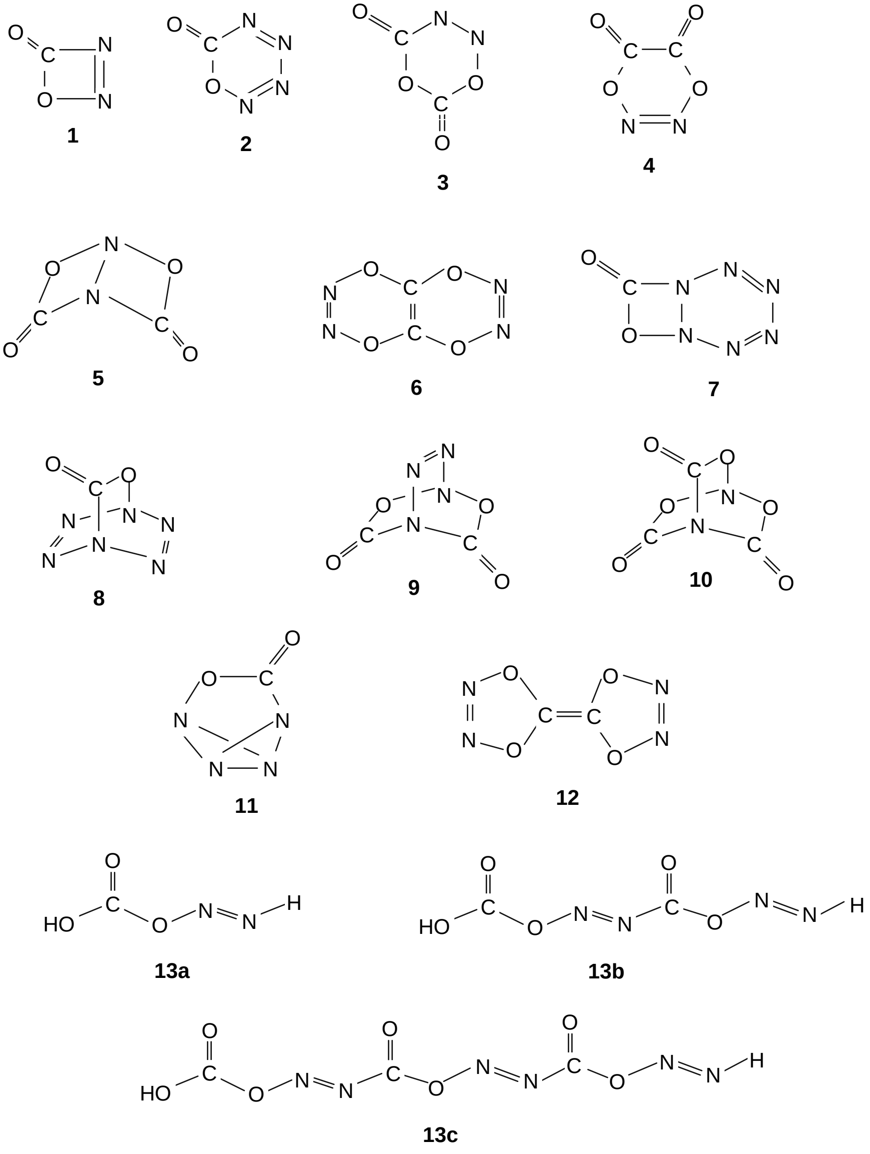


Fig. 11.2 The CO_2–N_2 "copolymers" considered in this chapter

studied computationally. B3LYP/6-31G* calculations indicate that this process has a barrier of 68.8 kJ mol^{-1} and a reaction energy of 83.1 kJ mol^{-1}. Thus this acyclic "dimer" seems to be less fragile and less energetic than the cyclic dimer (barrier 40.7, reaction energy 182 kJ mol^{-1}). Esters of the dimeric **3-CO_2**, dicarbonic acid or pyrocarbonic acid, are known and are stable (analogously to the fact that esters of

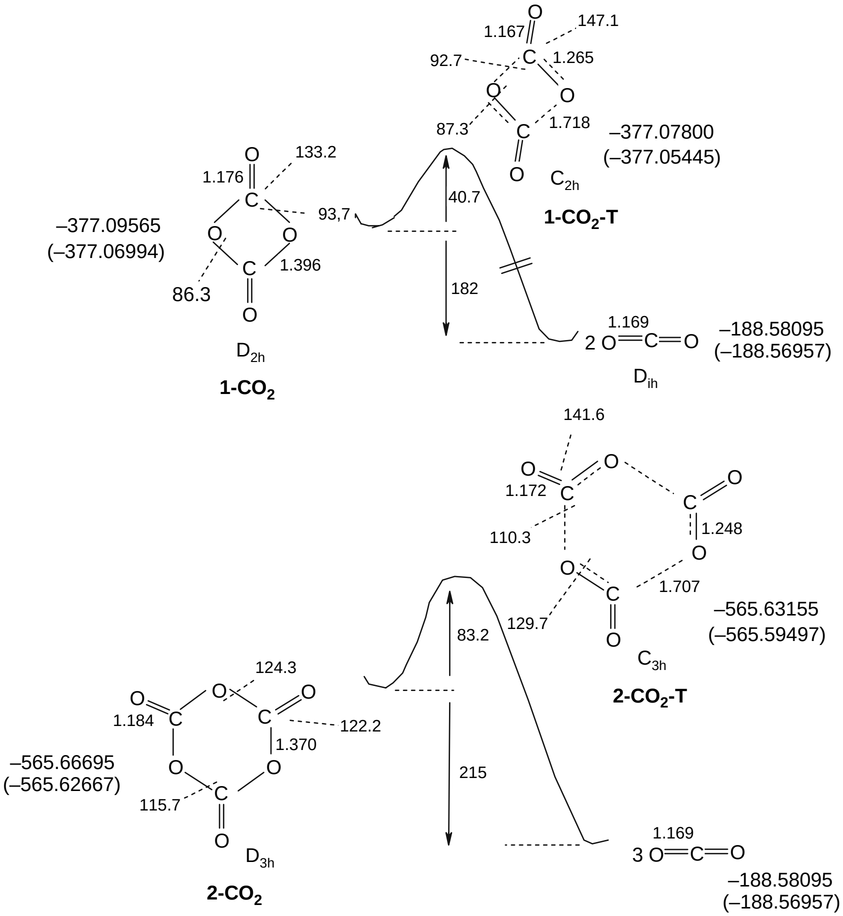


Fig. 11.3 Reaction profiles (including ZPE) of the dimers **1-CO$_2$** and **2-CO$_2$** at the B3LYP/6-31G* level. B3LYP/6-31G* energies in atomic units (hartrees) without and with (in parentheses) corrected ZPE are shown; the ZPE was corrected by multiplying it by 0.9806 [2]. Energy differences in hartrees were converted to kJ mol^{-1} by multiplying by 2626

the unstable carbonic acid are well-known); the diethyl ester is particularly prolific in the technical and patent literature, where it is touted as a food and beverage preservative.

The dimer **1-CO$_2$** and trimer **2-CO$_2$** were also looked at computationally (MP2, B3LYP) by Pyykko [7] and by Frapper and Saillard [8] who calculated the energy, geometry and IR spectrum of these and some other unusual C/O and C/S molecules. The trimer was studied by Mayor-Lopez et al. (MP2) [9], who calculated its geometry and IR spectrum and decomposition barrier and reaction energy, with essentially the same results as the author [1]; Mayor-Lopez et al. also studied trimers of SCO and HNCO. Semiempirical AM1 calculations on the trimer and another CO_2 oligomer have also been reported by Bodor and Huang [10]. Some sulfur analogues of unknown C/O molecules are known: references in [7, 8, 9].

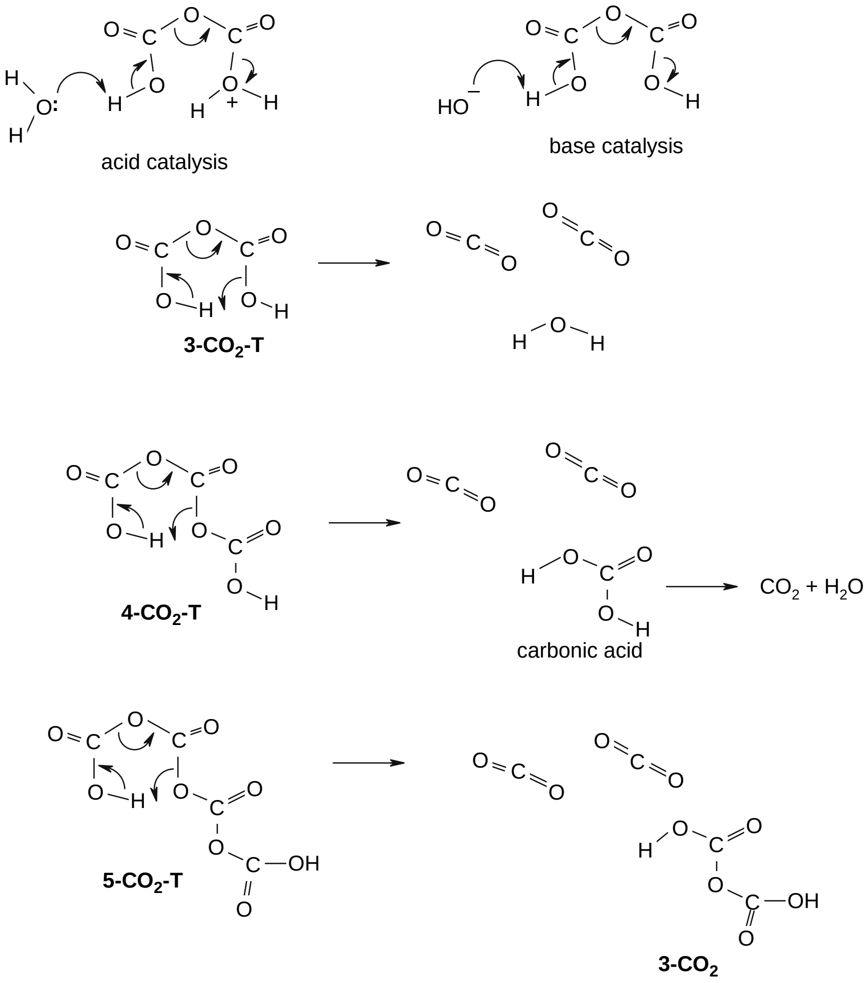
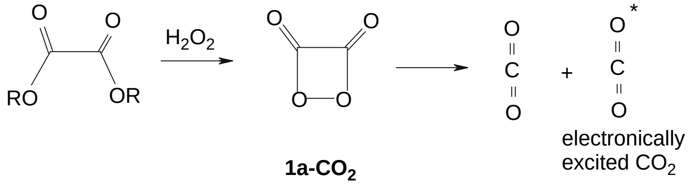


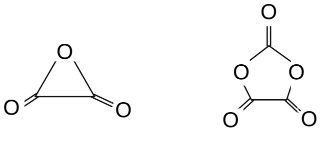
Fig. 11.4 Possible decomposition mechanisms for the acyclic CO_2 oligomers

The “head-to-head” isomer of **$1\text{-}CO_2$**, **$1a\text{-}CO_2$**, is important because it is evidently a highly unstable intermediate in oxalate ester-hydrogen peroxide chemiluminescece (cold light) reactions:



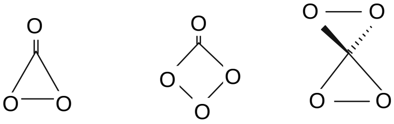
Fragmentation of **$1a\text{-}CO_2$** gives an electronically excited CO_2 molecule, which can transfer energy to a sensitizer which emits a photon of visible light. The presence of **1a-CO_2** in these reactions was indicated by mass spectrometry [11] and low-temperature ^{13}C NMR [12].

Cyclic oligomers $(CO_2)_n(CO)_m$ [13] and oxygen-rich carbon oxides CO_n [14] have been examined computationally by ab initio methods; some examples of these are:



14 **15**

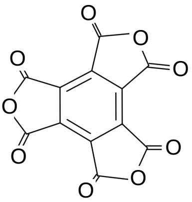
$(CO_2)_n(CO)_m$ molecules

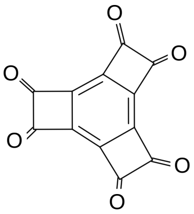


16 **17** **18**

CO_n molecules

Structures, vibrational frequencies, and reaction energies for decomposition, but not barriers, were calculated for these and other similar species. The CO_2/CO compounds were considered as possible high-energy materials [13] and the oxygen-rich compounds as possible intermediates in atmospheric reactions [14]. A trioxide of carbon has long been known, with a probable dioxacyclopropanone structure **16** [15, 16, 17, 18] and linear C_6O_2 has been tentatively observed in a matrix [19]. Carbon tetraoxide was studied computationally by Averyanov et al. and a trioxacyclobutanone structure **17** was found to be the lowest-energy one of the species investigated [20], but in a paper reporting the detection of a short-lived CO_4 molecule by neutralization-reionization mass spectrometry, Cacace et al. concluded that **17** had no barrier to dissociation, and the spiro structure **18** was tentatively assigned to the molecule detected [21]. Somewhat more prosaic but known carbon oxides are the anhydride of benzene hexacarboxylic acid (mellitic anhydride), and tris(dioxocyclobuta)benzene (hexaoxotricyclobutabenzene) [22, 23]:





The synthesis at very high pressures of extended polymeric quartzlike forms of carbon dioxide, lacking CO double bonds, has been reported, e.g. by Iota et al. [24] and Santoro et al. [25], and such materials have been analyzed computationally by the groups of Bodor [26] and Chiarotti [27].

CO_2–N_2 Compounds

We examined computationally the twelve cyclic and three acyclic "copolymers" shown in Fig. 11.2 [28]; except for **1**, which is discussed in some detail below, this appears to be the only published work on any of these fifteen species (Jones and coworkers have studied computationally oligomers and polymers of nitrogen oxides [29, 30, 31, 32]). We will survey here mainly the B3LYP/6-31G* results (the MP2/6-31G* results were generally similar [28]).

The ten structures **1**, **4**, **5**, **7** (with modification for **7**), **10**, **11**, **12**, and **13a–c** were relative minima ("real molecules") on the B3LYP/6-31G* (and MP2/6-31G*) potential energy surfaces, as shown by the absence of imaginary frequencies in the optimized geometries. The five structures **2**, **3**, **6**, **8**, and **9** were not relative minima on the B3LYP/6-31G* (and MP2/6-31G*) potential energy surface: two were stationary points (D_{2h} **6** was a hilltop with 2 imaginary frequencies, **8** was a transition state – 1 imaginary frequency – for dissociation to CO_2 and N_2) and **2**, **3**, and **9** were not even stationary points, but instead dissociated on attempted geometry optimization (**2** and **3** to CO_2 and N_2, **9** to NO_2, N_2, and OCNCO). Information on the fifteen structures **1–13c**, including the energies of the twelve that were stationary points, is summarized in Table 11.1, and Fig. 11.5 shows the

Table 11.1 Results of B3LYP/6-31G* calculations on the fifteen structures **1–13c**

Structure	Character	Energy of stationary point (hartrees, without ZPE)
1 Cs	relative min.	−297.93184
2 Cs	dissociates[a]	
3 Cs	dissociates[a]	
4 C_{2v}	relative min.	−486.46132
5 C_s	relative min.	−486.43953
6 D_{2h}	hilltop, 2 imag. freqs.[b](210i, 155i)	−595.75760
7 C_s	relative min.[c]	−516.80112
8 C_s	transition state[d](80i)	−516.77516
9 C_s	dissociates[e]	
10 C_{3v}	relative min.	−674.97969
11 C_s	relative min.	−407.29718
12 D_{2h}	relative min.	−595.82068
13 C_s	relative min.	−374.40511
13b C_1	relative min.	−672.37448
13c C_1	relative min.	−970.34291

[a] Dissociates to CO_2 and N_2;

[b] C_{2h} and C_i structures dissociate to CO_2 and N_2 on attempted optimization;

[c] One NN bond has broken: see Fig. 11.5;

[d] Transition state for dissociation to CO_2 and N_2;

[e] Dissociates to NO_2, N_2, and OCNCO.

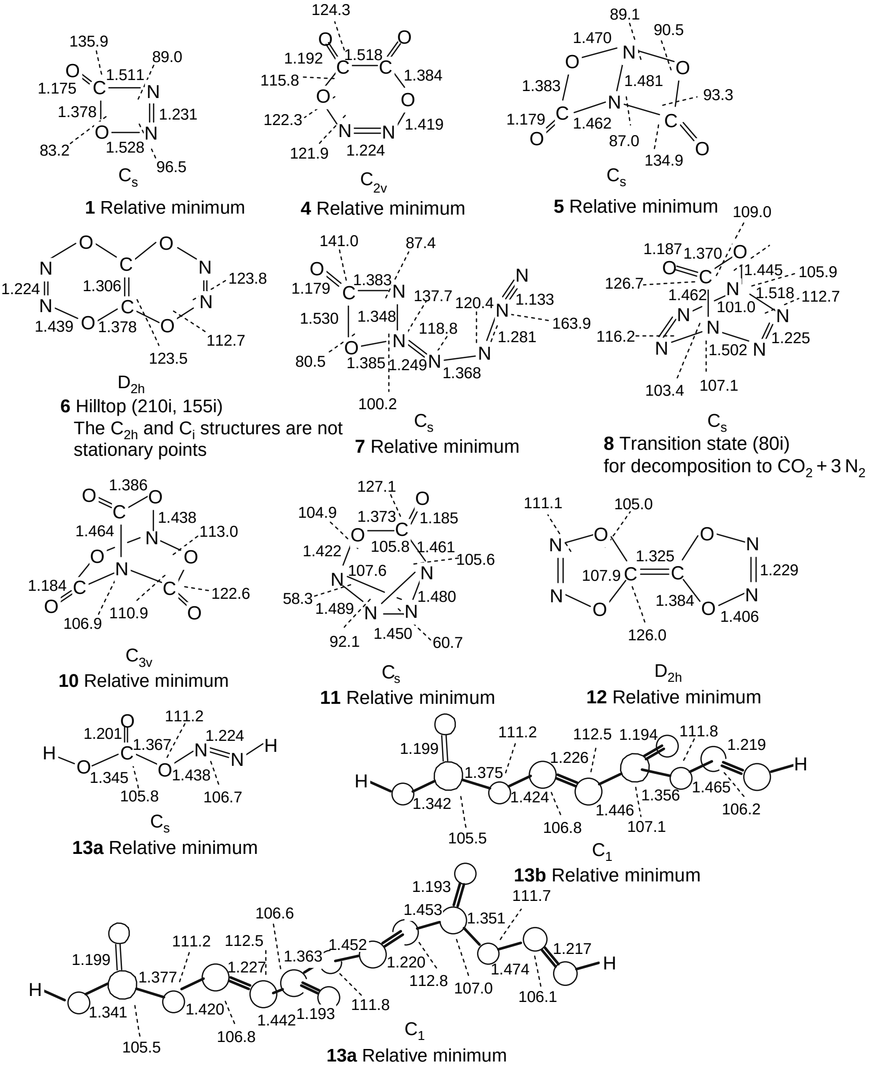


Fig. 11.5 Geometries of the twelve CO_2–N_2 "copolymers" from the set of fifteen **1**–**13c** (Fig. 2) that were stationary points at the B3LYP/6-31G* level, with symmetry designations and selected bond lengths (Å) and angles (degrees). The structures shown for the acyclics are only plausible conformations, with no imaginary frequencies, and not necessarily the lowest-energy conformations

structures of the twelve stationary points at the B3LYP/6-31G* level. The kinetics and thermodynamics of decomposition of the seven cyclic molecules **1**, **4**, **5**, **7**, **10**, **11**, and **12** are summarized in Fig. 11.6 at the B3LYP/6-31G* level, and in Fig. 11.7 at the MP2/6-31G* level.

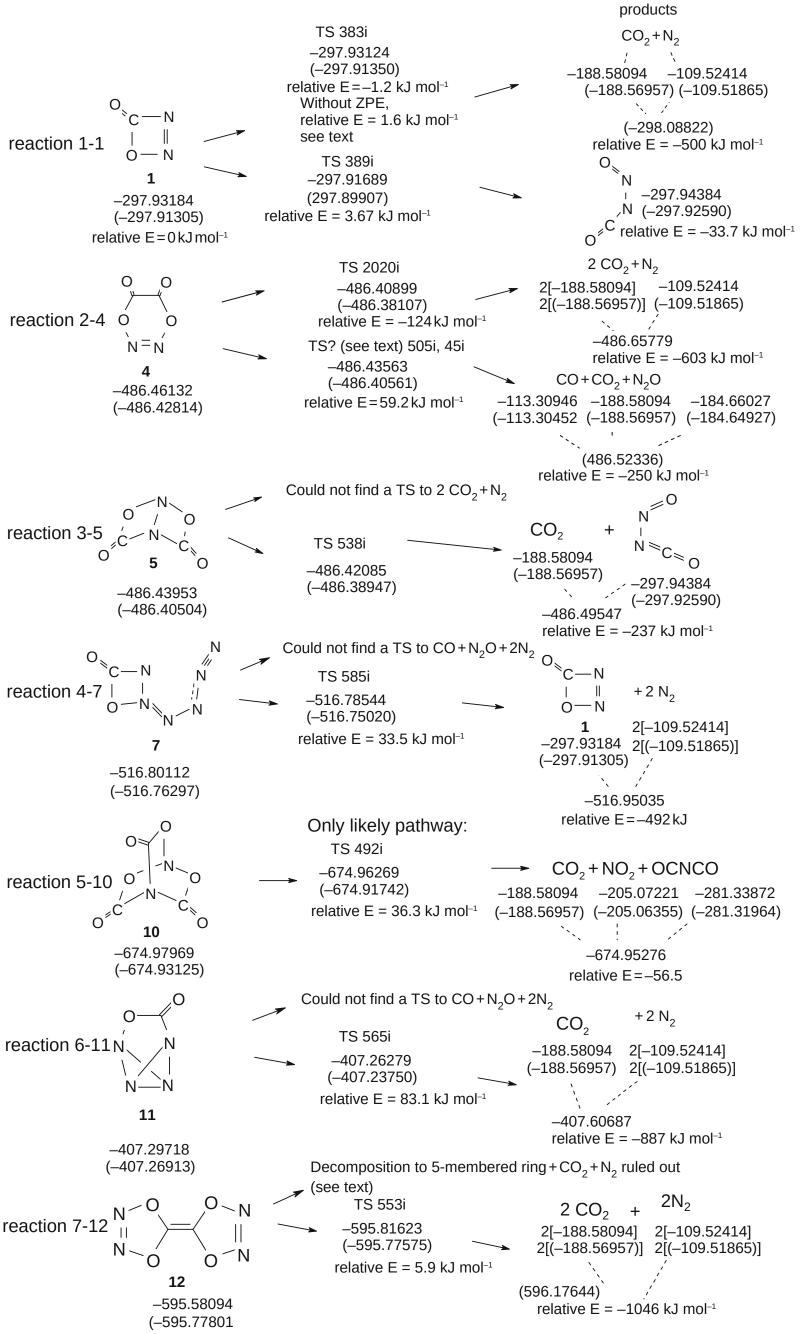


Fig. 11.6 B3LYP/6-31G* activation and reaction energies (including ZPE) of the cyclic CO_2–N_2 molecules. Energies in atomic units (hartrees) without and with (in parentheses) corrected ZPE are shown; the ZPE was corrected by multiplying it by 0.9806 [2]. Energy differences in hartrees were converted to kJ mol^{-1} by multiplying by 2626

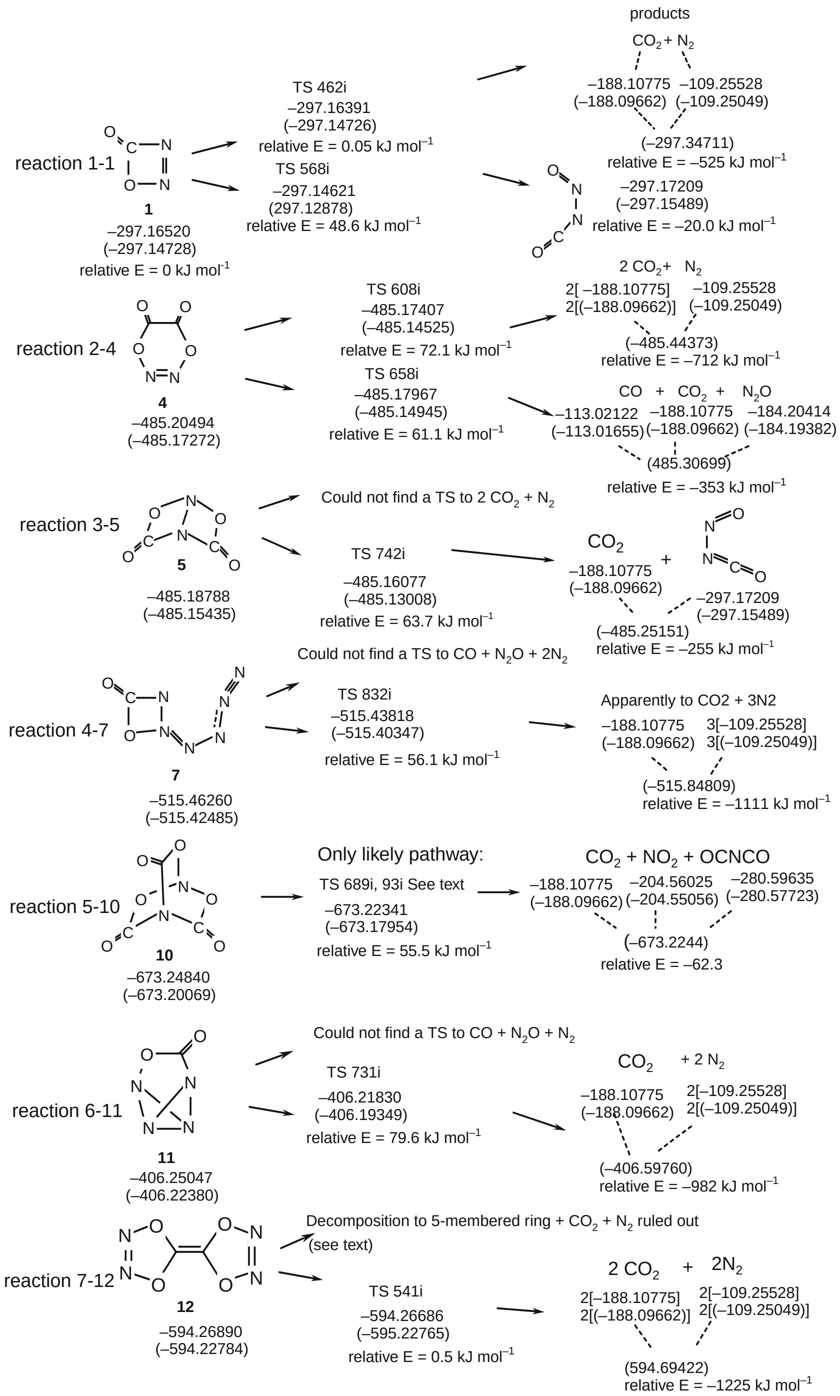


Fig. 11.7 (continued)

Structures (B3LYP/6-31G*) of the CO_2–N_2 Compounds (Fig. 11.5)

None of the ten molecules **1**, **4**, **5**, **7**, **10**, **11**, **12**, and **13a–c** shows any obvious unreasonable structural features that may be clues to kinetic instability, such as extraordinarily long bonds or highly distorted angles or dihedrals. The structures thus provide no a priori grounds for expecting them to be experimentally unrealizable, although the chemist might intuitively feel that a composite of CO_2 and N_2 moieties (**10** is an exception in that it is not topologically able to unravel into these) is likely to be fragile. Note that structure **7** in Fig. 11.2, on B3LYP/6-31G* optimization gave a structure in which the six-membered ring had opened, yielding a molecule with a four-membered ring and a pendant chain of four nitrogens (Fig. 11.5). This opened structure is the B3LYP/6-31G* (and MP2/6-31G*) relative minimum.

Decomposition Reactions (B3LYP/6-31G* and MP2/6-31G*) of the Cyclic CO_2–N_2 Compounds (Fig. 11.6)

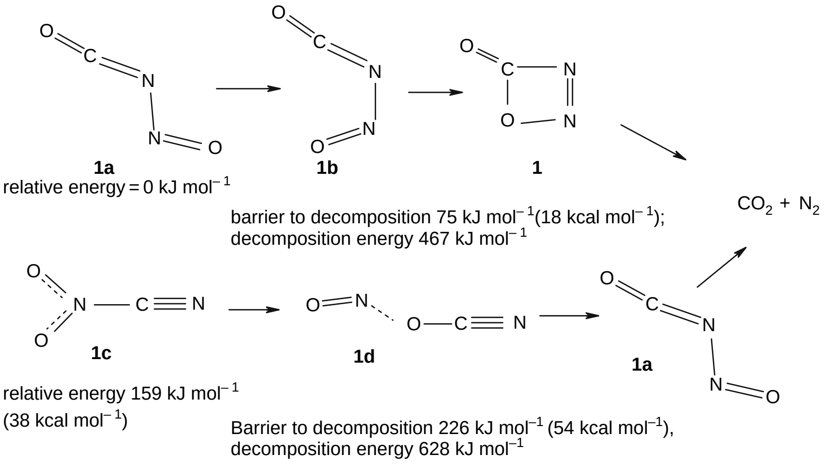
The seven cyclic molecules **1**, **4**, **5**, **7**, **10**, **11**, and **12** were examined, in reactions 1–1 to 7–12 respectively, for their activation and reaction energies, i.e. their kinetics and thermodynamics. In each case attempts were made to find transition states for the likely decomposition modes, usually to yield CO_2 and N_2 or CO_2 and N_2O. These molecules are discussed in turn and their energetics are then briefly summarized, with emphasis on the B3LYP/6-31G* results, followed by a brief comparison with the MP2/6-31G* ones.

The B3LYP/6-31G* Reaction Profiles (Fig. 11.6)

*Molecule **1*** is evidently extremely fragile: the barrier to fragmentation to CO_2 and N_2 is calculated to be slightly negative ($-1.2\ \mathrm{kJ\ mol^{-1}}$), which is presumably an artifact of inaccuracy in the ZPE; a similar phenomenon was found in the calculation of the barrier to decomposition of cyclic N_6 [33]. The barrier without ZPE correction is $1.6\ \mathrm{kJ\ mol^{-1}}$. Such a small barrier may place **1** beyond matrix isolation detection, or even imply that at some higher computational level it is not a relative minimum. The

Fig. 11.7 MP2/6-31G* activation and reaction energies (including ZPE) of the cyclic CO_2–N_2 molecules. Energies in atomic units (hartrees) without and with (in parentheses) corrected ZPE are shown; the ZPE was corrected by multiplying it by 0.9670 [2]. Energy differences in hartrees were converted to kJ $\mathrm{mol^{-1}}$ by multiplying by 2626 decomposition is quite exothermic: by 500 kJ mol^{-1}, somewhat below the comparably kinetically unstable cyclic N_6 (800–900 kJ mol^{-1}, Chapter 10). A diagnostic sometimes used as a probe for molecular stability, in lieu of direct calculation of the activation energy for decomposition, is the presence or absence of low-frequency vibrations (say, below 500 cm^{-1}) that would in the limit lead to dissociation.[2] This test is by no means infallible, but **1** does show a stretching mode at 380 cm^{-1} corresponding to dissociation to $CO_2 + N_2$. A transition state for ring opening to ONNCO was found, but with an activation energy of 36.7 kJ mol^{-1} it can scarcely compete with the almost barrierless fragmentation. A transition state leading to $CO + N_2O$ could not be found.

Molecule **1** is evidently the only member of the set **1–13c** which has appeared in the literature other than in our 1999 paper [28]. **1** and other several other CN_2O_2 [34] and CN_2O_3 [35] molecules were studied computationally by Korkin et al., in a detailed search for useful high-energy compounds; **1** is also of interest in connection with reactions occurring in the combustion of nitrogen-containing compounds and in a process for removing NO_x from exhaust gases, in which the NCO radical from HNCO reacts with NO (ref: in [34]). The barrier to decomposition of **1** was calculated to be no more than 2 kJ mol^{-1} (0.5 kcal mol^{-1}) [34]. The NCO–NO reaction was studied computationally in detail by Lin et al. [36], who implicated **1** as an intermediate. Reaction of NOCl with AgNCO was believed to form ON–NCO, nitrosyl isocyanate, an open-chain form of 1, which was studied by photoelectron spectroscopy [37]. Among the CN_2O_2 molecules studied by Korkin et al. [34] the lowest-energy one was nitrosyl isocyanate, ON–NCO, but its barrier to decomposition to CO_2 and N_2 was calculated to be only 75 kJ mol^{-1}; nitryl cyanide, $O_2N–CN$, lies 159 kJ mol^{-1} higher than nitrosyl isocyanate, but is evidently much stabler, with a barrier of 226 kJ mol^{-1}:



relative energy = 0 kJ mol^{-1}

barrier to decomposition 75 kJ mol^{-1}(18 kcal mol^{-1}); decomposition energy 467 kJ mol^{-1}

relative energy 159 kJ mol^{-1} (38 kcal mol^{-1})

Barrier to decomposition 226 kJ mol^{-1} (54 kcal mol^{-1}), decomposition energy 628 kJ mol^{-1}

With a decomposition energy of 628 kJ mol^{-1} (150 kcal mol^{-1}), the relatively stable (at least in the absence of bimolecular decomposition pathways) nitryl cyanide was considered a promising high-energy material.

*Molecule **4*** shows a barrier of 124 kJ mol^{-1} for decomposition to CO_2 and N_2, the reaction being exothermic by 603 kJ mol^{-1}. A more facile decomposition route leads to CO, CO_2, and N_2O, evidently with a barrier of 59.2 kJ mol^{-1} and is exothermic by 250 kJ mol^{-1}. The putative transition state for this route actually had, besides an imaginary vibration at 505i corresponding to the reaction coordinate, a small imaginary vibration at 45i (for distortion from planarity), and so is technically a second-order hilltop. We were unable to find a strictly correct transition state, and suspect that our species may be the victim of numerical errors which sometimes arise in DFT second derivatives because the algorithm utilizes a numerical grid [38]. The lower-barrier route appears to rule out the possibility of **4** being handled at room temperature. That the kinetically favored reaction is thermodynamically less favored is counterintuitive and probably the exception, but is not unprecedented.[3]

*Molecule **5*** was found to decompose with a barrier of 40.9 kJ mol^{-1} and the loss of 237 kJ mol^{-1} to CO_2 and ONNCO; as we saw above, this latter was calculated to decompose readily to CO_2 and N_2 with a barrier of 75 kJ mol^{-1} in a reaction exothermic by 467 kJ mol^{-1} (overall exothermicity = 237 + 467 kJ mol^{-1} = 704 kJ mol^{-1}). Interestingly, a transition state for decomposition to CO_2 and N_2 could not be found.

*Molecule **7*** (structure **7** in Fig. 11.5) seems to lose $2N_2$ with a barrier of 33.5 kJ mol^{-1} giving molecule **1**; we did not rule out the possibility that **7** goes directly to $CO_2 + 3N_2$, but in any case **1** decomposes to $CO_2 + N_2$ with an extremely low barrier (above). The formation of **1** is exothermic by 492 kJ mol^{-1}, and its decomposition is exothermic by 500 kJ mol^{-1}, for a total release of 992 kJ mol^{-1}.

*Molecule **10***, because of its connectivity, seems unlikely to decompose to CO_2 and N_2. We found a transition state for decomposition to $CO_2 + NO_2 +$ OCNCO, which corresponds to the connectivity. This reflects a barrier of 36.3 kJ mol^{-1} and a decomposition energy of 56.5 kJ mol^{-1}. The radical OCNCO is apparently unknown, although the cation is known [39, 40, 41].

*Molecule **11*** was found to lose CO_2 with a barrier of 83.1 kJ mol^{-1}; the other fragment(s) we suspect to be $2N_2$, although an N_4 species could not be ruled out (an IRC calculation to throw light on this failed). In any case an N_4 species is expected to decompose to $2N_2$ with a very low barrier (Chapter 10). The decomposition energy to $CO_2 + 2N_2$ is 887 kJ mol^{-1}. We could not find a transition state for decomposition to $CO + N_2O + N_2$.

*Molecule **12*** was calculated to decompose to $2CO_2 + 2N_2$ with a barrier of only 5.9 kJ mol^{-1} and a decomposition energy of 1046 kJ mol^{-1}. The possibility that **12** would lose just one mole of CO_2 and one mole of N_2 to form a carbene *cyclo*-CONNO was excluded, at least at the B3LYP/6-31G* level, by showing that this carbene is not a stationary point (it also does not exist at the MP2/6-31G* level).

To summarize the findings for the seven cyclic molecules **1**, **4**, **5**, **7**, **10**, **11**, **12**, all are relative minima on the B3LYP/6-31G* potential energy surface., and all should decompose exothermically to CO_2 and nitrogen (**7** and **11** may not go directly to these), except for **2**, **5**, and **10** (which form respectively CO + CO_2 + N_2, CO_2 + ONNCO, and CO_2 + NO_2 + OCNCO). Molecules **1** and **12** had extremely low decomposition barriers and may not be observable, or may even turn out at a higher computational level not to be real molecules. The highest barrier is for **11** (83.1 kJ mol^{-1}, which is suspiciously high for a molecule which seems to be more strained than any of these others except **1**) and the second highest is for **4** (59.2 kJ mol^{-1}); all the others are below 50 kJ mol^{-1}. Thus none of these seven is expected to be stable at room temperature.

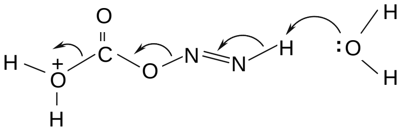
The MP2/6-31G* Reaction Profiles (Fig. 11.7)

Comparison of Figs. 11.6 and 11.7 shows that the B3LYP/6-31G* and MP2/6-31G* results are in essential agreement. All of the seven molecules are predicted to decompose exothermically with small barriers. Here molecule **7** appears to go to CO_2 and N_2, whereas with MP2 the proximate products were tentatively suggested to be **1** and N_2, a trivial difference in view of the instability of **1**. The MP2 "transition state" for decomposition of **10** has two imaginary frequencies and is thus technically a second-order hilltop. Unlike the case of **4** with B3LYP (above) this cannot be ascribed to numerical errors in "analytical" frequencies; were unable to remove the small second frequency by distorting the hilltop structure (close to C_s with a plane through the departing CO_2) but suspect that the transition state is close in energy and geometry to this somewhat aberrant structure.

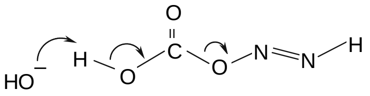
Both the B3LYP and MP2 methods may actually overestimate the stability of these molecules: comparison of experiment and calculations with small molecules indicates that unless quite high-level calculations are used, calculated bond lengths are too short, and thus possibly calculated implied bond strengths are too large, for N–O molecules [42].

Stability of the Acyclic CO_2–N_2 Compounds 13a, 13b, 13c

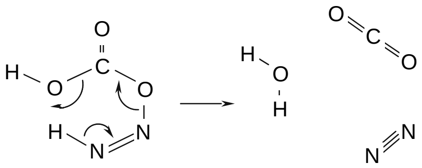
These three molecules were not examined directly for stability as were the seven cyclic species above. All three are B3LYP/6-31G* relative minima as shown by the absence of imaginary frequencies. Their kinetic stability is not expected to be high: as for the acyclic CO_2 species above, they should be susceptible to acid- or base-catalyzed decomposition, and to unimolecular decomposition through cyclic transition states, as shown here for **13a** (cf. Fig. 11.4):

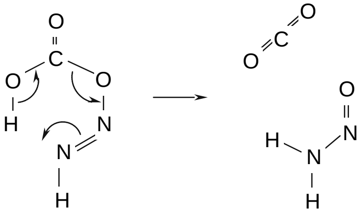


acid catalysis



base catalysis





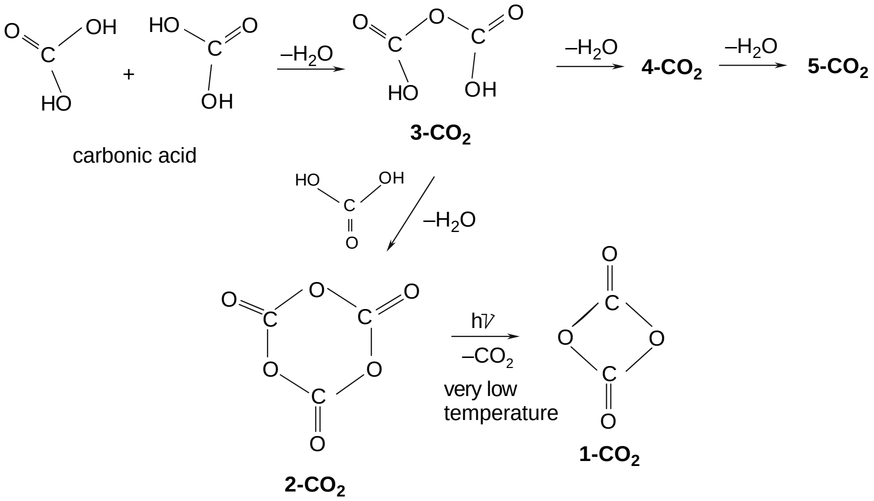
The HO–NN–H species implied as a product in the base catalysis decomposition has been implicated as an intermediate in the NH_2 + NO reaction, which is apparently a step in the process for removing NO_x from exhaust gases referred to above in connection with molecule **1**. In a study of this reaction, Wolf et al. concluded from ab initio calculations that HO–NN–H (which they calculated to have several stereoisomers of about the same energy, and also to be close in energy to its isomer H_2NNO, nitrosamine, shown in the second of the concerted reactions) loses water in a four-center reaction to form $H_2O + N_2$ (after all, it is hydrated dinitrogen!) [43], and Shin et al. have observed H_2NNO, the HO–NN–H isomer, in NO/NH_3 cationic clusters [44]. From our B3LYP/6-31G* calculations HO–NN–H loses water with a barrier of 110 kJ mol^{-1} and a decomposition energy of 264 kJ mol^{-1}, results roughly the same as from Wolf et al. [43].

Concerted decomposition of **13a** might occur to give $CO_2 + N_2 + H_2O$, or CO_2 + H_2NNO, as shown. The first mode, yielding $CO_2 + N_2 + H_2O$, is not available to **13b** and **13c**, which lack an NH hydrogen which can be transferred to an OH oxygen in a six-membered transition state (incidentally, this also needs a *cis* configuration of the groups on the N=N bond). We were unable to locate a B3LYP/6-31G* transition state for this mode. The second mode, yielding $CO_2 + H_2NNO$, was found to have a B3LYP/6-31G* barrier of a mere 7.5 kJ mol^{-1}, indicating that **13a**, and likely **13b** and **13c**, would be rather fragile compounds.

Synthesis

The CO_2 Compounds

Our suggested syntheses of the CO_2 dimer etc. start with carbonic acid, which it may be possible to use as a reagent in a nonaqueous solvent ("In spite of the chemist's belief, carbonic acid is surprisingly stable" [45, 46]; see too [47]). Dehydration of carbonic acid, e.g. with dicyclohexylcarbodiimide, DCC (cf. synthesis of fatty acids anhydrides [48]), or, if this is too mild to work at the low temperature that may be needed, a more aggressive dehydrating agent like thionyl chloride, $SOCl_2$, plays a key role in the syntheses suggested here:

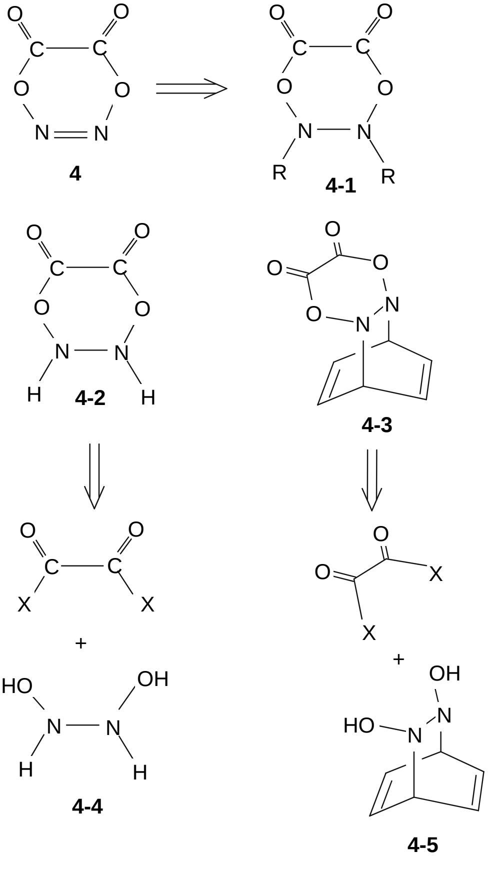


The CO_2 – N_2 Compounds

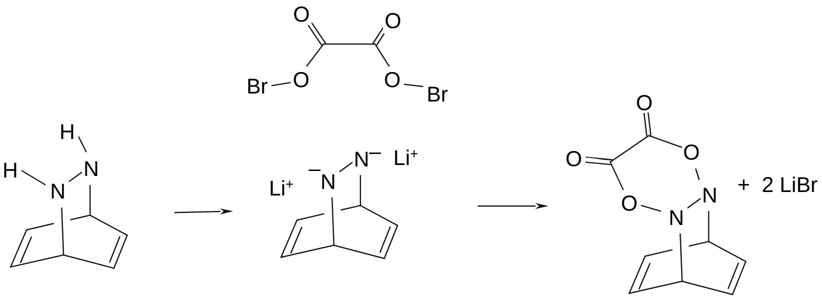
The dehydration approach suggested above for synthesizing the CO_2 dimer etc. would not work for the CO_2–N_2 compounds, because these contain O–N bonds. In contrast, the O–C bonds of the CO_2 molecules would result from nucleophilic attack of an OH oxygen on the electrophilic carbon of a COX moiety formed from an activated COOH; an activated nitrogen might be e.g. N–Halogen, but we will here avoid this approach (because of the uncertainties of nucleophilic substitution on nitrogen) and consider using N–OH groups to bond oxygen to electrophilic carbon.

Just one of the seven minima of Fig. 11.6, **4**, appears to be a reasonably accessible synthetic goal from the viewpoint of both structure and stability, although its lower calculated barrier to decomposition, $59.2\,\mathrm{kJ\,mol^{-1}}$ (Fig. 11.6), would not permit handling at room temperature (but might not demand matrix isolation conditions).

Molecule **4** suggests the possibility of synthesis from a hydrazine **4–1**, perhaps specifically **4–2** or **4–3**; hydrazines are known compounds, and lacking an NN double bond such a precursor may be stabler than **4**:

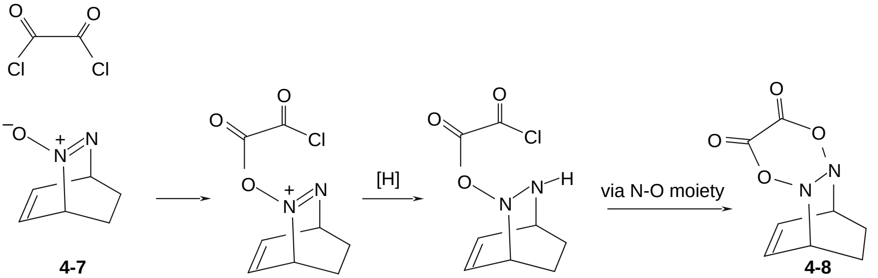


The route to **4–2** outlined here is unlikely to be profitable, because oxidation of hydrazine leads to diimide, HNNH, rather than the dihydroxy hydrazine **4–4** [49]. Precursor **4–3** is appealing because it might be possible to photochemically extrude the very stable molecule benzene from it, providing **4**. However, the bicyclic precursor to **4–5** suffers from the same kind of synthetic problem as **4–4**. Indeed, organic compounds with N–O bonds are uncommon, and the synthesis of **4–2** or **4–3** may require some audacity. One unorthodox approach would be the reaction of a hydrazine metal salt ("rather inaccessible species" [50]) with an acyl hypohalite [51], e.g. (surprisingly, **4–6** seems to be unknown):



4-6 **4-3**

Perhaps slightly more realistic is a scheme starting with the known **4–7** [52]:



4-7 **4-8**

Although compound **4–8** is a formal adduct of **4** with 1,3-cyclohexadiene, rather than with benzene like **4–3**, and so perhaps less propitious for extruding **4**, its pursuit may be worthwhile.

Summary

The CO_2 Dimer etc., Stability

B3LYP/6-31G* and MP2/6-31G* optimization/frequency calculations agree that of the five species examined, all are relative minima (real molecules, at least at these levels of computation). The decomposition barrier of the dimer (B3LYP 40.7 kJ mol^{-1}; MP2 40.8 kJ mol^{-1}) is too low to permit handling at room temperature, and this is probably also true for the trimer (B3LYP 83.2 kJ mol^{-1}; MP2 79.6 kJ mol^{-1}). The acyclic "dimer", "trimer" and "tetramer", actually hydrated $(CO_2)_n$, are probably also kinetically fragile (the "dimer" had a B3LYP barrier of 68.8 kJ mol^{-1} for decomposition through a cyclic transition state). All these compounds are expected to decompose exothermically to CO_2 or CO_2 and H_2O.

The CO_2–N_2 Dimer etc., Stability

B3LYP/6-31G* and MP2/6-31G* optimization/frequency calculations agree that:

(1) Of the fifteen CO_2–N_2 molecules examined, seven are relative minima (real molecules, at least at these levels of computation).
(2) None of the minima is kinetically very stable: the stablest is a tricyclic tetraaza species with a suspiciously high barrier (B3LYP, 83.1 $\mathrm{kJ\,mol^{-1}}$; MP2, 68.4 $\mathrm{kJ\,mol^{-1}}$), and the least stable the four-ring diaza species. All decompose exothermically, some to CO_2 and N_2, some to CO_2 and a nitrogen-containing molecule.

Synthesis

The cyclic CO_2 dimer is expected to require very low, possibly matrix isolation, temperatures for its observation, and a low-temperature photochemical synthesis by extrusion of CO_2 from the cyclic trimer was suggested. The trimer and the acyclic species may be isolable at somewhat higher temperatures, and may be preparable by dehydration of carbonic acid.

The synthesis of the CO_2–N_2 compounds is a formidable challenge, largely because of the synthetic difficulties associated with N–O bonds. Nevertheless, syntheses of the monocyclic $(CO_2)_2N_2$ were suggested.

Notes

1. Some barriers/room temperature halflives: (a) Decomposition of pentazole and (estimated) its conjugate base: 75 $\mathrm{kJ\,mol^{-1}}$/10 minutes and 106 $\mathrm{kJ\,mol}^{-1/2}$ days, respectively. V. Benin, P. Kaszynski, J. G. Radziszki, J. Org. Chem. 2002, *67*, 1354. (b) Decomposition of $(CF_3CO)OOO(COCF_3)$: 86.5 $\mathrm{kJ\,mol^{-1}}$/1 minute. S. v. Ahsen, P. Garciá, H. Willner, M. B. Paci, G. Argüello, Chem. Eur. J. 2003, *9*, 5135.
2. (a) *Kinetic Stability* section in Chapter 12. (b) Cf. calculations on nitrogen oligomers: R. Engelke, J. Am. Chem. Soc., 1993, *115*, 2961; R. Engelke, J. Org. Chem., 1992, *57*, 4841; R. Engelke, J. R. Stine, J. Phys. Chem., 1990, *94*, 5689.
3. Refs. 66–70 and accompanying discussion in ref. [34].

References

1. E. Lewars, J. Mol. Struct. (Theochem), 1996, *363*, 1.
2. A. P. Scott, L. Radom, J Phys Chem, 1986, *100*, 16502.
3. W. J. Hehre, “Practical Strategies for Electronic Structure Calculations”, Wavefunction, Inc., Irvine, CA, 1995; chapter 4.
4. J. W. Ochterski, G. A. Petersson, J. A. Montgomery Jr., J. Chem. Phys., 1996, *104*, 2598; J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, G. A. Petersson, J. Chem. Phys., 2000, *112*, 6532.
5. L. A. Curtiss, K. P. Redfern, J. Pople, J. Chem. Phys., 2000, *112*, 7374.
6. R. S. Sheridan, Org. Photochem., 1987, *8*, 159.
7. P. Pyykko, Chem. Commun., J. Chem. Soc., Chem. Commun., 1999, *6*, 495.
8. G. Frapper, J.-Y. Saillard, J. Am. Chem. Soc., 2000, *122*, 5367.

9. M. J. Mayor-López, J. Weber, H. P. Lüthi, K. Hegetschweiler, J. Mol. Model., 2000, *6*, 55.
10. N. Bodor, M.-J. Huang, Chem. Phys. Lett., 1992, *192*, 386.
11. H. F. Cordes, H. P. Richter, C. A. Heller, J. Am. Chem. Soc., 1969, *91*, 7209.
12. R. Bos, N. W. Barnett, G. A. Dyson, K. F. Lim, R. A. Russell, S. P. Watson, Anal. Chim. Acta, 2004, *502*, 141.
13. A. Gambi, A. G. Gimanini, P. Strazzolini, J. Mol. Struct. (Theochem), 2001, *536*, 9.
14. B. M. Elliot, A. I. Boldyrev, J. Phys. Chem. A., 2005, *109*, 3722.
15. N. G. Moll, D. R. Clutter, W. E. Thompson, J. Phys. Chem., 1966, *45*, 4469.
16. E. Weissberger, W. H. Breckenridge, H. Taube, J. Chem. Phys., 1967, *47*, 1764.
17. M. E. Jacox, D. E. Milligan, J. Chem. Phys., 1971, *54*, 919.
18. R. D. J. Froese, J. D. Goddard, J. Phys. Chem., 1993, *97*, 7484.
19. D. Strelnikov, W. Krätschmer, J. Phys. Chem. A, 2006, *110*, 12395.
20. A. S. Averyanov, Y. Khait, Y. V. Puzanov, J. Mol. Struct. (Theochem), 1996, *367*, 87.
21. F. Cacace, G. D. Petris, M. Rosi, Angew. Chem. Int. Ed. Engl., 2003, *42*, 2985.
22. P. W. Fowler, M. Lillington, J. Chem. Inf. Model., 2007, *47*, 905, and references therein.
23. H. Butenschön, Angew. Chem. Int. Ed. Engl., 2007, *46*, 4012; T. Hamura, Y. Ibusuki, H. Uekusa, T. Matsumoto, J. S. Siegel, K. K. Baldridge, K. Suzuki, J. Am. Chem. Soc., 2006, *128*, 10032.
24. V. Iota, C. S. Yoo, H. Cynn, Science, 1999, *283*, 1510.
25. M. Santoro, A. F. Gorelli, R. Bini, G. Ruocco, S. Scandolo, W. A. Crichton, Nature, 2006, *441*, 857.
26. N. Bodor, P. Buchwald, Chem. Phys. Lett., 2000, *319*, 645.
27. S. Sera, C. Cavazzoni, G. L. Chiarotti, S. Scandolo, E. Tosatti, Science, 1999, *284*, 788.
28. J. Bylykbashi, E. Lewars, J. Mol. Struct. (Theochem), 1999, *468*, 77.
29. W. H. Jones, J. Phys. Chem., 1992, *96*, 5184.
30. W. H. Jones, J. Phys. Chem., 1992, *96*, 594.
31. W. H. Jones, J. Mol. Struct. (Theochem), 1993, *103*, 299.
32. W. H. Jones, I. G. Csizmadia, Zeitschrift für Physik D, 1994, 32($^1/_2$), 145.
33. J. Fabian, E. Lewars, Can. J. Chem., 2004, *82*, 50.
34. A. A. Korkin, J. Leszczynski, R. J. Bartlett, J. Phys. Chem., 1996, *100*, 19840.
35. A. A. Korkin, A. Lowrey, J. Leszczynski, J. Lempert, R. J. Bartlett, J. Phys. Chem. A, 1997, *101*, 2709.
36. M. C. Lin, Y. He, C. F. Melius, J. Phys. Chem., 1993, *97*, 9124.
37. X. Zeng, M. Ge, Z. Sun, D. Wang, Inorg. Chem., 2005, *44*, 9283.
38. M. Malagoli, J. Baker, J. Chem. Phys., 2003, *119*, 12763.
39. S. H. Strauss, Chemtracts, 2000, 13, 145–151.
40. E. C. Meurer, R. Sparrapan, D. M. Tomazela, M. N. Eberlin, R. Augusti, J. Am. Soc. Mass Spectrom., 2005, *16*, 1602.
41. F. Turecek, Collect. Czech. Chem. Commun., 2001, *66*, 1038.
42. J. Demaison, A. G. Császár, A. Dehayem-Kamadjen, J. Phys. Chem. A, 2006, *110*, 13609.
43. M. Wolf, D. L. Yang, J. L. Durant, J. Phys. Chem. A, 1997, *101*, 6243.
44. D. N. Shin, M. Freindorf, T. R. Furlani, R. L. DeLeon, J. V. Garvey, Int. J. Mass Spectrom., 2006, *255–256*, 28.
45. L. Ludwig, A. Kornath, Angew. Chem. Int. Ed. Engl., 2000, *39*, 1421.
46. J. A. Tossell, Inorg. Chem., 2006, 45, 5961.
47. P. Ballone, B. Montanari, R. O. Jones, J. Chem. Phys., 2000, *112*, 6571.
48. Z. Selinge, Y. Lapidot, J Lipid Res, 1966, 7, 174.
49. C. R. Wellman, J. R. Ward, L. P. Kuhn, J. Am. Chem. Soc., 1976, *98*, 1683, and references therein (reference 8 here should say page 7647, not 7674).
50. I. A. Latham, G. J. Leigh, J. Chem. Soc. Dalton Trans., 1986, 399.
51. J. J. Reily, D. J. Duncan, T. P. Wunz, R. A. Parsiga, J. Org. Chem., 1974, *39*, 3291, and references therein.
52. J. P. Snyder, L. Lee, V. T. Bandurco, C. Y. Yu, R. J. Boyd, J. Am. Chem. Soc., 1972, 94, 3260.

Chapter 12
Polyprismanes. Flights of Fun and Fancy

Introduction

Polyprismanes is the name given to a class of molecules that can be viewed as stacked cycloalkanes [1]. Figure 12.1 shows some examples and illustrates the nomenclature. Minyaev et al. named these molecules by regarding the first member of a series as being the prism formed by stacking two cycloalkane units; thus structure **2, 3** with two stacked cyclopropane rings would be the first member of the stacked cyclopropane series, and they call it [3]prismane. Extending the stack by one layer gives structure **3, 3**, bi[3]prismane in their nomenclature, the bi- indicating the second member of the series, with *three* stacked cyclopropane rings, and the third member of the three-membered ring series is tri[3]prismane, with *four* stacked cyclopropanes. In this chapter I adopt a slightly different naming scheme: two numbers give, respectively, the number of rings being stacked and the size of the rings being stacked. Thus structure **2, 3**, with a stack of two cyclopropane rings, is here designated [2,3]prismane, and structure **3, 4** with three stacked cyclobutane rings, is named [3,4]prismane. The conventional prismanes (triprismane, cubane, pentaprismane) could be denoted as [2,n]prismanes, and running the risk of being pedantic, the “prisms” represented by the simple cycloalkanes would be [1,n]prismanes. The scheme used here has the advantage that the number of layers in a stack is clear at a glance, corresponding exactly to the first number in brackets. Of course, in all these prismanes there are several cyclobutane rings, for example **2, 3** has three such rings. The term *polyprismane* denotes a prismane with three or more layers, i.e. a [3,n]-, [4,n]-, etc. prismane.

Polyprismanes are interesting for at least two reasons:

(1) The carbon atoms not at the ends of the stack have a half-planar or butterfly-type disposition of their four bonds (Fig. 12.2). This makes them members of the unconventional non-tetrahedral assortment of tetracoordinate carbons to which also belong planar, pyramidal, and propellane (umbrella) carbon (Fig. 12.2; references to these carbon stereochemistries and to half-planar carbon in organometallic compounds, are given in [1]). Thus they excite the same kind of curiosity as that engendered by the planar carbon of Chapter 1 and the pyramidal carbon of Chapter 2.

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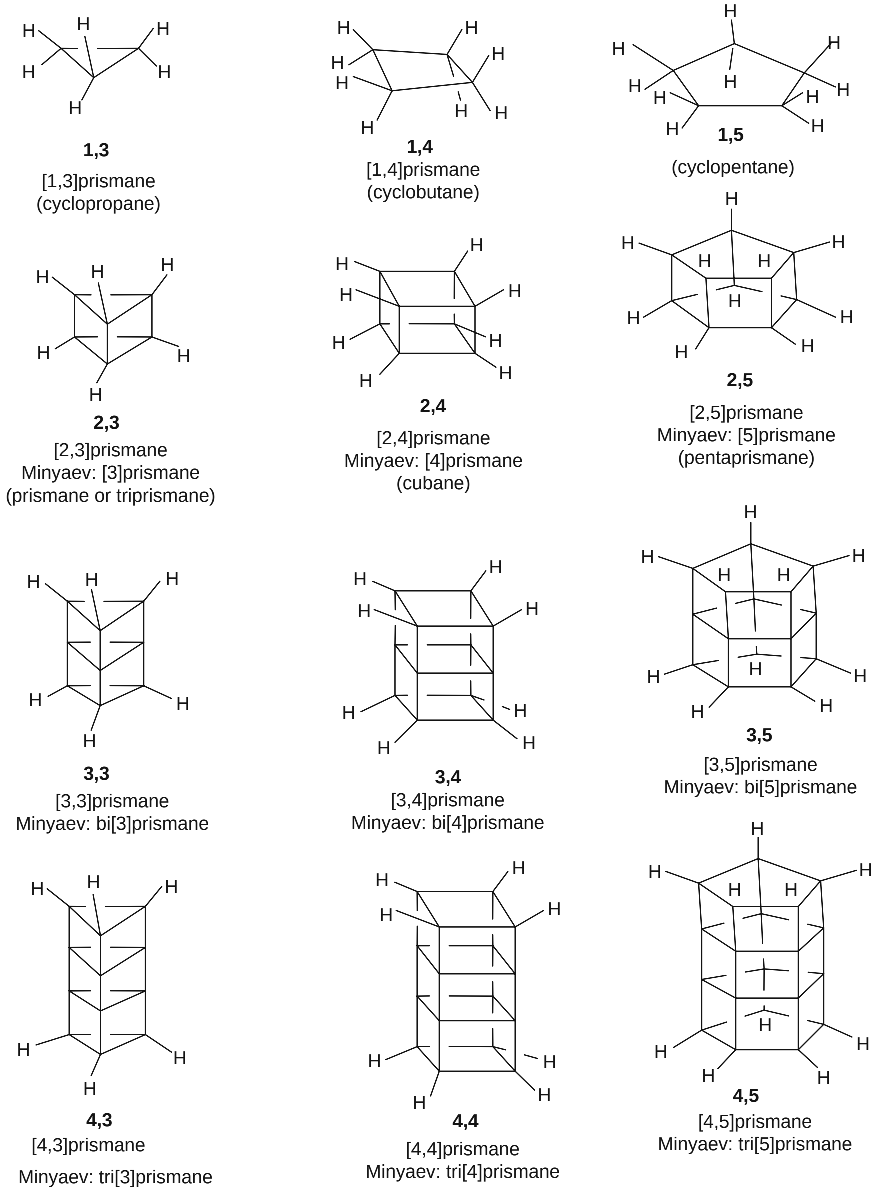


1,3
[1,3]prismane
(cyclopropane)

1,4
[1,4]prismane
(cyclobutane)

1,5
(cyclopentane)

2,3
[2,3]prismane
Minyaev: [3]prismane
(prismane or triprismane)

2,4
[2,4]prismane
Minyaev: [4]prismane
(cubane)

2,5
[2,5]prismane
Minyaev: [5]prismane
(pentaprismane)

3,3
[3,3]prismane
Minyaev: bi[3]prismane

3,4
[3,4]prismane
Minyaev: bi[4]prismane

3,5
[3,5]prismane
Minyaev: bi[5]prismane

4,3
[4,3]prismane
Minyaev: tri[3]prismane

4,4
[4,4]prismane
Minyaev: tri[4]prismane

4,5
[4,5]prismane
Minyaev: tri[5]prismane

Fig. 12.1 Prismanes and polyprismanes: structures and nomenclature. The [3]prismane, bi[3]-prismane, etc. names were used by Minyaev et al. [1]. Conventional names are in parentheses. The molecules have D_{nh} symmetry

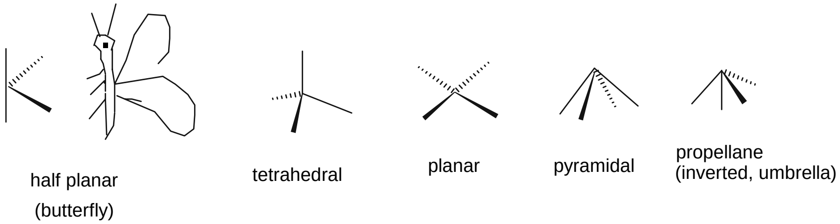


Fig. 12.2 The half-planar or butterfly stereochemistry of carbon atoms in polyprismanes. Besides this and the normal tetrahedral, other conceivable stereochemistries for carbon are the planar (Chapter 1), pyramidal (Chapter 2), and propellane. See refs. in [1]

(2) As rodlike molecules, polyprismanes enjoy the same kind of putative utility as carbon nanotubes [2], and are somewhat akin to staffanes and related rodlike molecules [3] and to ladderanes [4]. Stiff, rodlike molecules like these may find applications in materials science because of their mechanical and electrical properties.

In this chapter we shall briefly review “ordinary” prismanes ([2,n]prismanes), then examine polyprismanes; analogies with nanotubes, staffanes and ladderanes will be alluded to.

Simple Prismanes

To put help polyprismanes in perspective, particularly with regard to the challenge of synthesis, we begin with a brief look at “simple” prismanes, which do not have half-planar carbons; these have been ably reviewed by Hopf [5]. Triprismane (prismane), tetraprismane (cubane), and pentaprismane are known (**2,3**, **2,4**, and **2,5**, Fig. 12.1). Hexaprismane remains elusive, and the synthesis of higher prismanes has (understandably) probably not been diligently pursued. The syntheses will be outlined only, since this is not primarily an exposition of organic chemistry.

Triprismane (prismane) entered the literature in 1869, when it was proposed by Ladenburg as a possible structure for benzene [6, 7]. The synthesis of the genuine compound, first reported by Katz and Acton in 1973 [8], is outlined in Fig. 12.3. Benzvalene (**1**), made from lithium cyclopentadienide, dichloromethane, and methyllithium, was reacted with N-phenyltriazolinedione in a pathway that can be rationalized as proceding by formation of a zwitterionic carbocation **2** which relieves its strain by a C–C bond migration that converts a three- to a four-membered ring; closure of the zwitterion **3** gives a compound **4** short of prismane by only a C–C bond. Hydrolysis of **4** to a hydrazine (–NH–NH–) and oxidation gave an azo compound **5** which on photolysis lost dinitrogen to give prismane (**2,3**), a colorless liquid, explosive but stable at room temperature – in fact, for success the azo compound **5** must be heated during the photolysis!

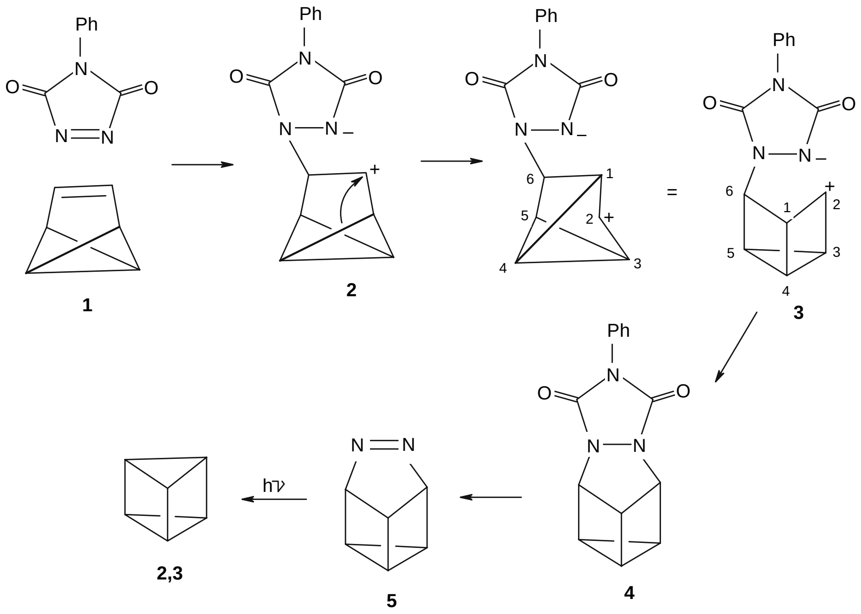


Fig. 12.3 The first synthesis of prismane [8]

Tetraprismane, i.e. cubane, was first synthesized by Eaton and Cole in 1964 [9]. This was a signal event, because cubane was the first molecular analogue of a Platonic solid [10, 11, 12] to be made. The synthesis is outlined in Fig. 12.4. The Diels-Alder dimer **6** of 2-bromocyclopentadienone, made from cyclopentenone by bromination-dehydrobromination reactions and spontaneous dimerization of the bromodienone, was converted to the monoketal **7**, which on photolysis underwent a [2+2] cycloaddition to form the cage molecule **8**, a bishomo cubane (it differs from the cubane system by having two one-carbon bridges). The bromo ketone moiety of **8** underwent Favorskii ring contraction with base to form the homocubane system of **9**, and this was decarboxylated to **10** by radical fragmentation of the *t*-butyl peroxy ester, with decarboxylation and abstraction of a hydrogen from the solvent by the alkyl-type radical. Removal of the ketal protecting group of **10** and another Favorskii ring contraction gave cubanecarboxylic acid, **11** (itself a valuable precursor to other cubane derivatives). Another decarboxylation sequence provided cubane, a stable colorless crystalline compound melting at 130–131°.

Pentaprismane was first made by Eaton, Or and Branca in 1981 [13]. The synthesis is more involved than that of cubane (which was more involved than that of prismane) because a prismane-type approach (extrusion of dinitrogen from the azo compounds **12** or **13**) fails, and a cubane-type photocyclization approach ([2+2] cycloaddition with **14**) did not work on **14**:

The successful synthesis is outlined in Fig. 12.5. The strategy of the Eaton group was to use photochemical [2+2] cycloaddition only right at the start, avoiding

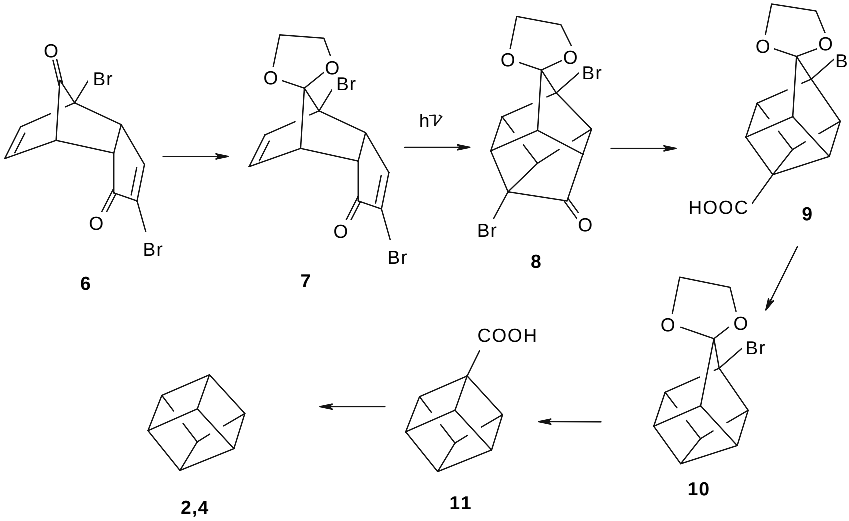
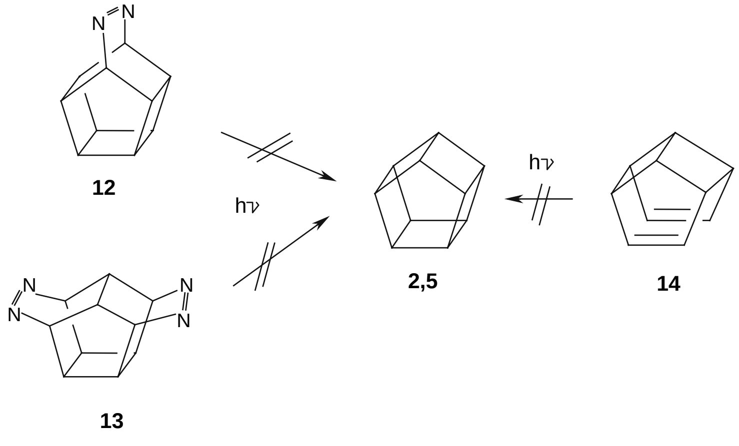


Fig. 12.4 The first synthesis of cubane [9]

disappointment in a final do-or-die step, and to eschew attempted CC bond formation by dinitrogen extrusion, relying rather on essentially conventional chemical reactions, a circumspect approach which does not detract from the experimental skill and persistence which was required to make it work. In the event (see below), a second photochemical cycloaddition was needed when a cyclobutane ring was inadvertently opened. The Diels-Alder adduct of *p*-benzoquinone and the dimethyl ketal of tetrachlorocyclopentadiene (**15**) on photolysis underwent a [2+2] cycloaddition to form the cage molecule **16**; this on reaction with lithium underwent reductive dechlorination and reduction of the ketone groups to hydroxyls, which latter on conversion to better leaving groups (tosylates, OTs, OSO$_2$C$_6$H$_4$Me-*p*) and reaction



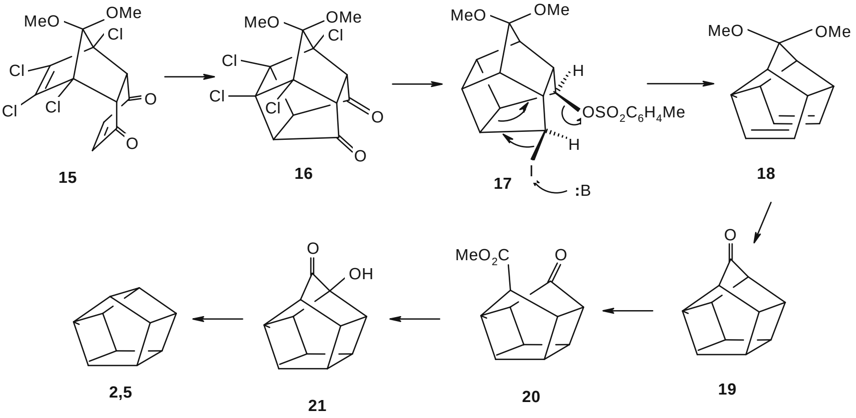
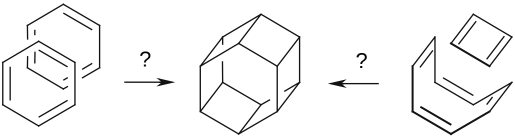


Fig. 12.5 The synthesis of pentaprismane [13]

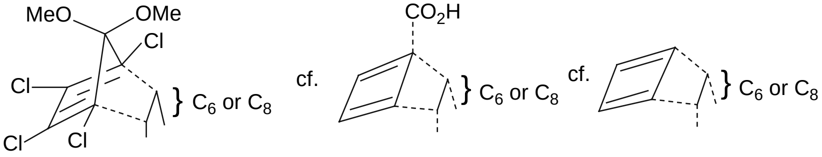
with iodide ion provided the iodo tosylate **17**. On reaction with *t*-butyllithium **17** unfortunately reacted by relieving strain by opening its cyclobutane ring, rather than by forming a new ring by nucleophilic attack of the iodine-bearing carbon on the proximate, tosylated carbon. Fortunately, the resulting dialkene **18**, in contrast to **14**, obligingly photocyclized, to the ketone **19**. This was not unexpected, since homo-**14**, **18** with CH_2 in place of $C(OMe)_2$, was known to undergo cyclization [14, 15]; such photoclosure is subject to subtle influences: the analogue of **18** with O in place of $C(OMe)_2$ could not be cyclized [15]. The conversion of **19** to pentaprismane was more circuitous than might have been thought, probably because the α-carbons of this ketone do not readily lend themselves to formation of an enol (which would have a very distorted CC double bond) or an enolate (which would have its lone pair unable to conjugate effectively with the carbonyl group). Reaction of **19** with a peroxy acid gave the characteristic insertion of an oxygen into a proximate CC bond (Baeyer-Villiger reaction) forming a lactone (CO–O bridge), and hydrolysis and oxidation afforded a keto acid which was methylated to give **20**. Reductive coupling of the ester and ketone groups with sodium (an acyloin reaction, usually applied to diesters) reintroduced the one-carbon bridge as a CH(OH) moiety which on oxidation provided a ketone bridge, but this time (contrast **19**) with a functional group on an α-carbon: the hydroxy ketone **21**, after tosylation of the OH to provide a good leaving group, underwent a Favorskii reaction with base (cf. the bromo ketone from **10** in the cubane synthesis) to afford pentaprismanecarboxylic acid, which was decarboxylated to the parent hydrocarbon (cf. **11** to cubane).

Let us close this account of simple prismanes with a look at hexaprismane. The synthesis of cubane was reported in 1964; pentaprismane was said (1974) to show “extraordinary synthetic inaccessibility” [16], but was made in 1981 [13]; and hexaprismane has so far (early 2007) resisted all attempts at synthesis [5]. As Hopf points out [5], hexaprismane can in principle be assembled from two benzene rings or from cyclobutadiene and cyclooctatetraene:



2,6

Benzene is of course abundant, cyclooctatetraene is commercially available, and cyclobutadiene is a known, if transient, synthetic intermediate. It is thus almost ironic that this very elusive prismane should show such a divergence between the topological allurement of these retrosynthetic disconnections [17] and the hard facts of chemical reactivity: benzene shows no tendency to be persuaded to be dimerized to hexaprismane, and cyclobutadiene and cyclooctatetraene do not react together in the [2+2] mode that would be required. Approaches to hexaprismane have thus been sequential elaborations of the desired scaffolding, akin to the syntheses of cubane and pentaprismane. A very close approach to the compound, by Mehta and Padma [18], is broadly outlined in Fig. 12.6. The Diels-Alder adduct of 1,5-cyclooctadiene and the dimethyl ketal of tetrachlorocyclopentadiene (**22**) here plays a role somewhat analogous to that of the adduct (**15**) of *p*-benzoquinone and the tetrachlorocyclopentadiene in the pentaprismane synthesis above (Fig. 12.5). In both syntheses the tetrachlorocyclopentadiene functions as a C_4 cyclobutadiene synthon [17] (a carbon is elided from the C_5 moiety toward the end of the synthesis); *p*-benzoquinone is a C_6 moiety for the construction of pentaprismane (C_4 + C_6) and 1,5-cyclooctatetraene is a C_8 moiety on the way to hexaprismane (C_4 + C_8):



The cyclooctene unit of **22** was allylically brominated and dehydrobrominated to furnish a 1,4-diene which underwent a Diels-Alder type reaction with singlet oxygen to give the peroxide **23**. The O–O bond of **23** was cleaved with lithium aluminum hydride, and the 1,4-diol (protected as the diacetate) was photocyclized, affording a cyclobutane ring; hydrolysis of the diacetate and reaction with methanesulfonyl chloride (mesyl chloride, MsCl, $MeSO_2Cl$) gave the dimesylate **24**. This was converted to **25** via a stepwise elimination process akin, overall, to the conversion of **17–18** in the pentaprismane synthesis (Fig. 12.5). Photocyclization and deketalization provided the ketone **26**, with two of the six needed cyclobutane rings. A Favorskii reaction (cf. **10–11** in the cubane synthesis) and methylation of the resulting acid afforded the ester **27**, with four hard-won cyclobutane face connectors. The superfluous carbon in **27** was removed by hydrolysis to the acid (esterification of the acid precursor of **27** was presumably a concession to experimental constraints, done for ease of handling) and decarboxylation to **28** with

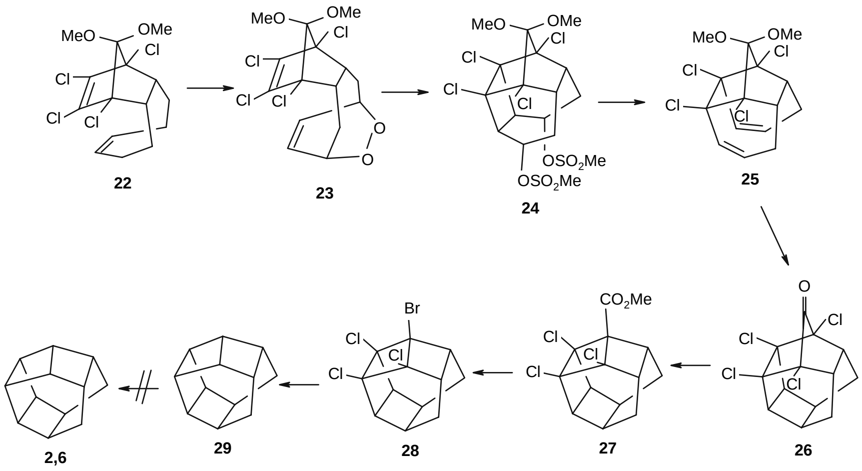


Fig. 12.6 A close approach to hexaprismane [17]

mercuric oxide-bromine-dibromomethane. This is a modern variation on the classical Hunsdiecker reaction in which a silver carboxylate R–COOAg reacts with bromine to form an acyl hypobromite R–COOBr, which homolytically ruptures the O–Br bond and loses CO_2 to give a radical $R^{\cdot}$ which reacts with bromine yielding RBr. Reductive dehalogenation of **28** furnished the hydrocarbon **29**, tantalizingly close to hexaprismane. Unfortunately, **29** subjected the experimenters to the fate of Tantalus in denying them the satisfaction they craved.

Polyprismanes

The energetics and electronic structure of the characteristic polyprismane, and other distorted, carbons. To get a feel for the price paid for distorting tetracoordinate carbon away from its canonical tetrahedral geometry in various ways (Fig. 12.7), let us calculate the energetics associated with these four distortions. Our approach is indicated in Fig. 12.7. The tetrahedral geometry is shown in two orientations A and B, to facilitate picturing the transformations that lead to the unorthodox dispositions of bonds (planar, half-planar, pyramidal, propellane). To facilitate following the transformations, the four bonds are labeled a, b, c, d, and the swinging motion required of the bonds in order to alter bond angles is indicated with short arrows. Each of these four transformations away from tetrahedral carbon was subjected to an analysis of the effect on energy of altering angles in tetrahedral methane, CH_4, which as the canonical normal carbon molecule was assigned a relative energy of zero kJ mol^{-1}. In a series of partial optimizations, the angles being varied were

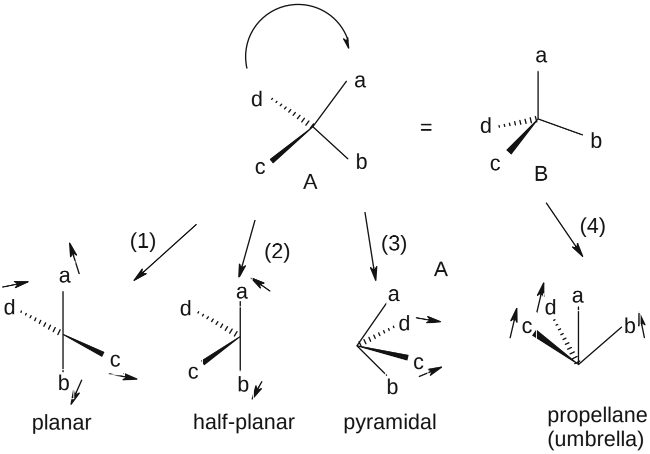


Fig. 12.7 The planar, half-planar and pyramidal strereochemistries are readily pictured as being derived from tetrahedral carbon in orientation A, by swinging the appropriate bonds as indicated by the short arrows on a, b, etc.; the propellane stereochemistry is pictured as arising from orientation B

fixed in increments of 10° and at each step the rest of the geometry was optimized at the moderately high MP2/6-31G* level [19] . The results for going from normal tetrahedral methane to planar, half-planar, pyramidal and propellane methane are summarized in Fig. 12.8, which is based on the data in Tables 12.1–12.4. As expected, the tetrahedral geometry is much the lowest-energy one for methane, but the lowest-energy half-planar structure (with equatorial HCH angle ca. 95°) is the next-lowest; its relative energy of ca. 264 kJ mol^{-1}, although considerably above the tetrahedral energy, is comfortably below the typical C–H bond energy of ca. 400–415 kJ mol^{-1} (contrast planar methane, Chapter 1), and far below the energies of planar methane (669 kJ mol^{-1}) and the lowest-energy pyramidal methane (ca. 575 kJ mol^{-1}). Of more direct relevance to polyprismanes is the observation that the strain energies of half-planar CH_4 with equatorial angles varying from 60° (corresponding to carbon in [n,3]prismanes) to 120° (corresponding to carbon in [n,6]prismanes) is, except for the 60° case, significantly below the typical C–C bond energy of ca. 350 kJ mol^{-1} (Fig. 12.8 and Table 12.2):

60°, 358 kJ mol^{-1}, [n,3]prismanes
90°, 264 kJ mol^{-1}, [n,4]prismanes
108°, ca. 280 kJ mol^{-1}, [n,5]prismanes
120°, 311 kJ mol^{-1}, [n,6]prismanes

These values provide some indication that polyprismanes with cyclopropane rings, and perhaps with cyclohexane rings, may be less stable than the cyclobutane and

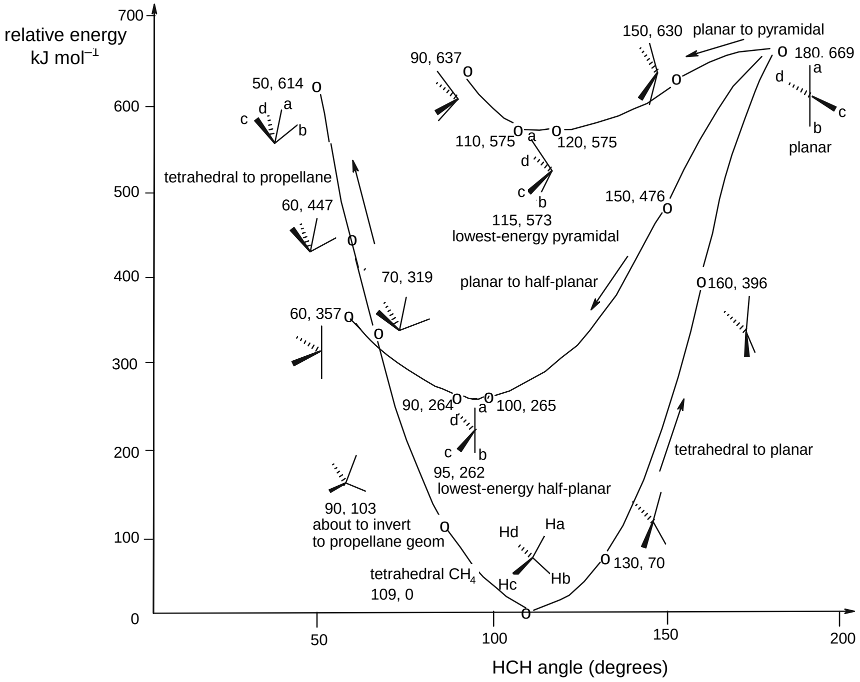


Fig. 12.8 Distorting CH_4 from the tetrahedral to the planar, half-planar, pyramidal and propellane (umbrella) geometries (cf. Fig. 12.7). The angles altered in each distortion are: tetrahedral to planar, HaCHb and HcCHd; planar to half-planar, HcCHd; planar to pyramidal, HaCHb and HcCHd; tetrahedral to propellane, HaCHb, HaCHc, and HaCHd. The numbers associated with points on the curves are relevant angles, and relative energies in kJ mol^{-1}; 95, 262 for the lowest-energy half-planar structure denotes an equatorial HCH angle of 95° and a relative energy of 264 kJ mol^{-1}, 115, 573 for the lowest-energy pyramidal structure denotes HaCHb = HcCHd = 115°, relative energy 575 kJ mol^{-1}, and 50, 614 for the propellane structure shown means HaCHb = HaCHc = HaCHd = 50° and relative energy = 614 kJ mol^{-1}. Calculations are at the MP2/6-31G* level, without ZPE

Table 12.1 Distorting tetrahedral CH_4 to the planar geometry (cf. Fig. 12.8). MP2/6-31G* calculations. Angles are in degrees and bond lengths in Å. MP2 energy is the ab initio energy without ZPE, in hartrees (atomic units) and relative energy is in kJ mol^{-1}

HCH	C–H	MP2 energy	Relative energy	
109.5	1.090	−40.33255	0	tetrahedral
120	1.091	−40.32548	18.6	
130	1.0935	−40.30606	69.6	
140	1.098	−40.27492	151	
150	1.104	−40.23294	262	
160	1.110	−40.18156	396	
170	1.110	−40.12387	548	
180	1.085	−40.07763	669	planar

Table 12.2 Distorting planar CH_4 to the half-planar geometry (cf. Fig. 12.8). MP2/6-31G* calculations. Angles are in degrees and bond lengths in Å. MP2 energy is the ab initio energy without ZPE, in hartrees (atomic units) and relative energy is in kJ mol^{-1}

HCH	Eq C–H	Axial C–H	MP2 energy	Relative energy	
180	1.085	1.085	−40.07763	669	planar
170	1.108	1.102	−40.09567	622	
160	1.117	1.105	−40.12368	548	
150	1.120	1.103	−40.15129	476	
140	1.119	1.100	−40.17821	405	
130	1.118	1.097	−40.19735	355	
120	1.118	1.095	−40.21398	311	
110	1.119	1.092	−40.22559	281	
100	1.122	1.090	−40.23171	265	
90	1.126	1.088	−40.23200	264	
80	1.133	1.086	−40.22621	279	
70	1.143	1.084	−40.21425	311	
60	1.157	1.082	−40.19629	358	3-ring angle

Tetrahedral CH_4, −40.33255, relative energy = 0 kJ mol^{-1}

Table 12.3 Distorting planar CH_4 to the pyramidal geometry (cf. Fig. 12.8). Angles are in degrees and bond lengths in Å. MP2 energy is the ab initio energy without ZPE, in hartrees (atomic units) and relative energy is in kJ mol^{-1}. The calculated (MP2/6-31G*) relevant CCC angle in (the still-unknown) pyramidane, **29**, is 76.7°

HCH	C–H	MP2 energy	Relative energy	
180.0	1.085	−40.07763	669	planar
170.0	1.086	−40.07952	664	
160.0	1.088	−40.08482	651	
150.0	1.093	−40.09251	630	
140.0	1.100	−40.10111	608	
130.0	1.110	−40.10883	587	
120.0	1.124	−40.11371	575	
110.0	1.141	−40.11373	575	
100.0	1.164	−40.10672	593	
90.0	1.194	−40.08998	637	
80.0	1.236	−40.05986	716	
70.0	1.303	−40.01227	841	

Tetrahedral CH_4, −40.33255, relative energy = 0 kJ mol^{-1}

Table 12.4 Distorting tetrahedral CH_4 to the propellane geometry (cf. Fig. 12.8) MP2/6-31G* calculations. Angles are in degrees and bond lengths in Å. MP2 energy is the ab initio energy without ZPE, in hartrees (atomic units) and relative energy is in kJ mol^{-1}. The calculated (MP2/6-31G*) relevant CCC angle in the known propellane, **30**, is 58.2°

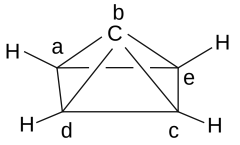
HCH	Central C–H	Peripheral C–H	MP2 energy	Relative energy	
109.5	1.090	1.090	−40.33255	0	tetrahedral
100	1.105	1.087	−40.32247	26.5	
90	1.131	1.086	−40.29401	101	
80	1.173	1.089	−40.25471	204	
70	1.238	1.099	−40.21094	319	
60	1.324	1.125	−40.16228	477	
50	1.438	1.176	−40.09888	614	

cyclopentane species. In the next section we will see evidence, from a comparison of homodesmotic and angle-distortion calculations, that half-planar CH_4 is a reasonable surrogate for the half-planar carbons of polyprismanes.

None of the three distorted methanes (planar, lowest half-planar, lowest pyramidal, Fig. 12.8) is a minimum on the potential energy surface. The planar structure is a fourth-order saddle point (four imaginary vibrational frequencies) [20] with the "biggest" frequency (arising from the most negative force constant) being $6857i$ cm^{-1}, apparently corresponding to distortion to a tetrahedral geometry. The lowest energy half-planar structure, unlike planar methane, is not a stationary point on the potential energy surface [20]: it was obtained by a constrained optimization, freezing the equatorial HCH angle at 95°. Optimization of this structure without constraints leads to tetrahedral methane (formally C_{2v} because the half-planar symmetry point group is maintained, but to all intents tetrahedral). In contrast, optimizing a planar CH_4 input structure (with D_{4h} symmetry) leads to a stationary point of the same symmetry (but a fourth-order saddle point, not a relative minimum). The lowest half-planar structure gave one imaginary frequency ($77i$ cm^{-1}), but this means little because the method used to calculate frequencies is based on the assumption that the species is a stationary point (although not necessarily a relative minimum), resting in the center of a quadratically curved portion of the potential energy surface [20]. Surprisingly, the lowest-energy pyramidal structure is a stationary point: unconstrained optimization leads to pyramidal methane with HCH (HaCHb, HcCHd) angles of 115°. This species is a third-order saddle point, with the "biggest" imaginary frequency, $1567i$, apparently corresponding to distortion to a tetrahedral geometry. Distortion along the propellane coordinate does not lead to a lowest-energy structure, but rather the energy rises monotonically, and a stationary point is not encountered. Subjecting CH_4 with a propellane geometry to unconstrained optimization leads to tetrahedral methane (formally C_{3v} because the propellane symmetry point group is maintained, but to all intents tetrahedral). At the MP2/6-31G* level the still-unknown pyramidane, **29**, (Chapter 2) has a CCC angle (shown) of 76.7° and the known [1.1.1]propellane [21, 22], **30**, has a CCC angle (shown) of 58.2°. The MP2/6-31G* and B3LYP/6-31G* [23] relative energies are not all that different, the B3LYP values being 20–40 kJ mol^{-1} lower:

planar (stationary point), HCH 180°
MP2, 669; B3LYP, 630
lowest-energy half-planar, MP2 HCH 95°
MP2, 262; B3LYP, 246
lowest-energy pyramidal (stationary point), MP2 HCH 114.8°
MP2, 573; B3LYP, 544
propellane with HCH 60° (CCC of [1.1.1]propellane)
MP2, 447; B3LYP, 426

The calculated (MP2/6-31G*) geometries of the five notable CH_4 structures arising from the calculations in Fig. 12.8 are shown in Fig. 12.9. Can these structures be regarded as templates that, being small, could be studied with relative ease



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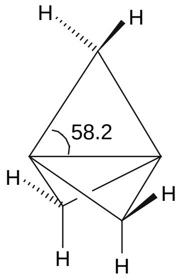
CaCbCc = CdCbCe = 76.7°



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to provide insight into the electronic structure of potentially realizable molecules containing the distorted carbon? To some extent this is the case. Let us briefly consider a few features identified with the aid of natural bond order (NBO) analyses [24] on each of the five (Fig. 12.9); for NBO calculations and Löwdin bond

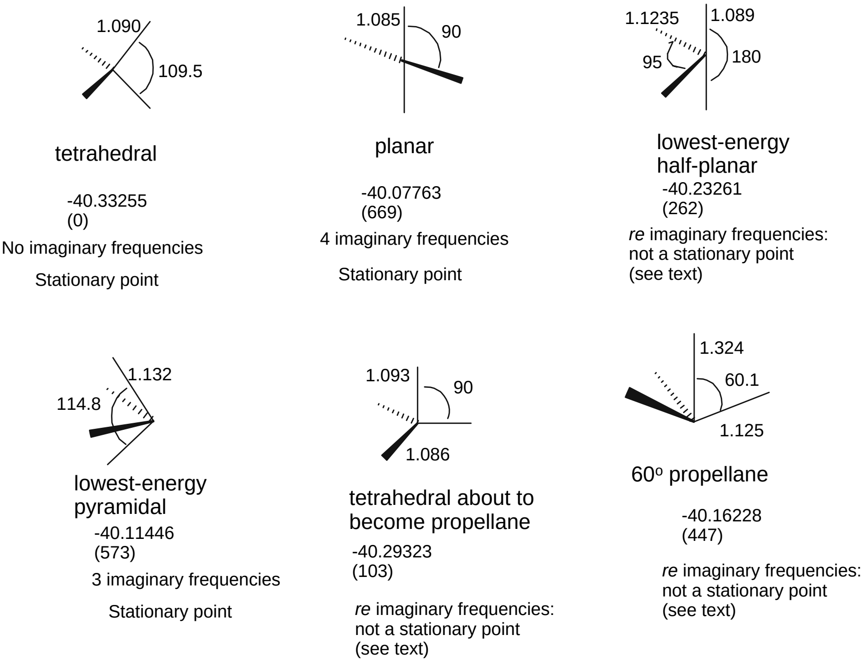


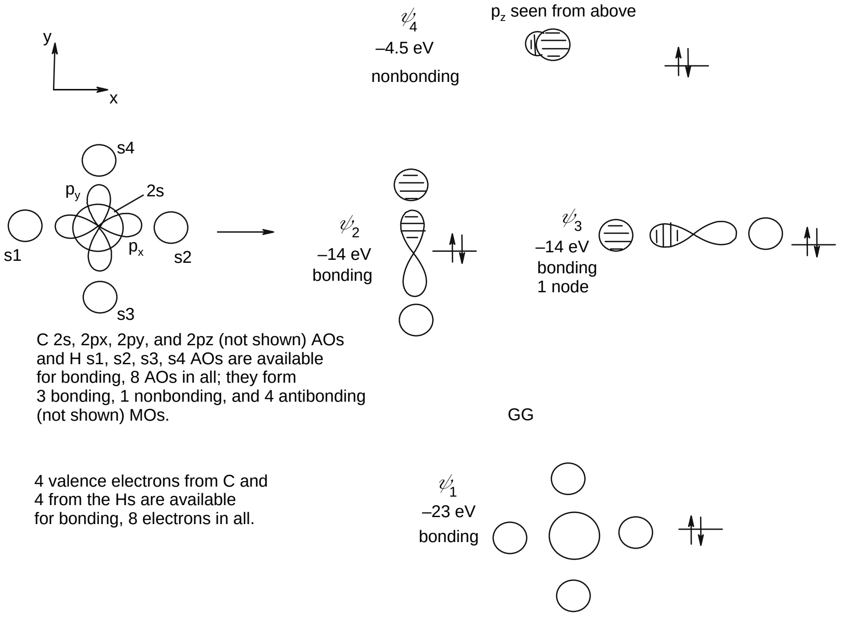
Fig. 12.9 The five notable CH_4 structures (two are shown for propellane CH_4), MP2/6-31G* geometries (cf. Fig. 12.8). Tetrahedral CH_4 is the only "real" molecule here and the standard with which the others are compared. Planar and pyramidal CH_4 are stationary points. The half-planar structure shown is a minimum along its distortion curve but is not a stationary point. No propellane structure is a distortion minimum or a stationary point; the 60° structure shown has an HCH angle similar to the corresponding CCC angle calculated for **30**, [1.1.1]propellane. The MP2/6-31G* energies in hartrees (atomic units) and relative energies (kJ mol^{-1}, in parentheses) are given

orders [25, 26, 27], STO-3G calculations[1] were done with Spartan[2] on MP2/6-31G* geometries:

(1) Tetrahedral CH_4 is familiar in electronic disposition: each hydrogen is bound to carbon by an sp^3-hybridized atomic orbital (AO), and each Csp^3/H1s localized molecular orbital (MO) is a normal electron-pair single bond (occupancy 2.0 electrons, bond order 1.00). Nonintuitively, the four equivalent *bonds* do not reflect four equivalent *valence AOs* on carbon, but rather are a mathematical construct based on *different* valence energy levels (−25, −14, −14, −14 eV at the STO-3G level), which can be experimentally detected [28, 29].

(2) (Figure 12.10). Planar CH_4 and planar carbon in a promising synthetic goal, dimethanospirooctaplane, were discussed in Chapter 1. Each hydrogen in planar CH_4 is bound to carbon by a moderately electron-deficient bond (Löwdin bond order 0.77). An orbital analysis of planar methane by Hoffmann et al. gave the perpendicular p orbital a lone pair [30].

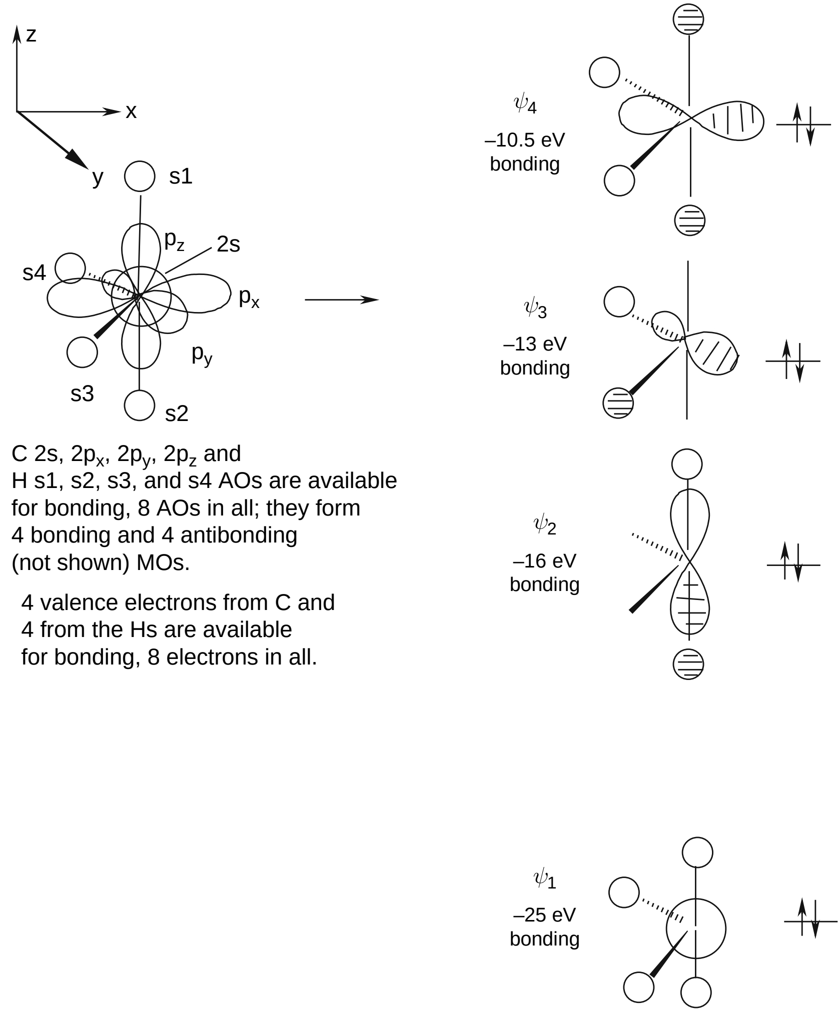
(3) (Figure 12.11). Half-planar CH_4 at the minimum-energy (equatorial HCH 90°) geometry has four full-fledged C–H bonds (Löwdin bond order 1.99), corresponding to two bonding MOs each of occupancy 1.99 (bonding the axial hydrogens) and 2.00 (bonding the equatorial hydrogens). To bond each axial hydrogen, carbon uses an approximately $sp^{1.6}$ (39% s) AO and for each equatorial



C 2s, 2px, 2py, and 2pz (not shown) AOs
and H s1, s2, s3, s4 AOs are available
for bonding, 8 AOs in all; they form
3 bonding, 1 nonbonding, and 4 antibonding
(not shown) MOs.

4 valence electrons from C and
4 from the Hs are available
for bonding, 8 electrons in all.

Fig. 12.10 Possible bonding in planar CH_4. The four hydrogens are bound to carbon by three bonding MOs and a total of six electrons (three pairs). This gives each C–H bond an order of 3/4 = 0.75; the calculated Löwdin bond order is 0.77. The HOMO is a p_z AO on carbon. The energy levels are from STO-3G calculations on the MP2/6-31G* geometry, which were also used to analyze the bonding



C 2s, $2p_x$, $2p_y$, $2p_z$ and
H s1, s2, s3, and s4 AOs are available
for bonding, 8 AOs in all; they form
4 bonding and 4 antibonding
(not shown) MOs.

4 valence electrons from C and
4 from the Hs are available
for bonding, 8 electrons in all.

Fig. 12.11 Possible bonding in the lowest-energy (equatorial HCH $\sim 95^\circ$) half-planar CH_4. The four hydrogens are bound to carbon by four bonding MOs and a total of eight electrons (four pairs). This gives each bond an order of essentially 4/4 = 1; the calculated Löwdin bond order is 0.98–0.99. The energy levels are from STO-3G calculations on the MP2/6-31G* geometry, used to analyze the bonding

hydrogen an approximately $sp^{7.7}$ (11% s) AO; this accords with the shorter axial bonds (1.089 Å cf. 1.124 Å), for bonds become stronger and shorter with increased s character [31]. The MO scheme deduced from the energy levels and by visualization of the orbitals is shown in Fig. 12.11. A similar orbital analysis of half-planar methane was given by Radius et al. in a paper discussing the effect of substituents on the energy gap between tetrahedral and half-planar methanes [32].

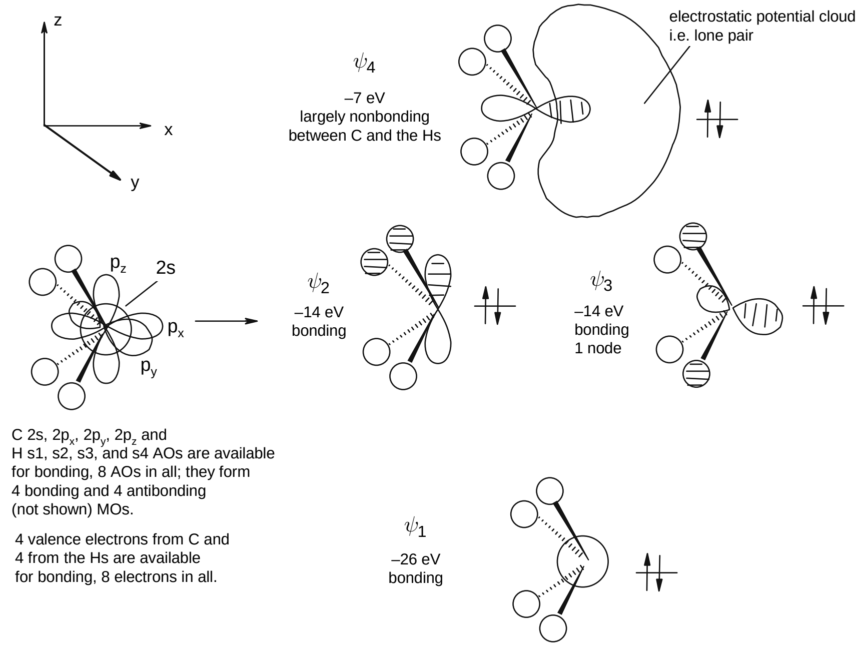
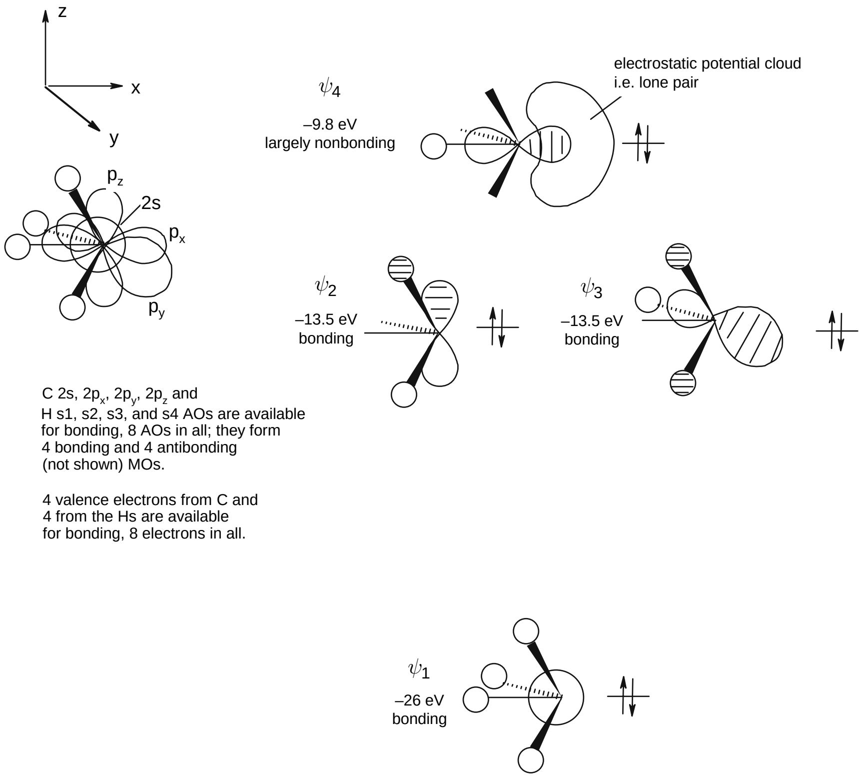


Fig. 12.12 Possible bonding in the lowest-energy (HCH, Fig. 12.9, 114.8°) pyramidal CH_4. The four hydrogens are bound to carbon by three bonding MOs and a total of six electrons (three pairs). This gives each C–H bond an order of 3/4 = 0.75; the calculated Löwdin bond order is 0.73. The highest-occupied molecular orbital (HOMO) engenders a very prominent region of net negative charge (electrostatic potential), corresponding to a lone pair on carbon

(4) (Figure 12.12). Pyramidal CH_4 at the minimum-energy geometry (HCH, Fig. 12.9, 114.8°) has four moderately electron-deficient bonds (Löwdin bond order 0.73). The MO scheme deduced from the energy levels and by visualization of the orbitals is shown in Fig. 12.12. A striking feature of this structure is a very prominent lone pair on carbon, which is also one of the remarkable calculated properties of pyramidane, $C(CH)_4$, a realistic synthetic goal (Chapter 2). Of the five distorted methanes, only the pyramidal and the propellane (below) have this lone pair. Almost exactly the same kind of electrostatic potential lone pair is seen in conventional molecules like NH_3.

(5) (Figure 12.13). Propellane CH_4 has no minimum energy arrangement along the distortion curve in which three C–H bonds are swivelled toward a central bond (Fig. 12.8). The transition from tetrahedral to propellane CH_4 occurs when three C–H bonds are in a plane, with the fourth bond normal to the plane, and this is the lowest-energy propellane structure. The species with HCH angles 60° (Fig. 12.9), similar to those in the known propellane (**30**, [21, 22], 58.2° from an MP2/6-31G* optimization) was analyzed in a manner similar to the above four CH_4 structures.



C 2s, $2p_x$, $2p_y$, $2p_z$ and
H s1, s2, s3, and s4 AOs are available
for bonding, 8 AOs in all; they form
4 bonding and 4 antibonding
(not shown) MOs.

4 valence electrons from C and
4 from the Hs are available
for bonding, 8 electrons in all.

Fig. 12.13 Possible bonding in propellane CH_4 with HCH 60° (Fig. 12.9). The four hydrogens are bound to the carbon by three bonding and one largely nonbonding MOs and a total of eight electrons (four pairs) but the central (axial) hydrogen is bound by a somewhat weaker bond than the three others, Löwdin bond order is 0.75, length 1.324 Å, cf. 1.00, 1.125 Å for the other three C–H bonds

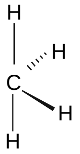
The C-central H bond is moderately electron-deficient (Löwdin bond order 0.75) and the three other bonds are of conventional order (1.00), which accords with the calculated bond lengths of 1.325 Å (central) and for the other three, 1.125 Å, although these three are a bit long (the MP2/6-31G* C–H length for tetrahedral CH_4 is 1.090 Å). The MO scheme deduced from the energy levels and by visualization of the orbitals is shown in Fig. 12.13.

Some Computed Properties of Polyprismanes

We'll review the salient points in the inaugural paper [1] and augment this (anticipatory to experiment) knowledge of polyprismanes with a few more calculations.

Strain

Minyaev et al. estimated the angle strain of the half-planar carbons in polyprismanes by comparing the energy of half-planar (partial optimization with the axial angle set to 180° and the equatorial set to various ring angle values) and tetrahedral methane. The authors chose **31** as an approximate representative of the strain energy (SE) of the polyprismane quaternary carbon, since steric compression should be small or absent here, in contrast to the situation in **32**, **33**, and **34**. Evidently using the B3LYP/6-311G(2df.p) level, they estimated the angle strain due to the half-planar centers in the "three-stack" polyprismanes [3,3]-, [3,4]-, [3,5]-, and [3,6]-prismanes (cf. Fig. 12.1) at ca. 650–1300 kJ mol^{-1} (3× 218 −6× 218 kJ mol^{-1}; ca. 160–310 kcal mol^{-1}).



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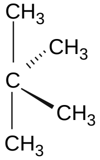

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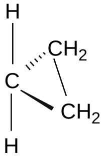

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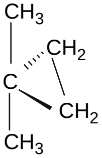

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The total strain in [3,3]-, [3,4]-, [3,5]-, and [3,6]-prismanes was calculated by homodesmotic reactions, hypothetical reactions with the same number of each kind of bond in reactants and products; homodesmotic reactions are a refinement of isodesmic reactions [33], and have been extensively used to estimate strain energies [34, 35]. The exothermicity of such a reaction is a measure of the SE of the molecule whose rings are being broken. Consider [3,4]prismane, for which a homodesmotic reaction is shown in Fig. 12.14. The energetics of this reaction at the B3LYP/6-31G* level are (my calculations, a.u. or hartrees, omitting ZPE):

[3,4]prismane	−461.55095
CH_3CH_3	−79.83042
$HCMe_3$	−158.45881
CMe_4	−197.77309

$$\begin{aligned}\Delta E_{\text{reaction}} &= E(\text{Products}) - E(\text{reactants}) = [4\,\text{CMe}_4 + 8\,\text{HCMe}_3]\\ &\quad - [[3,4]\text{prismane} + 20\,\text{CH}_3\text{CH}_3]\\ &= [4(-197.77309) + 8(-158.45881)] - [-461.55095 + 20(-79.83042)]\\ &= -2058.76284 - [-2058.15935] = -0.60349 = 1585\,\text{kJ}\,\text{mol}^{-1}.\end{aligned}$$

The reaction is calculated to be exothermic (this is a 0 K enthalpy change) by 1585 kJ mol^{-1}, which we take as the SE. At the considerably "higher" B3LYP/6-311(2df, p) level [1] the value was 1561 kJ mol^{-1} (373 kcal mol^{-1}), essentially

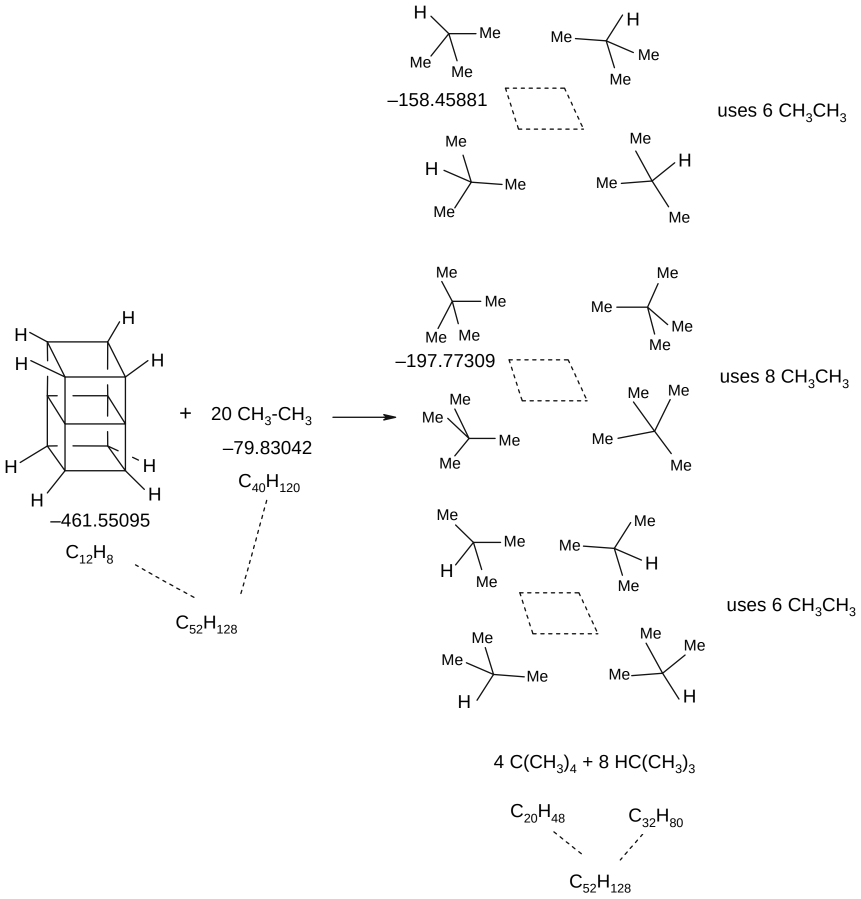


Fig. 12.14 A homodesmotic reaction on [3,4]prismane. Formally each side of the equation has the same number of each kind of bond, regarding for example an $HCMe_3$ molecule as equivalent to an HC moiety bonded to four carbons in the polyprismane (we have glossed over the fact, strictly speaking, ethane-type C–C bonds are not among the products). The reaction is calculated to be exothermic by 1585 kJ mol^{-1} at the B3LYP/6-31G* level; the deviation from zero exothermicity represents the strain in the molecule

the same as that found here. That such an arithmetically unwieldy kind of calculation, involving the subtraction of large, similar numbers,[3] should nevertheless give reasonable results [33, 34, 35], essentially unchanged with a much bigger basis set (for the prismane, 408 cf. 196 basis functions), is cogent testimony to the utility of homodesmotic reactions.

Let's compare strain in [3,4]prismane with that in the known [9] molecule cubane, [2,4]prismane. Estimating the SE of cubane by homodesmotic reactions at the B3LYP/6-31G* level, as for [3,4]prismane:

cubane	-309.46047
CH_3CH_3	-79.83042
$HCMe_3$	-158.45881
CMe_4	-197.77309

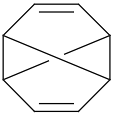
$$\Delta E_{\text{reaction}} = E(\text{products}) - E(\text{reactants}) = [8\,\text{HCMe}_3] - [\text{cubane} + 12\,\text{CH}_3\text{CH}_3]$$
$$= [8(-158.45881)] - [-309.46047 + 12(-79.83042)]$$
$$- 1267.67048 - [-1267.42551] = -0.24497 = -643\,\text{kJ}\,\text{mol}^{-1}.$$

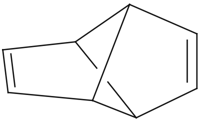
We take the SE to be 643 kJ mol^{-1}, essentially the same as the value of 657 kJ mol^{-1} (157 kcal mol^{-1}) obtained by comparing the experimental heat of combustion with that calculated with group increments [36]. This gives for cubane SE/C–C bond = 643/12 kJ mol^{-1} = 54 kJ mol^{-1}. From the total SE of 1585 kJ mol^{-1} for [3,4]prismane (above), the SE/C–C bond of this species is 1585/20 kJ mol^{-1} = 79 kJ mol^{-1}. Were no factors at work peculiar to the half-planar bonds, the SE of the prismane should be ca. $20 \times 54 = 1080$ kJ mol^{-1}. If the extra $1585 - 1080 = 505$ kJ mol^{-1} is ascribed to the eight half-planar bonds, then each such bond represents a SE of 505/8 kJ mol^{-1} = 63 kJ mol^{-1}. Note that this value was obtained using homodesmotic ring-opening, at the B3LYP/6-31G* level; now, compare this with the SE/bond of half-planar 90° CH_4, obtained by comparing that species with tetrahedral CH_4. Half-planar 90° CH_4 has a B3LYP/6-31G* SE of $-40.42471 - (-40.51839) = 0.09368 = 246$ kJ mol^{-1}, or 246/4 = 61.5 kJ mol^{-1} per bond. The excellent agreement between homodesmotic and angle-distortion calculations, 63 cf. 61.5 kJ mol^{-1}, if not somehow substantially fortuitous, indicates that half-planar CH_4 is a good model for the formally analogous carbons in polyprismanes.

Thermodynamic Stability

Strain energy (above) is an indication of thermodynamic stability, because a high value implies, tacitly at least, that the species in question can be transformed into a lower-energy product, with release of energy. We imagine (possibly hypothetical) reactions such that, overall, the bonds formed in the products are stronger than those broken in the reactants. Strain is not really a *measure* of thermodynamic stability, because by itself it does not give a value of the enthalpy or the free energy change for any particular reaction, but affords rather a feel for the energy released when the reaction *has* occurred. Whether strain energy is also relevant to kinetic stability, i.e. to the sluggishness or the alacrity with which reactions occur, depends on whether the transition state for a plausible reaction resembles the products: only then would release of strain on reaction be relevant to the *rate* of reaction. Intuitively, it is clear that to the extent that strain might affect reaction rate, it should increase it. Kinetic stability is a subtler matter than thermodynamic stability, and its quantitative evaluation requires examination of relevant transition states.

A hydrocarbon with a large strain energy will always be susceptible to *some* highly exothermic reaction (certainly combustion), but it may or may not be kinetically unstable. Consider cubane and (the known [37]) tricyclo[3.3.0.0^{2,6}]octa-3,7-diene, **35**; both are $(CH)_8$ molecules:





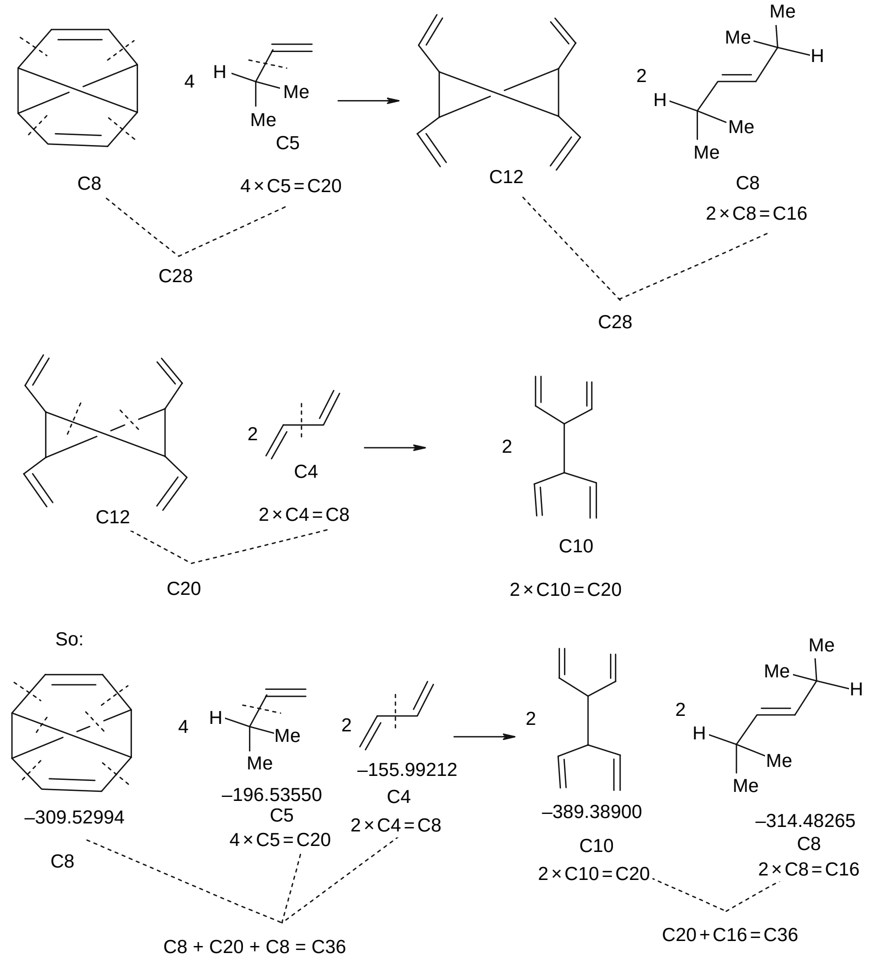
35

Using B3LYP/6-31G* homodesmotic calculations, we found above for cubane a SE of 643 kJ mol^{-1}; Fig. 12.15 shows the scheme for a homodesmotic reaction on **35**, which yields a SE of 229 kJ mol^{-1}. Here sp^2–sp^3 bonds are conserved and the substitution pattern on tetracoordinate carbons are similar; a simpler isodesmic scheme breaking tricyclooctadiene bonds with CH_3–CH_3 gave a presumably less accurate strain energy of 280 kJ mol^{-1}: exchanging sp^3–sp^2 bonds for the weaker sp^3–sp^2 leads to a more exothermic reaction and thus a bigger SE. Cubane is thus calculated to be much more strained than **35**, yet it "is extraordinarily stable, surviving essentially unchanged at temperatures up to ca. 200°C", requiring no special humoring in its synthesis and handling [9, 38]. In contrast, the less-strained **35** is quite unstable kinetically, (and of course unstable thermodynamically): in solution, NMR peaks due to **35** "*rapidly decreased in intensity* [emphasis in original] at room temperature" [37].

So what can we conclude about the stability of polyprismanes from strain calculations? We carried out the above illustrative calculations on [3,4]prismane. Here are results of the homodesmotic strain calculations of Minyaev et al. [1] at the B3LYP/6-311G(2df,p) level; [stack height, ring size], nomenclature of Fig. 12.1, SE and SE/C–C, in kJ mol^{-1}:

[2,3] 569, 63; [2,4] 632, 53; [2,5] 540, 36; [2,6] 682, 38
[3,3] 1247, 83; [3,4] 1561, 78; [3,5] 1582, 63; [3,6] 1946, 65
[4,3] 1912, 91; [4,4] 2423, 87; [4,5] 2536, 72; [4,6] 3130, 74

It appears reasonable to examine just the SE/C–C bond (since, obviously, the bigger a polymeric molecule the bigger its *total* strain energy should be) and to compare this with the SE/C–C of cubane, the canonical stable prismane, for which the SE/C–C is 53 kJ mol^{-1}. The [2,n] series are simple prismanes, rather than polyprismanes, and of the four treated above all except [2,6]prismane (hexaprismane, discussed above) are known. [2,3]Prismane (triprismane, prismane; SE/C–C 63 kJ mol^{-1}) is explosive but stable at room temperature [8]. Of the eight polyprismanes listed here, two have SE/C–C values of 63 and 65 kJ mol^{-1} ([3,5] and [3,6]) and all the others have higher values, with the [3,3], [4,3] and [4,4] being above 80 kJ mol^{-1}. This indicates that all the polyprismanes examined here would be



$$\Delta_{\text{reaction}} = [2(-389.38900) + 2(-314.48265)] - [-309.52994 + 4(-196.53550) + 2(-155.99212)]\text{a.u.}$$

$$= [-1407.74330] - [-1407.65618]\ \text{a.u.} = -0.08712\ \text{a.u} = -229\ \text{kJ mol}^{-1}$$

Fig. 12.15 A homodesmotic reaction on a $(CH)_8$ isomer of cubane, tricyclo[3.3.0.0^{2,6}]octa-3,7-diene, also $(CH)_8$. The strain energy of the tricyclooctadiene is calculated to be 229 kJ mol^{-1} at the B3LYP/6-31G* level

thermodynamically high-energy materials, which may or may not be stable at room temperature. The cyclopropane and cyclobutane species are predicted (as expected) to be most energetic, and are the most problematic with regard to kinetic stability. Noteworthy is the increase in SE/C–C with increasing stack height along any given ring size series (e.g. cyclopropane, [2,3], [3,3], [4,3]: 63, 83, 91 kJ mol^{-1}). Does this trend level off, or do higher polyprismanes suffer self-immolation under unbearable strain? Here are our SE/C–C results (kJ mol^{-1}) for B3LYP/6-31G* calculations on the cyclopropane and cyclohexane series, from stack heights of 5–7, combined with the results of Minyaev et al. (B3LYP/6-311G(2df,p) [1]) for stack heights 2–4; recall that our B3LYP/6-31G* SE/C–C for [3,4]prismane was 79 kJ mol^{-1}, compared to 78 kJ mol^{-1} reported for the B3LYP/6-311G(2df,p) level, so the two basis sets evidently give essentially the same SE/C–C:

[2,3] 63, [3,3] 83, [4,3] 91, [5,3] 96, [6,3] 98, [7,3] 100
[2,6] 38, [3,6] 65, [4,6] 74, [5,6] 79, [6,6] 82, [7,6] 84

A graphical presentation of these values, Fig. 12.16, clearly shows that the SE/C–C levels off for the cyclopropane series at about 100 kJ mol^{-1}, and for the cyclohexane series at about 85 kJ mol^{-1}.

Another factor, besides strain, that can destabilize a molecule is an unfavorable electronic interaction, for example that manifested as antiaromaticity, in, say cyclobutadiene [39], but unlike strain, electronic interactions can be favorable and stabilizing. Minyaev et al. proposed that orbital interactions between the two capping $(CH)_n$ and the adjacent C_n moieties stabilize [3 n]- and [4,n]-prismanes by σ-overlap of π-type ring orbitals, and precedent for such stabilization in simple

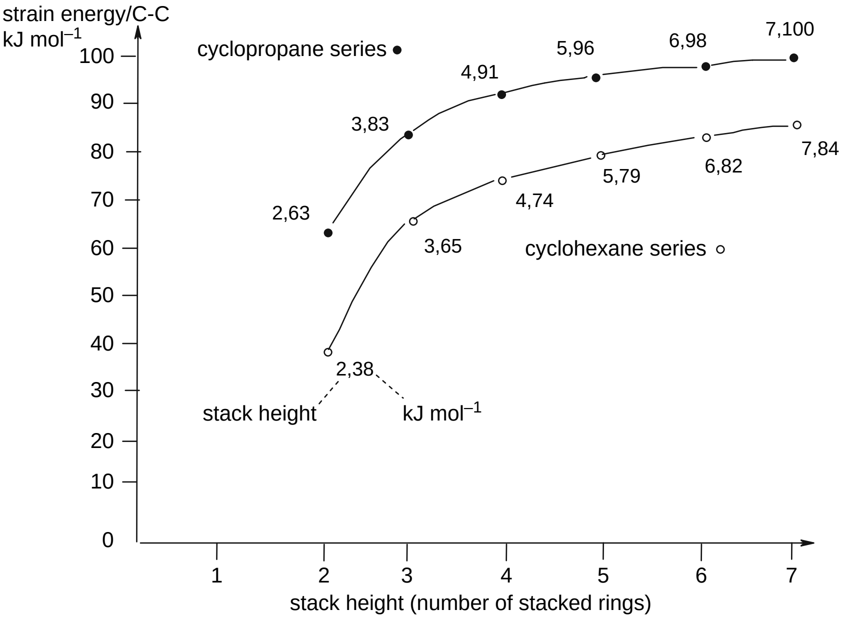


Fig. 12.16 Variation of strain energy per C–C bond with number of stacked rings, for the cyclopropane ([2,3]- to [7,3]prismane) and cyclohexane ([2,6]- to [7,6]prismane) prismane series. Calculated by homodesmotic reactions (cf. Fig. 12.14) at the B3LYP/6-311G(2df,p) (for stack heights 2–4, [1]) and B3LYP/6-31G* (for stack heights 5–7, this work) levels; the two basis sets give essentially the same SE/C–C, see text. The SE/C–C levels off for the cyclopropane series at about 100 kJ mol^{-1}, and for the cyclohexane series at about 85 kJ mol^{-1}

prismanes and other systems was cited [1]. The interactions were examined qualitatively, with the aid of extended Hückel calculations [40]. As for the case of angle strain, such interactions should affect stability in a thermodynamic sense (but stabilize rather than, like strain, destabilize). Whether they exert a kinetic influence will depend on the extent to which energy changes in the reactant are mirrored in the transition state: a reaction pathway in which stabilization of the reacting prismane is lost in the transition state experiences an increase in barrier height (relative to the corresponding reaction involving a – perhaps hypothetical – unstabilized reactant).

Some quantitative assertions about the thermodynamic stability of polyprismanes were made by comparing the energies of polyprismanes with energies of some isomeric molecules [1]. This procedure is most relevant when the comparison is with a molecule that might reasonably arise from or be converted into the one of interest, and valence tautomers are the epitome of such molecular siblings. Examples of such transformations are shown in Fig. 12.17. The "equations" are mainly to show the connection between the polyprismanes and the valence isomers, but were the latter compounds to be higher in energy than the polyprismanes, the Figure might really depict possible syntheses. Unfortunately, B3LYP/6-311G(2df,p) calculations show that the tautomers in fact lie below the corresponding polyprismanes [1]. For example, these relative energies (kJ mol^{-1}) were obtained:

[3,3] cf. **36**, 0, −55; **[3,4]** cf. **37**, **38**, **39**, 0, −34, −135, −25.

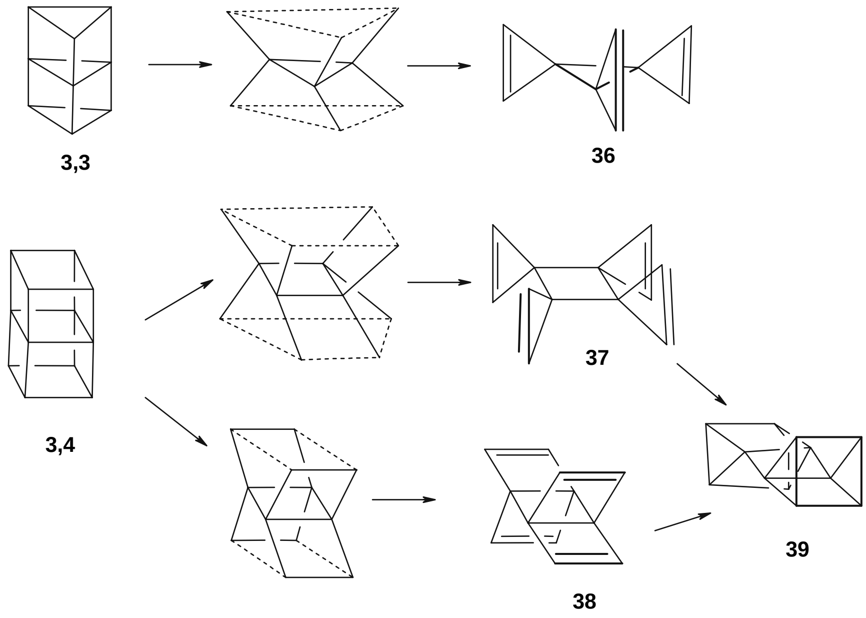
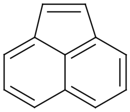


Fig. 12.17 Some valence tautomers of polyprismanes. The "intermediates" shown are mainly a correlating heuristic to make clear that only electronic reorganization and modest atomic movements connect the polyprismanes with the tautomers **36**–**39**

Somewhat surprisingly, perhaps, the [3,3]prismane is more strained than the (tris)cyclopropene **36**, and [3,4]prismane is more strained than the (tetrakis)cyclopropene **37**, the (tetrakis)cyclobutene **38**, and even the (bis)prismane **39**. The structures of these compounds and strain factors were examined in some detail [1]. If the barriers to rearrangement are not too high, it seems possible that the polyprismanes could rearrange to such cyclopropene and cyclobutene molecules (intuitively, prismane structures like **39** appear unlikely). The question of barriers to reaction is examined in the next section. These valence isomers do seem somewhat exotic, if not fanciful, and known, more prosaic isomers such as acenaphthylene (**40**) and biphenylene (**41**) were also examined, and turned out to be much lower in energy than isomeric polyprismanes (**40** and **41**, $C_{12}H_8$, are respectively 343 and 309 kJ mol^{-1} lower than [3,4]prismane at the B3LYP/6-311G(2df,p) level) [1]. Although these benzenoid molecules have, like [3,4]prismane, the $(CH)_8C_4$ motif, unlike **37**, **38** and **39** they do not share any simple topological (i.e. connectivity) kinship with the isomeric polyprismane, and it is not clear that such compounds could actually arise from it in vitro.



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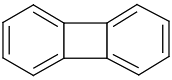
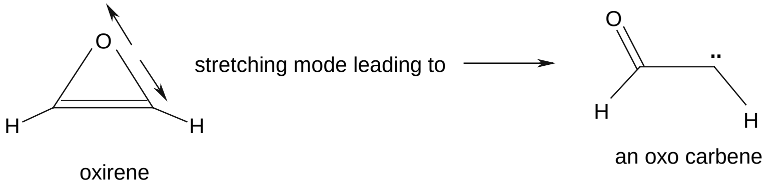


41

Kinetic Stability

The disconnection between thermodynamic and kinetic stability seen for the highly strained but conventionally “stable” cubane, in contrast to the less-strained but very reactive (conventionally unstable) tricyclooctadiene $(CH)_8$ isomer **35** (above), shows that there is no necessary connection between the two kinds of stability. Thermodynamic stability is an important guide to what a molecule may ultimately do; kinetic stability tells us how long it will take to do it. An extreme case of the antithesis between the two criteria of stability is provided by diamond and graphite! Thermodynamic stability is, as we saw, easy to calculate reliably, but cannot be used to confidently predict kinetic stability. Yet this latter is important because a thermodynamically unstable compound may, like cubane, be quite robust from the viewpoint of synthesis and handling. Minyaev et al. [1] did not directly calculate kinetic stabilities for polyprismanes; this difficult task would have required identifying likely reaction pathways, locating transition states, and calculating activation energies. An alternative procedure that is sometimes presented as a simple way to obtain an indication of the kinetic stability of a molecule is to calculate its vibrational frequencies. A very low-frequency mode corresponding to a possible reaction pathway indicates that the molecule will be kinetically unstable. This assertion can be justified by considering the fact that a stationary point on a potential energy surface (PES) that has *no* kinetic stability must be a transition state or a higher-order saddle point, and therefore will have one or more imaginary frequencies, corresponding to negative curvature along some reaction mode [20]. If we imagine these destabilizing curvatures becoming less negative, the PES along these directions flattens out, then it becomes barely positively curved just as a barrier to these modes arises. Since an imaginary vibration corresponds to negative curvature of the PES and thus a negative force constant, these changes correspond to a transition from negative to barely positive force constants, i.e. from imaginary to barely real frequencies. Continued stabilization (a higher barrier) along any reaction mode is reflected in a more positive force constant, i.e. a larger vibrational mode. A good example of the use of low-frequency vibrations as a guide to kinetic stability is provided by oxirene (Chapter 3). At most computational levels the lowest-frequency normal mode of this molecule corresponds to ring-opening to form an oxo carbene (ketocarbene) and is real, but as the computational level is raised this mode becomes smaller, corresponding to a decreasing force constant. This leaves open the possibility that at some very high level the frequency may become imaginary, revealing a negative force constant for this mode and thus exposing oxirene as a mere transition state [41, 42], which would be consonant with experiment.



The relatively high values of the lowest normal-mode vibrations (and of course the absence of imaginary frequencies) were taken as evidence that polyprismanes sit in “relatively deep...local minima” on the potential energy surfaces [1]. For example, these frequencies (cm^{-1}) were, for some of the polyprismanes (B3LYP/6-311G(2df,p) [1]/B3LYP/6-31G* our work):

[3,3]- (241/243), [4,3]- (133/133)
[3,4]- (337/339), [4,4]- (191/195)
[3,5]- (385/389), [4,5]- (245/247)
[3,6]- (394/400), [4,6]- (270/271)

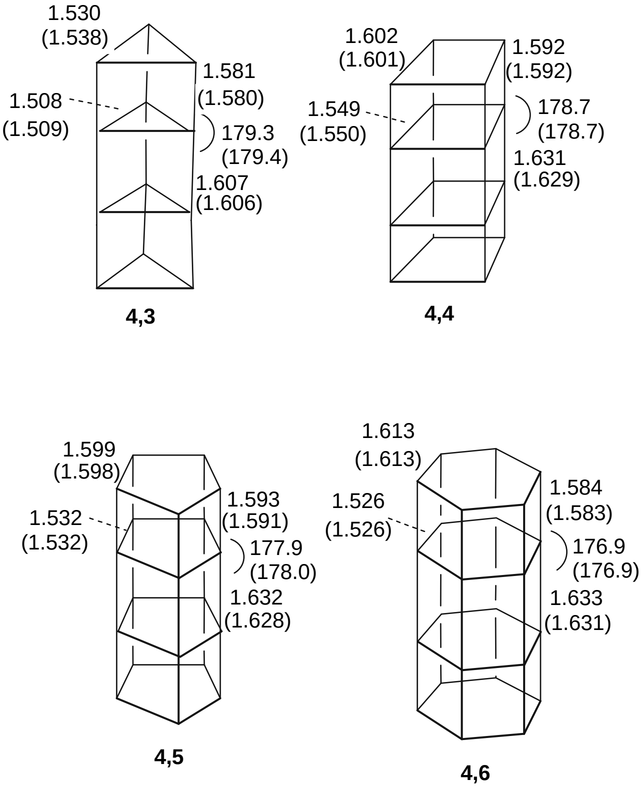
Note that the B3LYP/6-31G* frequencies are essentially identical to the B3LYP/6-311G(2df,p) ones. For all these molecules except [3,6]prismane, these lowest-frequency vibrations correspond to bending of the stack; for [3,6]prismane they correspond to a breathing motion of the “tube”, and the next two higher modes (410 and 410 cm^{-1}; like all the bending modes these too are twofold degenerate) are for bending. The bending motions do not obviously correspond to any reaction (in contrast to the case of oxirene), but carried to an extreme they could conceivably break the stack. One sees that in this set of molecules, for a given stack height the potentially disruptive frequency becomes less threatening as the ring size increases from three to six (from [3,3] to [3,6], 241–394 cm^{-1}, from [4,3] to [4,6], 133–270 cm^{-1}) and for a given ring size, as the height decreases from four to three (e.g. from [4,3] to [3,3] from 133–241 cm^{-1}). These suggested stability trends are intuitively reasonable: from organic chemical experience, one expects reactivity to be at a maximum for the cyclopropane series and a minimum for the cyclopentane or cyclohexane series, and it is plausible that for a given ring size shorter stacks would be stabler than taller ones.

How good a surrogate for actual calculation of barrier heights are the lowest vibrational frequencies? Here are the lowest B3LYP/6-31G* frequencies (cm^{-1}) for hexaprismane ([2,3]prismane, prismane, **2,3**), cubane ([2,4]prismane, **2,4**), and the tricyclooctadiene **35**:

hexaprismane
651, twisting movement (rotation of top ring with respect to bottom ring).
cubane
627, 627, twisting movement (rotation of top ring with respect to bottom ring).
tricyclooctadiene
354, 354, up-down movement of one cyclopentene snout (see **35**) with respect to the other.

Hexaprismane is far less stable kinetically than cubane, yet both molecules have low-frequency vibrations with similar values. On the other hand, for the tricyclooctadiene, which is much less stable than its isomer cubane, the low-frequency vibrations are significantly lower than for cubane. This (and other cases) shows that inspection of the lowest vibrational frequencies is a guide to kinetic stability that must be treated with caution. Oxirene (above) is a special case (still unresolved), because the lowest vibration corresponds clearly to ring-opening, it falls reasonably monotonically and fairly quickly with increasing computational level, and at all the DFT levels tried it is imaginary [41, 42]. One must conclude that the frequency calculations for these polyprismanes do not tell us how reactive (kinetically) they will be, although they do strongly indicate, indeed almost prove, that they should be isolable compounds.

Another calculable and experimentally observable property of molecules that might have been expected to serve as a predictor of kinetic instability is bond length. The typical C–C bond length between tetracoordinate carbons is about 1.54 Å [43] and the B3LYP/6-31G* calculated C–C interstack length in [2,3]prismane (which has no half-planar atoms) is 1.558 Å. The half-planar/half-planar C–C bonds of [4,n]prismanes were calculated to be 1.61–1.63 Å (Fig. 12.18) [1], i.e. ca. 1.62 Å, which is 4–5% longer than normal, so these bonds could be considered slightly abnormally long. A good, simple correlation between bond length and bond strength (bond dissociation energy, BDE) has been found for the gamut of single, double and highly strained CC bonds:



4,3 **4,4** **4,5** **4,6**

Fig. 12.18 C–C bond lengths and angles of some [4,n]prismanes, calculated at the B3LYP/6-311G(d,p) [1] and (in parentheses, this work) the B3LYP/6-31G* levels

$$r = 1.748 - 0.002371(\text{BDE}),$$

where r is in Å and BDE is in kcal mol^{-1} [43]. Inserting a bond length of 1.62 Å into this equation yields a BDE of 54 kcal mol^{-1} or 226 kJ mol^{-1}. The typical tetracoordinate carbon C–C bond has a BDE of ca. 88 kcal mol^{-1} or 368 kJ mol^{-1}, so the exotic bonds of the polyprismanes seem to be about 60% as strong as "normal". The longest possible C–C bond is calculated from the above equation to be 1.748 Å, when the BDE becomes zero (the longest known conventional C–C bond seems to be 1.724 Å [44]), so these polyprismane bonds are only ca. 100(1.62−1.54)/(1.748−1.54) = 38% along the way toward zero bonding; alternatively they could be said to be about 60% normal in length. A correlation between CC stretch in the IR spectrum and BDE was also found for *uncoupled* CC stretching vibrations (frequency(cm^{-1}) = 171.9(BDE) − 632 [43]), but this is not rigorously applicable here as truly uncoupled CC stretch was not seen in the animated calculated B3LYP/6-31G* spectra. Our calculations on 95° half-planar CH_4 (Fig. 12.11

and accompanying discussion) gave an axial bond that was *shorter* than the equatorial, in contrast to the situation for the polyprismanes in Fig. 12.18. The cause of the somewhat anomalously long and, evidently, weak axial half-planar/half-planar C–C bonds may not lie in some exotic electronic phenomenon, but rather could be simply that closer proximity of adjacent rings would lead to excessive geminal ring-ring type steric repulsion, analogous to the H–C–H and C–C–C repulsion proposed by Gronert for the weakening of C–H and C–C bonds, for which the standard explanation has been hyperconjugation [45].

The presence of long, and therefore weak, bonds suggests that polyprismanes would be more prone to radical-type reactions, like polymerization and dioxygen-induced reactions (autooxidation) than are normal alkanes. Incidentally, the converse is not true: low kinetic stability is by no means always a reflection of the presence of weak bonds. A facile reaction mode may have nothing to do with bond strength. For example, cyclobutadiene is extremely reactive, undergoing a Diels-Alder dimerization in the absence of another options [39], which may be associated with a small HOMO–LUMO gap [46]. The single and double bonds of cyclobutadiene are calculated to be of essentially unexceptional length, 1.578 Å and 1.335 Å (B3LYP/6-31G*). The unknown tetrahedrane is a more apposite reference compound, because its expected reactivity may be associated with homolytic C–C cleavage (Chapter 6). Nevertheless, its C–C bonds are calculated (B3LYP/6-31G*) to be 1.479 Å, somewhat *shorter* than “normal” (ca. 1.54 Å). Interestingly too, the five lowest low-frequency modes of tetrahedrane are calculated (B3LYP/6-31G*) to correspond to C–H bending, and only with the sixth and seventh (862 cm^{-1}, degenerate) is a potentially disruptive C–C stretching mode reached. In a nutshell, however, the long, somewhat weak bonds of polyprismanes does not portend well for their being stable materials; this is especially true of those with three- and four-membered rings.

Two Simple Reactions: Attack by a Hydride Ion and by a Proton

Minyaev et al. examined the products of nucleophilic and electrophilic attack on [3,3]prismane, using hydride ion and a proton [1]. The results for their work with hydride and our results with proton attack are shown in Fig. 12.19. The “outer” (CH) and “central” (quaternary, half-planar) carbons of [3,3]prismane had Mulliken charges of -0.15 and 0.11, respectively; attack of hydride ion on the central carbon was computed to give an anion **41a** which undergoes degenerate bond-switching through a transition state **41b–41c**, with a barrier of 115 kJ mol^{-1} (27.4 kcal mol^{-1}) [1]. Attack of a proton on [3,3]prismane seems more likely than hydride attack, since hydrocarbon chemistry, at least for more prosaic alkanes, is replete with acid-initiated reactions [47], so we investigated in some detail proton addition to this prismane. At the B3LYP/6-31G* level four cations with only limited deviation (other $(\mathrm{CH})_7\mathrm{C}_2$ cations are possible) from the [3,3]prismane structure were found, **42**, **43**, **44**, and **45**, in order of increasing energy. The energies shown in Fig. 12.19 are without ZPE, but this is essentially the same, 332 ± 2 kJ mol^{-1}, for all four cations. These are all relative minima on the potential energy surface (all

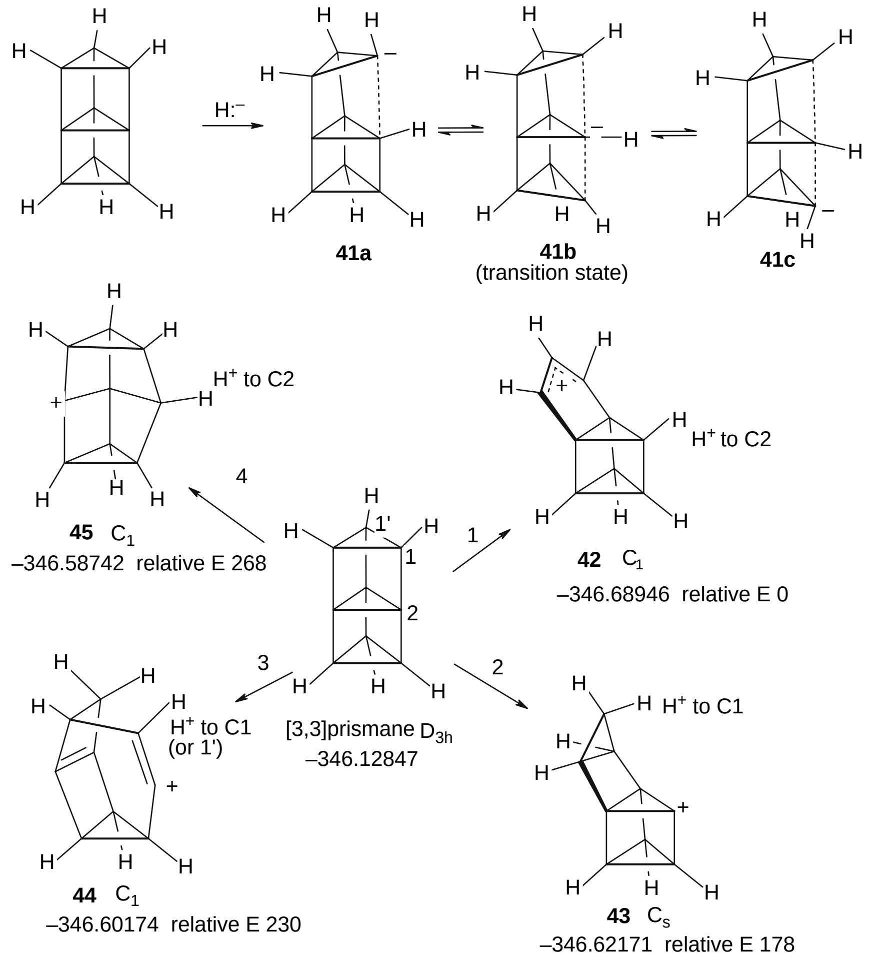
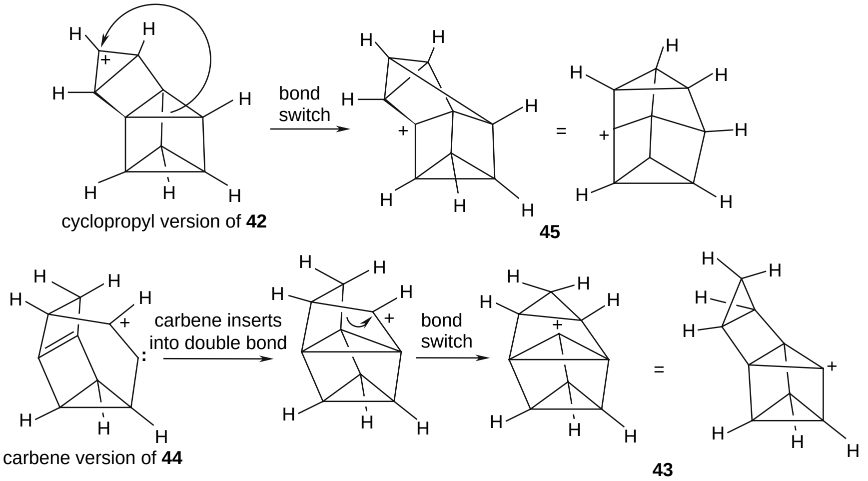
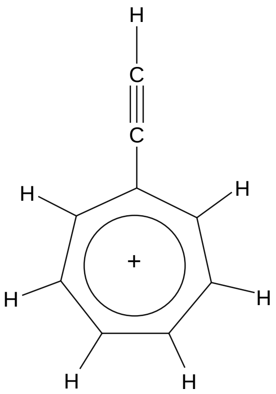


Fig. 12.19 Computed results for attack on [3,3]prismane of a hydride ion and a proton. Hydride ion attack gives **41a** which interconverts with **41c** through transition state **41b** [1]. Proton attack was found (this work) to give four possible carbocations, **42**, **43**, **44**, and **45** (increasing energy), for which the symmetries and the B3LYP/6-31G* energies (not corrected for ZPE, which for all is 332±2 kJ mol^{-1}) are shown. Lewis structures were drawn from computed geometries to show the most reasonable bonding based on bond lengths. Relative energies are in kJ mol^{-1}

vibrational frequencies are real). Cations **42** and **45** both result from protonation on the central carbon but have different structures, **42** being formally convertible to **45** by closing the allyl cation to a cyclopropyl cation and switching a C–C bond (below). Cations **43** and **44** result from protonation on the outer carbon, but have different structures; **44** can be formally converted to **43** by imagining a carbene contributor to the vinyl cation inserting into the distal cyclobutene double bond to create a cyclopropylmethyl cation which switches a C–C bond to form **43**:



The actual pathways (intermediates and activation energies) by which these cations may interconvert was not investigated. Minkin et al. compared cations **43** and **45** which they designated **15a** and **15b**, respectively, and represented slightly differently, omitting long C–C bonds of ca. 1.7 Å which in our depiction complete cyclopropane rings [1]. They found **45** to lie 92 kJ mol^{-1} (22 kcal mol^{-1}) above **43** at the B3LYP/6-311G(d,p) level; at our B3LYP/6-31G* level the difference is 268−178 kJ mol^{-1} = 90 kJ mol^{-1}. Note that our allylic cation **42** is calculated to be by far the stablest of these four cations, lying 178 kJ mol^{-1} below **43**. As hinted above, stabler isomeric cations are possible, for example, the aromatic ethynylcycloheptatrienyl cation,[4] **46**, which is not just C_9H_7 but like **42** $(CH)_7C_2$, is calculated (B3LYP/6-31G*) to lie ca. 382 kJ mol^{-1} below **42**. It is not clear how **42** might rearrange to **46**, but this suggests the possibility that [3,3]prismane might react with acid to form **46**.



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To compare the basicities of polyprismanes with those of other molecules we can use the simple energy difference $E(\mathrm{M}) - E(\mathrm{MH}^+)$. The zero-point energies were taken into account, although these are only marginally significant here, the ZPE of MH^+ being generally about 35–40 kJ mol^{-1} greater than that of M. Thermal corrections to the 0 K energies were ignored as was done by, e.g. Chamorro et al. (who also ignored ZPE) [48]). This gives a gas-phase *proton affinity* (PA) scale at 0 K, where PA is defined as the negative of the enthalpy change for the reaction

$$\mathrm{M} + \mathrm{H}^+ \rightarrow \mathrm{MH}^+, \ \mathrm{PA} = -\Delta H^\circ$$

(to calculate the room temperature, 298 K, proton affinity, the enthalpy of the proton, 5/2RT = 6.20 kJ mol^{-1}, should be taken into account for strict thermodynamic propriety [49].) The results of some B3LYP/6-31G* calculations are shown in Fig. 12.20 and Table 12.5. [3,3]prismane and indeed "ordinary" prismane ([2,3]prismane, hexaprismane) would seem to be rather basic for neutral hydrocarbons (PA 1437 and 1172 kJ mol^{-1}, respectively), comparing them with methane, ethene, and cyclopropane, which have calculated PAs of 525, 690, and 814 kJ mol^{-1},

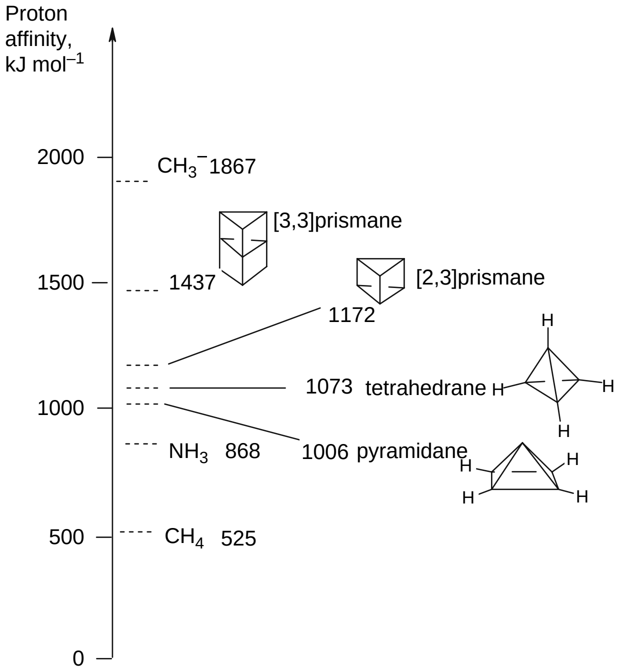
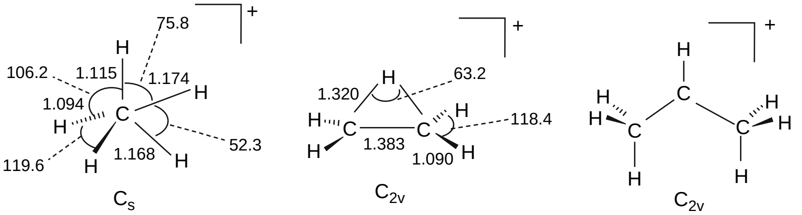


Fig. 12.20 Calculated (B3LYP/6-31G*) basicities (as 0 K gas-phase proton affinities) of some molecules. For reference points, methane is an extremely weak base and the methyl anion is extremely strong, while ammonia is moderately strong. Cf. the proton affinities in Chapter 2, Fig. 2.7

Table 12.5 B3LYP/6-31G* results for basicities (gas phase 0 K proton affinities, PA) of some molecules (see Fig. 12.20)

Molecule	"Raw" energy, ZPE; corrected energy	PA (hartrees, kJ mol^{-1})
CH_3^-	−39.79026, 0.02789; −39.76237	0.71078
CH_4	−40.51843, 0.04528; −40.47315	1867
[3,3]	−346.12888, 0.11276; −346.01612	0.54725
$[3,3]H^+$	−346.68946, 0.12609; −346.56337	1437
[2,3]	−232.05570, 0.09773; −231.95797	0.44624
$[2,3]H^+$	−232.51515, 0.11094; −232.40421	1172
tetrahedrane, C_4H_4	−154.63679, 0.05994; −154.57685	0.40858
tetrahedraneH^+, $C_4H_5^+$	−155.06088, 0.07545; −154.98543	1073
pyramidane, C_5H_4	−192.73009, 0.06706; −192.66303	0.38315
pyramidaneH+, $C_5H_5^+$	−193.12668, 0.08050; −193.04618	1006
NH_3	−56.54791, 0.03450; −56.51341	0.33063
NH_4^+	−56.89393, 0.04989; −56.84404	868
CH_4	−40.51843, 0.04528; −40.47315	0.19992
CH_5^+	−40.72350, 0.05043; −40.67307	525

respectively, using as the protonated structures for these latter three the B3LYP/6-31 G* relative minima shown here [50, 51, 52]. The cations from methane and ethene have nonclassical structures while protonated cyclopropane is taken here as the secondary cation formed by proton migration in an unstable or incipient primary cation.

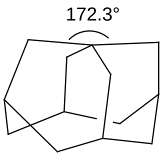


from methane,	from ethene,	from cyclopropane,
ZPE-corrected E –40.67307	ZPE-corrected E –78.79911	ZPE-corrected E –118.12329
methane,	ethene,	cyclopropane,
ZPE-corrected E –40.47315	ZPE-corrected E –78.53625	ZPE-corrected E = –117.81345
PA = 0.19992 h = 525 kJ mol^{-1}	PA = 0.26286 h = 690 kJ mol^{-1}	PA = 0.30984 h = 814 kJ mol^{-1}

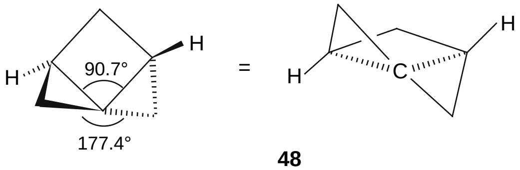
We should however be cautious about comparing the basicities of these various molecules, as the proton affinities do not all reflect the same thing. Species like the methyl anion, ammonia, and, apparently (the still unknown, Chapter 2) pyramidane and other "hemispiro" type molecules [53] are protonated and deprotonated simply by clicking or unclicking a proton on to a lone electron pair, ethene uses a highest-occupied π-electron "lone" pair, and even the unconventional base methane can be viewed as using a σ-bonding pair in a similar way in lieu of a lone pair. In all these protonations, except perhaps for methane, there is but little structural rearrangement of the base. The prismanes and tetrahedrane, in contrast, react with a proton in a more deep-seated way, by breaking a C–C bond to form a cation with a different carbon skeleton. This indicates that for the "electron-pair" bases proton affinity is a reflection of the inherent availability of an electron pair for donation to a proton, but for the "rearrangement bases" it shows the extent to which a stabler product can be formed by protonation and structural rearrangement, this latter process being a chemical reaction driven by release of strain. The basicity of tetra-*t*-butyltetrahedrane has been measured experimentally to be 1035 kJ mol^{-1} [54]; this is a Gibbs free energy change and so not exactly the same thing as the proton affinity, but it is reassuringly similar to the PA of 1073 kJ mol^{-1} calculated here for tetrahedrane. Other calculations gave tetrahedrane a PA of 1053 kJ mol^{-1} [55].

Other Candidates for Half-Planar or Linear C–C–C Carbons

The half-planar carbon geometry of the polyprismanes is characterized by an essentially linear C–C–C bond angle perpendicular to a plane with some other C–C–C angle (60° for cyclopropane, 90° for cyclobutane, etc.). Other ways of attaining a geometry with some of these features (and the planar and pyramidal arrangement) were investigated computationally by Rasmussen and Radom [53] who in their quest for planar carbon (Chapter 1) performed calculations on **47** and related molecules, in which a very roughly planar carbon caps a ring, and by Dodziuk and coworkers [56, 57, 58, 59, 60, 61, 62, 63], who examined molecules like **47** and **48**.

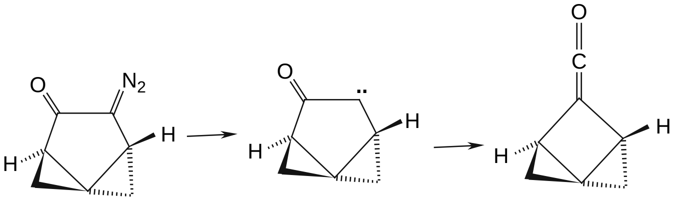


47

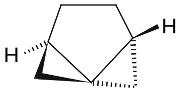


48

At the B3LYP/6-31G* level **47** ("bowlane") has a relevant C–C–C angle of 172.3°, and **48**, tricyclo[3.1.0.$0^{1,3}$]hexane, 177.4°, which is very close to being the ideal linear angle. Note, however, that **48** does not have an equatorial plane normal to the C–C–C line. Interestingly, while B3LYP/6-31G* (177.4°), MP2/6-31G* (177.6°), and AM1 (177.9°) give for **48** a C–C–C angle close to 180°, molecular mechanics (Merck Molecular Forcefield, MMFF; Sybyl) [64], often excellent for hydrocarbon structures and energies, fails here, yielding angles of only 159.7° and 159.2°, respectively. A derivative of **48** has evidently been synthesized: Wiberg and Snoonian found that UV irradiation of the diazo ketone **49** in Nujol at ca. 20 K formed, presumably by Wolff rearrangement via the carbene **50**, a compound with an IR band at 2117 cm^{-1} to which they assigned the ketene structure **51**, which contains the framework of **48** [65].

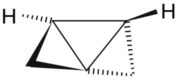


49 **50** **51**



48

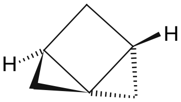
The tricyclic skeleton analogous to that of **48** but with a five- instead of a four-membered ring, tricyclo[4.1.0.01,3]heptane, **52**, is apparently much stabler than **48**, as shown by the fact that **49** and other derivatives could be handled at room temperature [65]. These authors also calculated (at the MP2/6-31G* level) strain energies and geometries of several similar tricyclic systems, including **53**, **48**, **52**, and **54**, using a group equivalents method:



53

573 kJ mol^{-1}

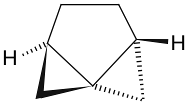
quaternary C: pyramidal



48

485 kJ mol^{-1}

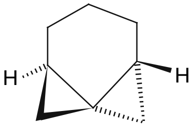
CCC ~180°



52

331 kJ mol^{-1}

CCC158°



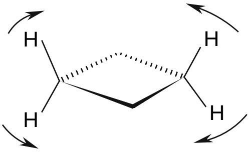
54

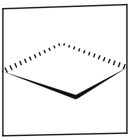
276 kJ mol^{-1}

CCC149°

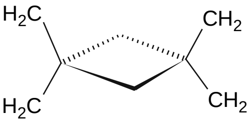
One derivative of **48** has apparently been made and several derivatives of **52** are known, as indicated above, and derivatives of **54** have also been synthesized [65]. In a study explicitly designed to investigate the variation of energy and geometry as one goes from tetrahedral toward linear carbon, the strain in **53**, **48**, and **52** was studied by Takeuchi et al. [66], using homodesmotic reactions [34, 35]; they obtained essentially the same energies as Wiberg and Snoonian.

An approach which may yield a half-planar carbon like that in a polyprismane is to bend backwards the C–H bonds of a cycloalkane; applying this to cyclobutane by using two C_2 clamps gives us **55**, tricyclo[2.2.1.1^{1,4}]octane.





55



56

Computational results on this molecule are somewhat ambiguous: at the HF/6-31G* level **55** is a genuine relative minimum (a real molecule), albeit with rather long clamping C–C bonds of 1.794 Å , an axial C–C–C angle of 175.2° (bending slightly toward the cyclobutane ring) and an equatorial C–C–C angle of 102.9°, not too different from the situation in the [n,4]prismanes, $n > 2$. However, at correlated levels **55** is a transition state or not even a stationary point: attempted B3LYP/6-31G* optimization stretches and breaks the two clamping C–C bonds, apparently giving a tetraradical **56** which is a second-order saddle point (two imaginary frequencies) at this level, and at the MP2/6-31G* level **55** is a transition state with rather long (1.850 Å) clamping bonds, whose imaginary vibration (225*i*) corresponds to contraction of one clamping C–C and breaking of the other.

Some Other Rodlike Molecules: Carbon Nanotubes, Staffanes, Ladderanes

At the start of this chapter it was stated that polyprismanes owe their interest to the electronic disposition of the half-planar carbons, and to the possible utility in materials science of properties arising from a stiff, rodlike structure.

Carbon nanotubes [2] have excited tremendous interest since they were described in 1991 [67]. This is due not so much to their theoretical interest as to their potential technological applications: a nanotube (or fullerene tubule – see [2] is a folded graphite sheet Fig. 12.21), and although some new properties, like one-dimensional conductivity, may arise in going from a two-dimensional to a one-dimensional (both geometrically idealized, of course) molecular system, the nanotube atoms remain essentially conventional sp^2-hybridized carbons. Nanotubes are made by chemical vapor deposition (CVD): carbon vapor from gas-phase decomposition of a small organic compound is deposited on a substrate, e.g. SiO_2 or Al_2O_3.

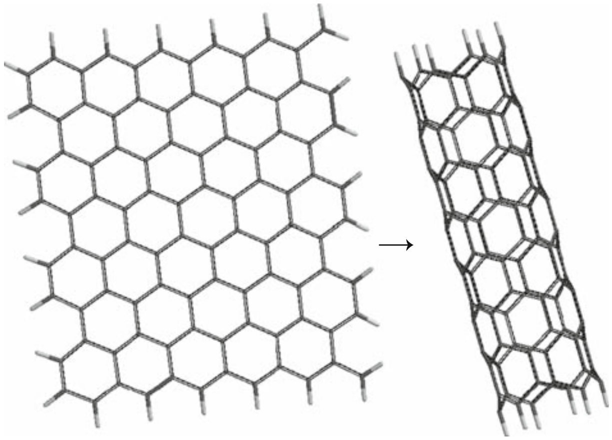


Fig. 12.21 Folding a graphite sheet and joining the free bonds (from removing appropriate hydrogens) gives a carbon nanotube or a fullerene tubule. The subtle distinction and the manner of capping the tubes is discussed in [2]

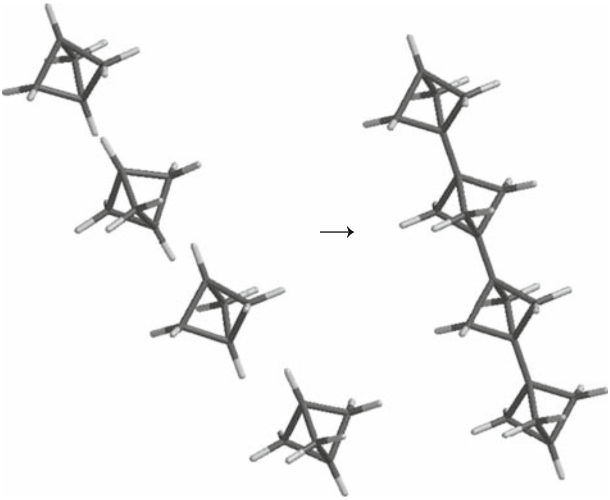
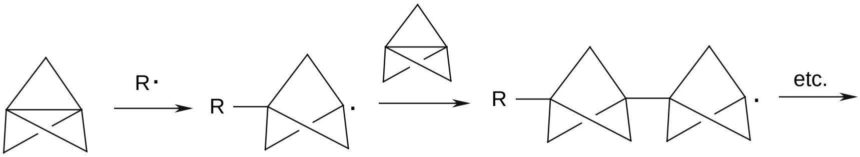


Fig. 12.22 Staffanes are conceptually formed by joining bicyclo[1.1.1]pentane units

Staffanes are based on bicyclo[1.1.1]pentane units (Fig. 12.22). They and other rodlike molecules based on linking polycyclic monomers along an axis have been reviewed [3]; staffanes are singled out here for special mention because they appear at present to be fairly readily made and to be reasonably stable. As with nanotubes, the interest in staffanes arises from their possible applications in materials science. Staffanes can be made by oligomerizing [1.1.1]propellane in a free radical reaction:



Ladderanes are molecules composed of fused cyclobutane rings (Fig. 12.23) [4]. Like nanotubes and the rodlike molecules of [3], they have been considered as possibly having electronic applications. Ladderanes have been made by oligomerization of a (transient) cyclobutadiene [68], and by solid-state photooligomerization of polyenes [4] (Fig. 12.23).

Of the rodlike molecules mentioned in this section, the closest gross structural similarity to prismanes is, clearly, shown by carbon nanotubes. This kinship is, however, not shared at the level of their carbon atoms, for nanotubes are based on the garden variety of carbon found in benzene, while polyprismanes demand an exotic half-planar species. This dichotomy is likely to be reflected in the sphere of synthesis: nanotubes are made by allowing nature to take a broad course in

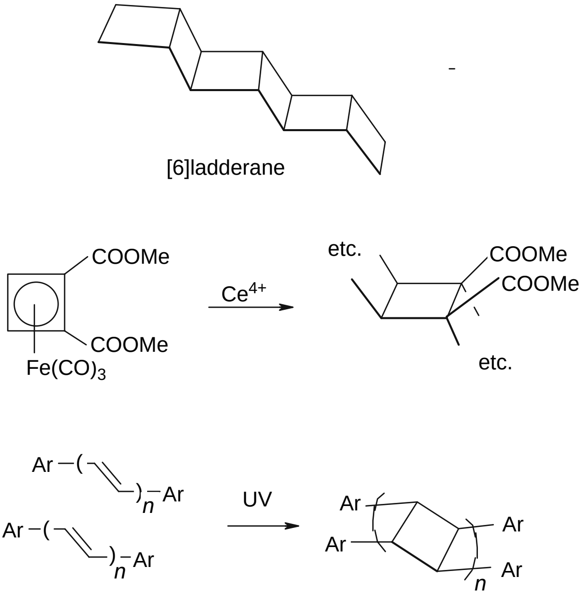


Fig. 12.23 Ladderanes are based on cyclobutane units. They have been made by oligomerization of a transient cyclobutadiene [68] and by solid-state photooligomerization of polyenes [4]

assembling carbon atoms in a vapor deposition process, while the construction of polyprismanes may very likely require micromanagement by the full synthetic powers of the organic chemist.

Polyprismanes: Synthesis

The synthesis of a polyprismane has not yet been reported, but the syntheses of the simple prismanes (*Simple Prismanes*, above) provide some clues to an approach that may work for some polyprismanes. The preparation of hexaprismane ([2,3]prismane, **2,3**), Fig. 12.3, is sui generis, but there may be some useful hints in the syntheses of cubane (**2,4**), Fig. 12.4, pentaprismane (**2,5**), Fig. 12.5, and *seco*-hexaprismane (**29**), Fig. 12.6. A somewhat conventional plan might start with a simple prismane system and attempt to attach another tier; since cubanes are readily available, let us consider such a possible route to [3,4]prismane. Figure 12.24 sketches a scheme in which the highly reactive intermediate cubene, **57** [69] undergoes a Diels-Alder addition with the dimethyl ketal of tetrachlorocyclopentadienone (**58**) to form **59**, which is deketalized to the ketone **60**. The commercially available ketal **58** is a surrogate for the highly reactive cyclopentadienone (or a chlorinated cyclopentadienone); the probability of a transient cubene molecule being intercepted by a *transient* cyclopentadienone would be very low. A Favorskii-type reaction (cf. Fig. 12.6, **26** → **27**) yields **61**, which is trimmed down to **62** (cf. **27** → **29**).

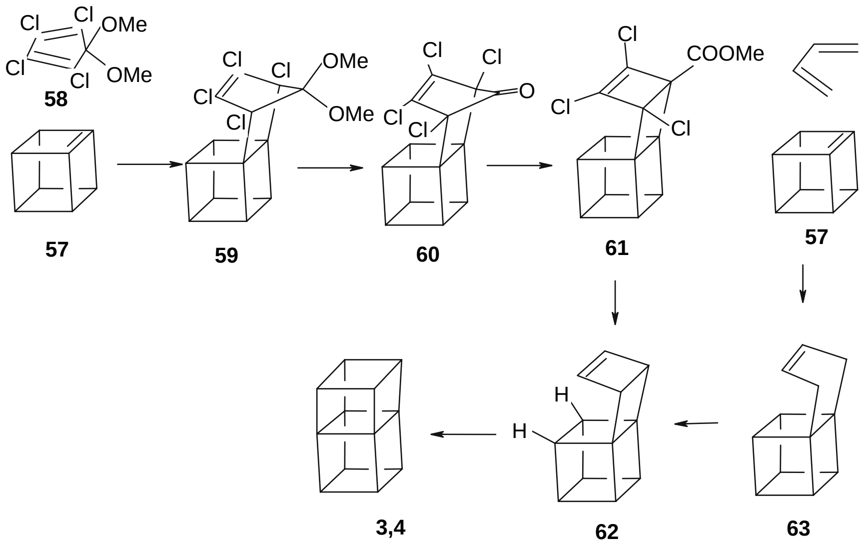


Fig. 12.24 Speculative synthesis of [3,4]prismane from cubene, **57**

An alternative putative route to **62** is from **63**, an adduct of cubene with the poorer Diels-Alder diene 1,3-butadiene. In **62**, the proximity of the double bond to the two hydrogens which must be removed for formation of two new CC bonds may enable, possibly with the aid of a transition metal reagent, closure of the cyclobutene cap onto the cubane moiety to give [3,4]prismane. One could imagine halogenating [3,4]prismane (assuming it were in hand, and stable enough to be manipulated!) and generating from it the corresponding cubene for a repetition of these reactions, but the synthesis of a [4,n]prismane by any such sequential tour de force is quite problematic. Perhaps more promising is an approach using the known **64** [70] (Fig. 12.25). Joining the two pairs of allylic carbons, which are presumably activated by the double bonds, and effecting closure (not necessarily one-step – note the failure of photoclosure of **14** to **2,6**, above) to a cyclobutane ring yields [3,4]prismane (on paper).

In contrast to piece-by-piece *consecutive* or *linear* syntheses like these, other things being equal a *convergent* synthesis, in which two at least roughly equally-sized halves of a molecule are joined, is more efficient [71]. A very speculative illustration of this is the assembling of the two cubane units of **65** to give [4,4]prismane (Fig. 12.25). Here a tetraester, in principle preparable from a tetrol and a tetracarboxylic acid, is decarboxylated, perhaps photochemically and at low temperature, to [4,4]prismane. Unfortunately, cubanes tetrafunctionalized in the pattern needed to prepare the alcohol and acid precursors of **65** appear to be unknown. The micromanagement alluded to at the end of the previous section will require synthetic chemists skilled in planning and executing a rather challenging task.

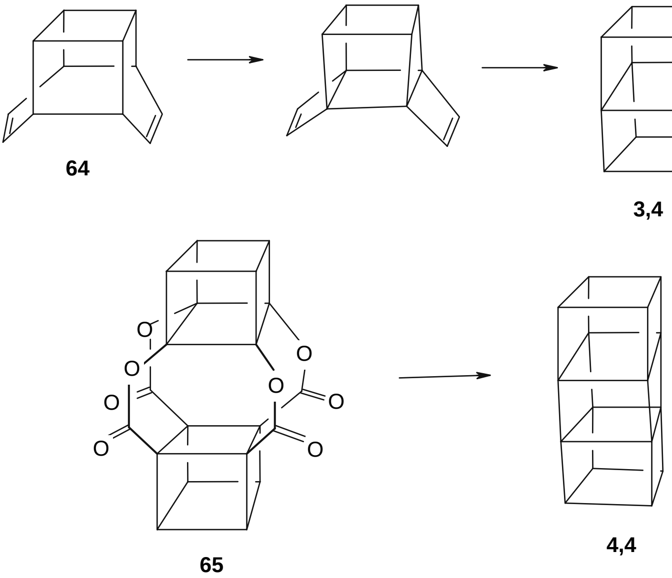


Fig. 12.25 Speculative syntheses of prismanes from the known **64** and the unknown **65**

Conclusions

Polyprismanes are interesting mainly because they embody a theoretically intriguing half-planar carbon atom. Their somewhat weak half-planar-C–C bonds are potential causes of instability, and because of logistical difficulties inherent in assembling stacked rings they pose formidable synthetic challenges.

Notes

1. The "low-level" STO-3G basis set is still used sometimes, to simplify bonding analysis, e.g. S. Inagaki, Y. Ishitani, T. Kakefu, J. Am. Chem. Soc., 1994, *116*, 5954.
2. Spartan '04, Wavefunction Inc., 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612, USA.
3. *Re* Coulson's remark on weighing the captain by weighing the ship with and without him (C. A. Coulson, "Valence", Second Ed., Oxford University Press, London 1961; p. 91): E. Lewars, "Computational Chemistry", Kluwer, Boston, 2003; p. 263.
4. Cycloheptatrienyl cations are stable aromatic species: F. Pietra, Chem. Rev., 1973, *73*, 293.

References

1. R. M. Minyaev, V. I. Minkin, T. N. Gribanova, A. G. Starikov, R. Hoffmann, J. Org. Chem., 2003, *68*, 8588.
2. P. M. Ajayan, Chem. Rev., 1999, *99*, 1787.

3. P. F. Schwab, M. D. Levin, J. Michl, Chem. Rev., 1999, *99*, 1863.
4. X. Gao, T. Friščić, L. R. MacGillivray, Angew. Chem. Int., 2004, *43*, 232, and references therein.
5. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; Chapter 4.
6. A. Ladenburg, Berichte, 1869, *2*, 140.
7. J. A. Berson, “Chemical Discovery an the Logicians’ program”, Wiley, Weinheim, New York, 2003; Chapter 4.
8. T. J. Katz, N. Acton, J. Am. Chem. Soc., 1973, *95*, 2738.
9. P. E. Eaton, T. W. Cole, J. Am. Chem. Soc., 1964, *86*, 3157.
10. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; Chapter 5.
11. P. Ball, “Elegant Solutions. Ten Beautiful Experiments in Chemistry”, Royal Society of Chemistry, Cambridge, UK, 2005; Chapter 10.
12. H. P. Schultz, J. Org. Chem., 1965, *30*, 1361.
13. P. E. Eaton, Y. S. Or, S. J. Branca, J. Am. Chem. Soc., 1981, *103*, 2134.
14. P. E. Eaton, L. Cassar, R. A. Hudson, D. R. Hwang, J. Org. Chem., 1976, *41*, 1445.
15. A. P. Marchand, T.-C. Chou, J. D. Ekstrand, D. van der Helm, J. Org. Chem., 1976, *41*, 1438.
16. E. L. Allred, B. R. Beck, Tetrahedron Lett., 1974, *5*, 437.
17. E. J. Corey, X.-M. Cheng, “The Logic of Chemical Synthesis”, Wiley, New York, 1989.
18. G. Mehta, S, Padma, Tetrahedron, 1991, *47*, 7783.
19. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; section 5.4.2.
20. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 2.
21. K. B. Wiberg, F. H. Walker, J. Am. Chem. Soc., 1982, 104, 5239.
22. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; section 6.1.
23. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 7.
24. A. E. Reed, L. A. Curtis, F. Weinhold, Chem. Rev., 1988, *88*, 899.
25. L. C. Cusachs, P. Politzer, Chem. Phys., 1968, 1, 529.
26. M. A. Natiello, J. A. Medrano, Chem. Phys., 1984, *105*, 180
27. M. A. Natiello, J. A. Medrano, Chem. Phys., 1984, *110*, 445.
28. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; p. 98.
29. M. S. Banna, D. A. Shirley, Chem. Phys. Lett., 1975, *33*, 441.
30. R. Hoffmann, R. W. Alder, C. F. Wilcox, Jr., J. Am. Chem. Soc., 1970, *92*, 4992.
31. F. A. Carey, R. J. Sundberg, “Advanced Organic Chemistry”, Fourth Ed., Kluwer, New York, 2000; section 1.2.1.
32. U. Radius, S. J. Silverio, R. Hoffmann, R. Gleiter, Organometallics, 1996, *15*, 3737.
33. W. J. Hehre, L. Radom, P. von R. Schleyer, J. A. Pople, “Ab Initio Molecular Orbital Theory”, Wiley-Interscience, New York, 1985; section 6.5.6.
34. P. George, M. Trachtman, C. W. Bock, A. M. Brett, Tetrahedron, 1976, *32*, 317.
35. P. R. Khoury, J. D. Goddard, W. Tam, Tetrahedron, 2004, 60, 8103.
36. B. D. Kybett, S Carroll, P. Natalis, D. W. Bobbell, J. L. Margrave, J. L. Franklin, J. Am. Chem. Soc., 1966, *88*, 626.
37. J. Meinwald, H. Tsuruta, J. Am. Chem. Soc., 1969, *91*, 5877.
38. G. W. Griffin, A. P. Marchand, Chem. Rev., 1989, *89*, 997.
39. G. Maier, Angew. Chem. Int. Ed. Engl., 1988, *27*, 309.
40. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; section 4.4.
41. G. Vacek, J. M. Galbraith, Y. Yamaguchi, H. F. Schaefer, R. H. Nobes, A. P. Scott, L. Radom, J. Phys. Chem., 1994, *98*, 8660.
42. G. Vacek, B. T. Colegrove, H. F. Schaefer, Chem. Phys. Lett., 1991, *177*, 468.
43. A. A. Zavitsas, J. Phys. Chem. A, 2003, *107*, 897.
44. G. Kaupp, J. Boy, Angew. Chem. Int., 1997, *36*, 48.
45. S. Gronert, J. Org. Chem., 2006, *71*, 1209.

46. N. S. Mills, A. Levy, B. F. Plummer, J. Org. Chem., 2004, 69, 6623.
47. G. A. Olah, G. K. Surya Prakesh, “Carbocation Chemistry”, Wiley-Interscience, New York, 2004.
48. E. Chamorro, C. A. Escobar, R. Sienra, P. Pérez, J. Phys. Chem. A, 2005, *109*, 10068 and references therein.
49. E. I. von Nagy-Felsobuki, K. Kimura, J. Phys. Chem., 1990, *94*, 8041.
50. X. Huang, A. B. McCoy, J. M. Bowman, L. M. Johnson, C. Savage, F. Dong, D. J. Nesbitt, Science, 2006, 311, *60*, and references therein.
51. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; p. 232.
52. M. B. Smith, J. March, “Advanced Organic Chemistry”, Fifth Ed., 2001, Wiley, New York; pp. 988–990 and references therein.
53. D. R. Rasmussen, L. Radom, Chem. Eur. J., 2000, *6*, 2470.
54. R. Notario, O. Castaño, J. L. Andrés, J. Elguero, G. Maier, C. Hermann, Chem. Eur. J., 2001, *7*, 342.
55. R. Notario, J. Elguero, J. Chem. Soc., Chem. Commun., 1995, 1543.
56. H. Dodziuk, Tetrahedron, 1988, *44*, 2951.
57. H. Dodziuk, J. Mol. Struct. (Theochem.), 1990, *239*, 167.
58. H. Dodziuk, K. S. Nowinski, J. Mol. Struct. (Theochem.), 1994, *311*, 97.
59. H. Dodziuk, J. Leszczynski, K. S. Nowinski, J. Org. Chem., 1995, *60*, 6860.
60. H. Dodziuk, J. Leszczynski, K. S. Nowinski, Theochemistry, 1997, *391*, 201.
61. H. Dodziuk, J. Leszczynski, K. Jackowski, J. Org. Chem., 1999, *64*, 6177.
62. H. Dodziuk, G. Dolgonos, J. Leszczynski, Tetrahedron, 2003, *59*, 2561.
63. H. Dodziuk, G. Dolgonos, J. Leszczynski, Tetrahedron, 2003, *59*, 10013.
64. D. Young, “Computational Chemistry. A Practical Guide from Applying Techniques to Real World Problems”, Wiley-Interscience, New York, 2001; Chapter 6.
65. K. B. Wiberg, J. R. Snoonian, J. Org. Chem., 1998, 63, 1390.
66. Takeuchi, A. Horiguchi, S. Inagaki, Tetrahedron, 2005, *61*, 2601.
67. S. Iijima, Nature, 1991, *354*, 56.
68. G. Mehta, M. B. Viswanath, A. C. Kunwar, J. Org. Chem., 1994, *59*, 6161.
69. K. Lukin, P. E. Eaton, J. Am. Chem. Soc., 1995, *117*, 7652.
70. N. C. Yang, M. C. Horner, Tetrahedron Lett., 1986, *27*, 543.
71. M. B. Smith, “Organic Synthesis”, Second Ed., McGraw-Hill, Boston, MA, 2002; p. 829.

Chapter 13
A Menagerie of Molecules from Michl and Balaji: Superstrained Molecules

Introduction

In 1988 Balaji and Michl published an analysis of a set of seven strained molecules which represent, moving along the series, a progressively greater challenge to theory and synthesis (Fig. 13.1) [1]. Using **1** (bicyclo[1.1.1]pentane) as the starting point, successive removal (conceptually!) of pairs of distally positioned hydrogens leads to **2** (tricyclo[1.1.1.0^{1,3}]pentane, [1.1.1]propellane) or **3** (tricyclo[2.1.0.0^{2,5}]pentane), then to **4** (tetracyclo[2.1.0.0^{1,3}.0^{2,4}]pentane) or **5** (tetracyclo[2.1.0.0^{1,3}.0^{2,5}]pentane, pyramidane), on to **6** (pentacyclo[2.1.0.0^{1,3}.0^{2,4}.0^{2,5}]pentane), and finally to **7** (hexacyclo[2.1.0.0^{1,3}.0^{2,4}.0^{2,5}.0^{3,5}]pentane), which has no hydrogens. We shall tend to eschew the ponderous systematic names [2][1] of these polycycles. These molecules are interesting because starting from the moderately strained **1** we soon encounter extraordinarily high levels of strain, and strain is a phenomenon that has long fascinated chemists [3, 4].[2] Furthermore, at least some of these structures embody intriguing bonding phenomena, and might even be justly described by an experienced organic chemist as being (no reproach intended) bizarre. We shall examine **1**–**7**, concentrating on the still-unknown **4**, **5**, **6**, and **7**.

We shall first examine the synthesis and properties of the known **1**, **2**, and **3** then move on to more speculative ground by evaluating the theoretical verdict on **4**, **5**, **6**, and **7**. Molecules **1**–**7** will be combined in a comparative survey of some salient characteristics, such a geometry, strain, spectroscopic properties, and finally (for **4**–**7**) possible synthetic routes will be suggested.

Molecules 1, 2, and 3 (Known Species)

Molecule ***1****, C_5H_8* The conceptual construction of the series **1**–**7** begins with a look at the known **1**, bicyclo[1.1.1]pentane (Fig. 13.1). This is now a well-known compound, with ca. 150 references in *Chemical Abstracts* as of early 2007. The first preparation was reported in 1964 by Wiberg and Conner [5, 6], who made it in low yield by reducing 1-bromo-3-bromomethylcyclobutane with metals or sodium naphthalenide; electrochemical reduction proved better although the yield was still

E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_13,

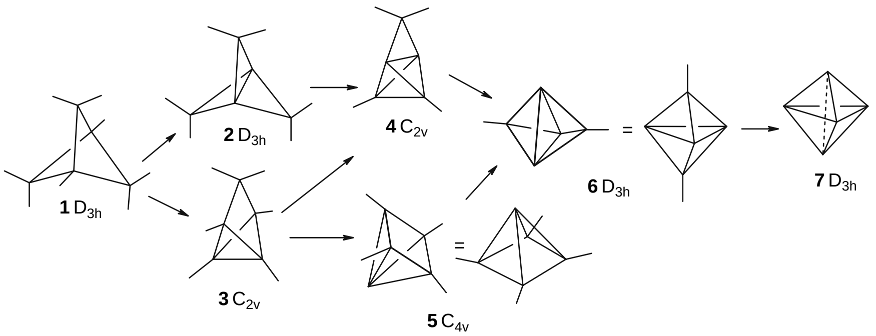
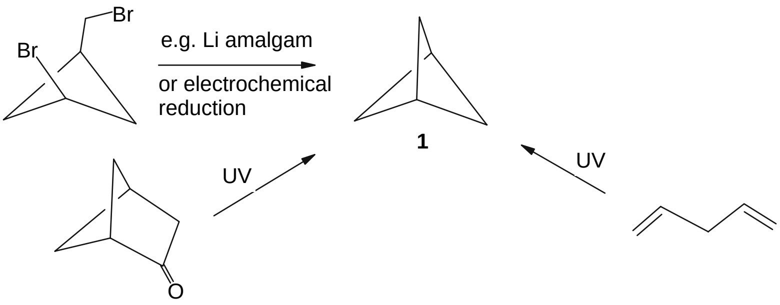


Fig. 13.1 Seven strained C_5 molecules. Starting with **1** (C_5H_8), pairs of hydrogen atoms are successively removed to create a new bond (the location and orientation of C–H bonds is shown for clarity).The process ends with **7** (C_5), in which the removal of the last pair of hydrogens has created a long (formal?) bond. The structures are drawn from MP2/6-31G* geometries

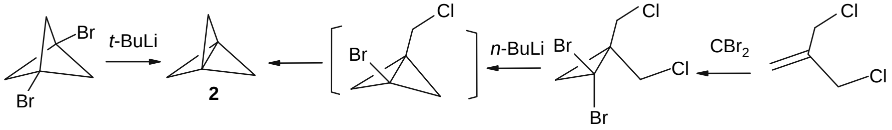
low [7].[3] It can also be made by photolysis of bicyclo[2.1.1]hexane-2-one [8] and by photolysis of 1,4-pentadiene [9].



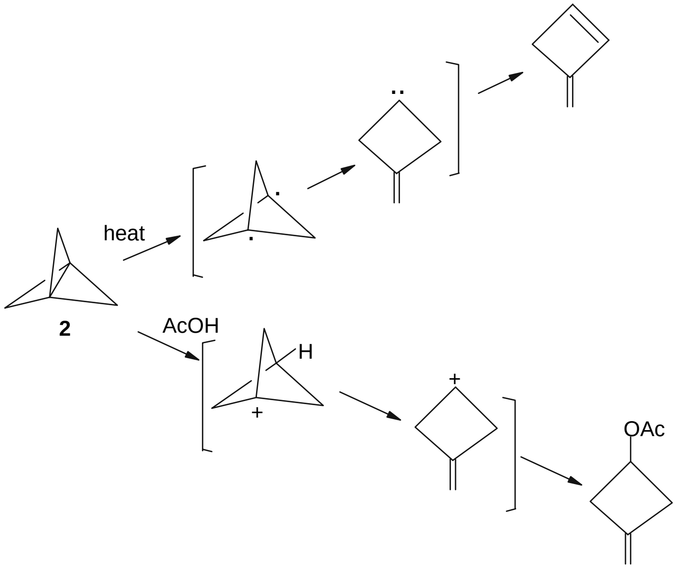
These and many other syntheses of the parent and derivatives have been reviewed [10]. The best route to **1** is perhaps reduction of the readily-available[1.1.1] propellane **2** (below) [11]. Bicyclo[1.1.1]pentane, a liquid with an estimated boiling point of 36°C, is very stable thermally: heating it at 305°C for 9 hours gave a 1:1 mixture of the starting compound and 1,4-pentadiene [5, 6].

Molecule ***2****,* *C_5H_6* The next molecule in the (conceptual!) hydrogen-removal series, **2**, tricyclo[1.1.1.$0^{1,3}$]pentane, is almost always known as [1.1.1]propellane (Fig. 13.1). It too also represents a well-known compound, with ca. 180 references in *Chemical Abstracts* as of early 2007. Let us note at the outset that its two bridgehead atoms are tetracoordinate carbons with a highly unorthodox umbrella (Chapter 12, Figs. 12.7 and 12.8) disposition of their bonds. The first preparation was reported in 1982 by Wiberg and Walker [12], who made it by debromination of 1,3-dibromobicyclo[1.1.1]pentane with *t*-butyllithium. A subsequent, more practical synthesis, by Szeimeis and coworkers [13] from the commercial compound

3-chloro-2-chloromethyl-1-propene made [1.1.1]propellane readily available; in fact, it is now a viable precursor to the more prosaic bicyclopentane system **1** [10, 11, 14,15]:



This propellane **2** was so stable that it could be handled at room temperature and purified by gas chromatography at 50°C; the half-life at 114°C was ca. 5 minutes, whereupon it rearranged to methylenecyclobutene, and the compound was sensitive to acids [12]. Clearly the central bond is the reactive site, and possible reaction paths are indicated here.



In contrast to the lowest propellane **2**, [2.2.2]propellane has a half-life at 20°C of only an hour [16], and [4.1.1]- [17], [3.1.1]- [18, 19] and [2.1.1]-propellane [20] polymerize rapidly. This stability of **2** is astonishing in view of its pair of inverted carbons, and its robustness compared to other small-ring propellanes is quite counterintuitive. Indeed, prior to its synthesis some organic chemists with sound credentials viewed it, as a synthetic target, with skepticism [21, 22].[4] Wiberg and Walker however, evidently anticipated this anomalous stability with a series of calculations on small-ring propellanes [12]. They found that the energy needed to homolytically open the reactive propellane central bond *increased* in the order [2.2.1]-, [2.1.1]-, [1.1.1]propellane: quite surprisingly, [1.1.1]propellane is predicted to be most resistant to the thermal reaction-initiating diradical formation. Since the

[2.2.1]- and [2.1.1]-propellanes were known, this boded well for the synthesis of the [1.1.1] compound, and as shown above debromination of a dibromo bicyclic precursor achieved the anticipated result. The computational method of used by Wiberg and Walker to estimate the stabilities of the three propellanes is delineated in Fig. 13.2 for [1.1.1] propellane. It avoids direct calculation of the energy of the diradical **8**, which can be an involved process as this is not a closed-shell molecule.[5] The calculation invokes the bridgehead C–H bond energy, which is taken here as in [12] to be that of the methane C–H [23]; should this be a poor choice, the trend found for the series should still be correct. The calculated energies for breaking the central bond of these three propellanes, along with various energy values, are summarized in Table 13.1. In our calculations on molecules in the series **1**–**7** we

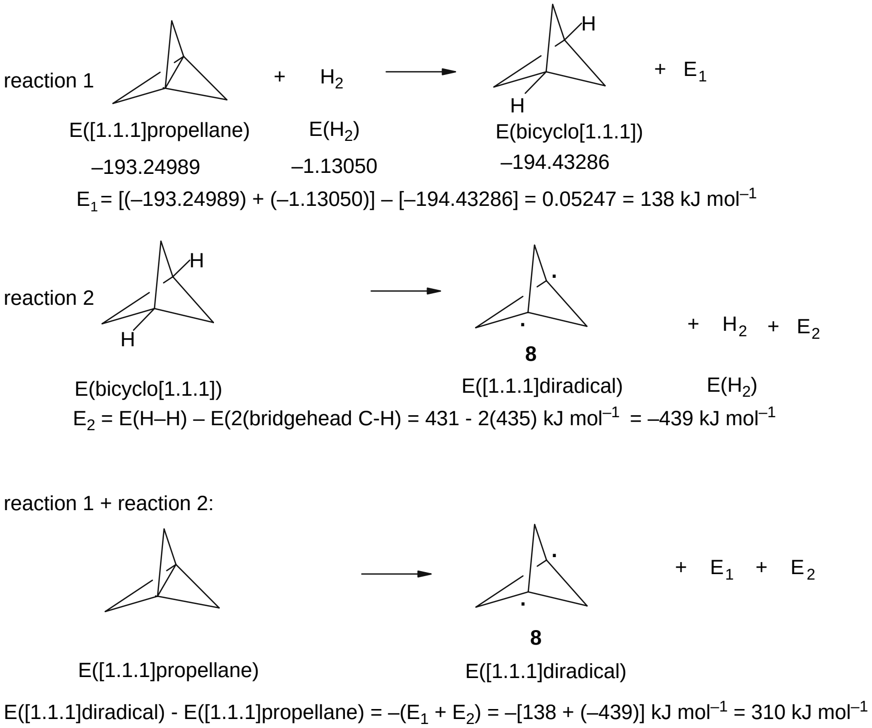


Fig. 13.2 Estimation of the enthalpy required to convert [1.1.1]propellane into the bridgehead diradical (the endothermicity of central C–C bond cleavage), using the method of Wiberg and Walker [12]. The calculation avoids direct calculation of the enthalpy of the diradical **8**, which is not routine (see text). The energies used here are 298 K enthalpies at the MP2/6-31G* level; the Wiberg-Walker calculations used HF/6-31G* 298 K enthalpies, and their reported propellane-to-diradical energy was ~272 kJ mol^{-1} (~65 kcal mol^{-1}), cf. 310 kJ mol^{-1} above. As in [12] the bridgehead C–H bond energy was taken to be that of methane, 435 kJ mol^{-1}. The C–H and H–H bond energies (431 kJ mol^{-1}) are standard values [23] (the H–H energy need not have been explicitly used, as it cancels in adding reactions 1 and 2). The reaction enthalpies for [1.1.1]-, [2.1.1]-, and [2.2.1]propellane are summarized in Table 13.1

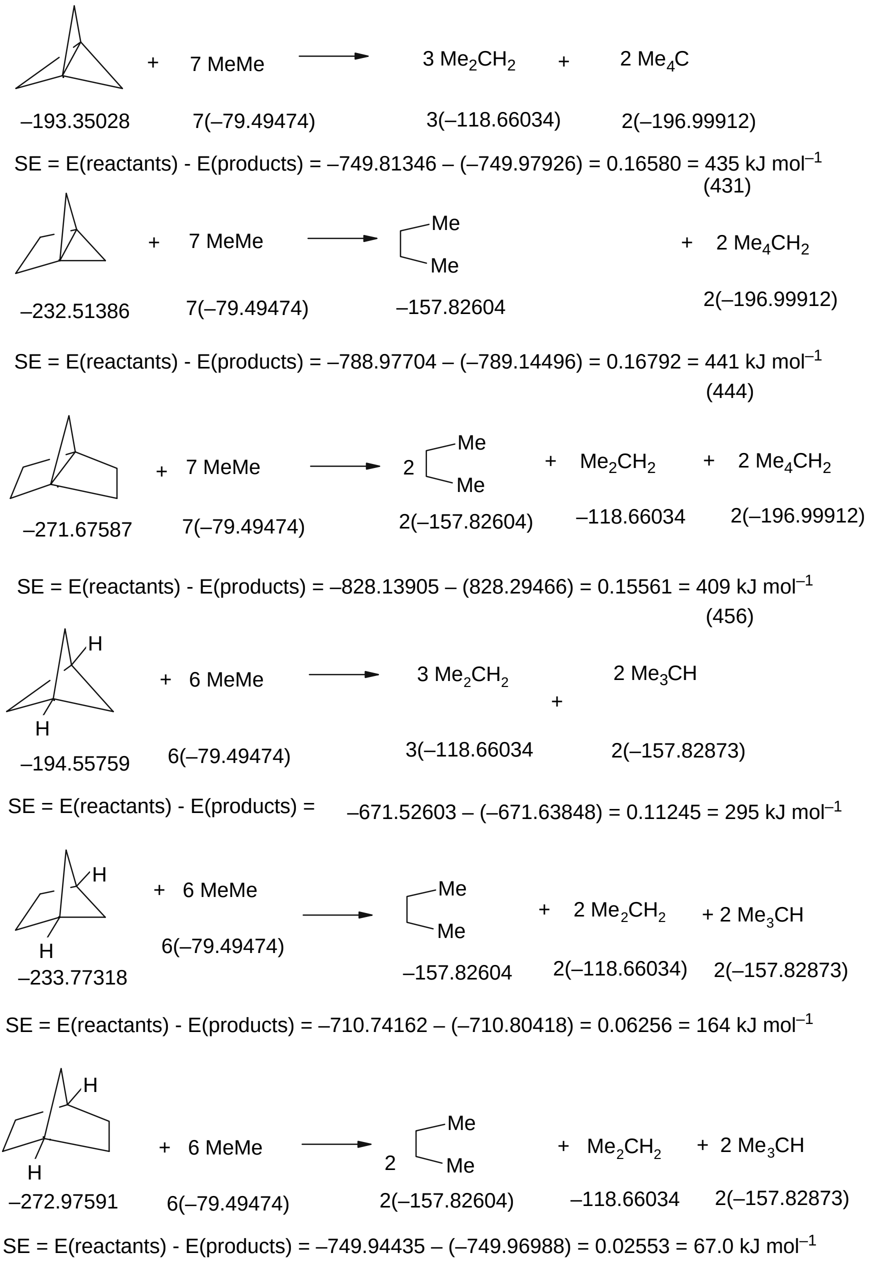


Fig. 13.3 Strain energies (SE) of propellanes from homodesmotic reactions [26, 27, 28] at the MP2/6-31G* level, without ZPE. The three SEs in parentheses are from [29]. Quantities are atomic units (hartrees) and kJ mol^{-1}

Table 13.1 Enthalpy of cleavage at 298 K of the central C–C bond of propellanes to give a singlet diradical (i.e. the endothermicity of cleavage of the central C–C bond), data and results. The calculations are at the MP2/6-31G* level, and were carried out as shown for [1.1.1]propellane in Fig. 13.2. Quantities are in atomic units (hartrees) and (298 K cleavage ΔH) kJ mol^{-1}; values in parentheses are from HF'6-31G* calculations by Wiberg and Walker [12]. The 0 K energies shown exclude ZPE. The central C–C bond of [1.1.1]propellane is calculated to be the strongest, requiring the highest enthalpy input to cleave

Molecule	0 K energy	298 K H	298 K cleavage ΔH
[1.1.1]propellane	−193.35028	−193.24989	310 (∼272)
[2.1.1]propellane	−232.51386	−232.38309	168 (∼126)
[2.2.1]propellane	−271.67597	−271.51551	66.0 (∼21)
bicyclo[1.1.1]pentane	−194.55759	−194.43286	
bicyclo[2.1.1]hexane	−233.77318	−233.61670	
bicyclo[2.2.1]heptane	−272.97591	−272.78801	

give precedence to MP2/6-31G* geometries and energies over the other perhaps viable alternatives, HF/6-31G* and B3LYP/6-31G* because correlation effects can be decisively important in studying exotic species, and because a priori a purely ab initio method seems likely to be (marginally?) more trustworthy than one with a semiempirical component [24]; that **1**–**7** are small makes MP2 competitive with the faster (DFT) method. At both the MP2/6-31G* and B3LYP/6-31G* levels all seven are potential energy surface relative minima (real molecules). The bond cleavage energy increases dramatically from [1.1.1]-, to [2.1.1]-, to [2.2.1]propellane. What is the cause of this trend? Wiberg and Walker point out that the strain energies of these propellanes are all about the same, but the strain energies of their bicyclic counterparts fall markedly. These strain energies and the reactions used here to calculate them are shown in Fig. 13.3 (the strain energies referred to in [12] were obtained by comparing calculated enthalpies with idealized values from summing group equivalents [25]). Figure 13.3 shows the use of homodesmotic equations [26, 27], a technique with wide applications for calculating strain energies [28]. Strain energies calculated by Wiberg on HF/6-31G* geometries using calculated hydrogenolysis energies and certain approximations [29] are also shown in Fig. 13.3. The homodesmotic strain energies of the propellanes are all about 410–430 kJ mol^{-1}, but the values for the corresponding bicycloalkanes fall from 205, through 164, to 67 kJ mol^{-1} (bicyclo[1.1.1]-, [2.1.1]-, and [2.2.1]alkanes). Regarding the bicycloalkanes as surrogates for the diradicals as far as strain goes (we expect much the same geometry for both), we expect the same trend, at least semiquantitatively, for the diradicals. Clearly, then, the propellane → diradical reactions should become thermodynamically more favorable as the energy of the ring-opened intermediate diradical falls and the enthalpy of the reactant propellane remains essentially unchanged (in these rigid systems entropy changes should be small). That the bicycloalkanes become less strained in the series bicyclo[1.1.1]-, [2.1.1]-, and [2.2.1]- is entirely expected, because here we find successively a 1-carbon bridged cyclobutane, cyclopentane, and cyclohexane: the rings being constrained are increasingly less strained, resulting in structures with less total strain. The reason that all three propellanes have about the same strain is unclear: that the trend is no trend shows that opposing factors are at work, but their nature is unclear. The MP2/6-31G* geometries of the carbon framework and the bond orders (Löwdin bond orders [30, 31, 32] at the HF/6-31G* level) of the critical central bond of the three propellanes are shown in Fig. 13.4. The *least* reactive propellane has the *lowest* central bond order and although the bond orders increase monotonically, the bond lengths, rather than decreasing, increase, and do so irregularly. Propellanes have been reviewed by Levin et al. [10] and by Hopf [33]. For thermochemical and geometry calculations on, and an analysis of bonding in [1.1.1]-, [2.1.1]-, and [2.2.1]propellanes, see [29]. The nature and indeed the existence of the central C–C bond is unsettled: these leading references show that some studies claim that there is a bond, of some more or less novel kind [34, 35, 36, 37] and others claim that there is no bond [38, 39, 40]. The "no-bonding" assertions are hedged with the claim of some interaction between the carbons [38, 39] or no "direct" bonding [40]. Our findings with routine procedures are summarized in Fig. 13.5: using the MP2/6-31G* geometry we found a normal if slightly anemic (Löwdin bond order [30, 31, 32] 0.77; HF/6-31G* single-point calculation) central C–C bond, and a standard NBO analysis [41] (using the STO-3 G basis for simplicity) pronounced this bond to be the result of p–p overlap, in accord with which each bridgehead carbon uses an sp^2 orbital to bond to each of its three other neighbors. Each of these methylene carbons uses an essentially sp^4 orbital to bond to each bridgehead carbon and a roughly sp^2 orbital to bond to each of its hydrogens; enriching hybrid orbitals with p character for ring bonds and with s character for bonding to hydrogen is standard for cyclopropane rings [42]. A HF/6-31G* single-point calculation of orbital energies and visualization showed the central bond to be the HOMO (−9.81 eV). A perhaps more satisfying analysis of propellane bonding is implicit in the treatment of "propellane methane" in Chapter 12, Fig. 12.13, where, in particular, the prominent regions of electrostatic charge (electrostatic potential) around the bridgehead carbons are seen to arise from essentially nonbonding electron pairs (lone pairs) (cf. Chapter 2, Fig. 2.5).

*Molecule **3**, C_5H_6* Removal (conceptually) of a pair of distal hydrogens from **1** can yield an alternative to **2**, namely **3**, tricyclo[2.1.0.0^{2,5}]pentane (Fig. 13.1). This has not prompted nearly as much experimental and theoretical activity as its

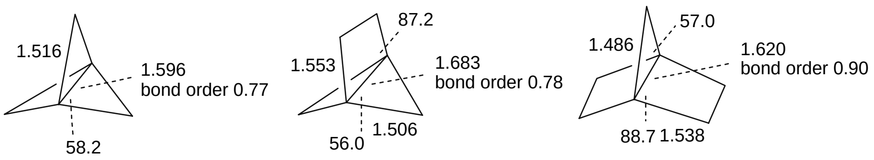


Fig. 13.4 MP2/6 geometries and central-C–C bond orders of [1.1.1]-, [2.1.1]- and [2.2.1]propellane. The bond orders are Löwdin [29] HF/6-31G* on the MP2 geometries. Bond lengths are in Å and angles in degrees

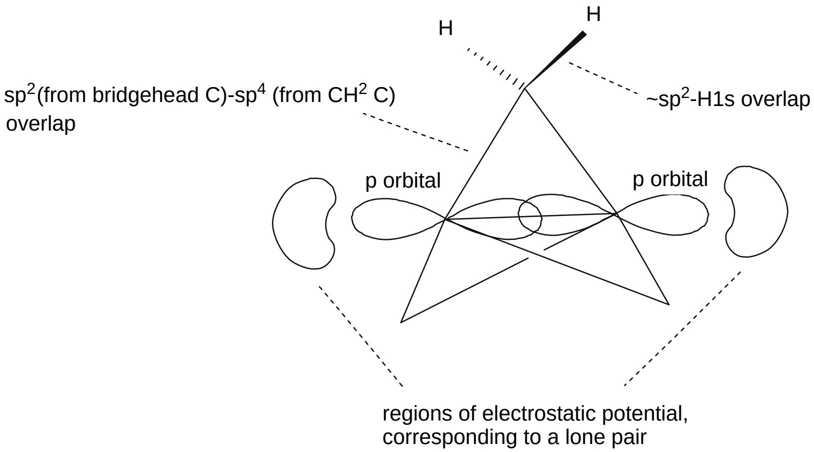
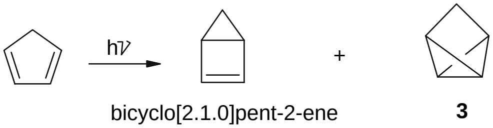


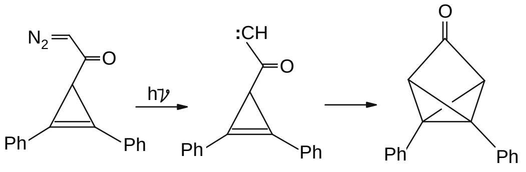
Fig. 13.5 Bonding in [1.1.1]propellane (**2**) as indicated by NBO [41] STO-3 G analysis on the MP2/6-31G* geometry

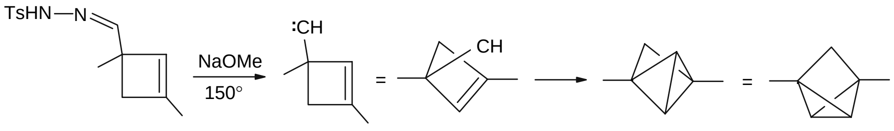
isomer, [1.1.1]propellane, eliciting only 23 references in *Chemical Abstracts* as of early 2007. The first preparation of the parent compound was reported in 1977 by Andrews and Baldwin [43] who, in a study of photoinduced skeletal rearrangements in cyclopentadiene discovered that besides the previously-known [44, 45, 46] major photoproduct bicyclo[2.1.0]pent-2-ene, **3** is present:



3

Ratio of cyclopentadiene: The formation of bicyclopentene is formally an electrocyclic reaction like that which converts the benzene system to a Dewar benzene [47], and the formation of **3** is "crossed cycloaddition" like that which converts benzene to benzvalene [48]. Structural derivatives of **3** were known prior to the isolation of the parent: Masamune prepared 1,5-diphenyl tricyclo[2.1.0.0^{2,5}]pentan-3-one by photolysis of a diazocyclopropenyl ketone [49] (X-ray analysis of a derivative confirmed the structure in the face of skepticism [50, 51] and Closs and Larrabee prepared 2,4-dimethyltricyclo[2.1.0.0^{2,5}]pentane [52] by heating the sodium salt of a cyclobutenyl tosylhydrazone; both kinds of reactions are known to generate carbenes or carbe-noids, and presumably involve insertion of a carbene-type carbon into a carbon–carbon double bond:





Both groups of workers misnamed the tricyclo[$2.1.0.0^{2,5}$]pentane system; this kind of solecism with polycyclics was common before Meinwald and Crandall's admonitory note [53], which seems to have acted like a nomenclatural epiphany; for example, footnote 2 in [50] corrects the original nomenclature and cites among others reference [53]. Tricyclopentanes with this skeleton, among other strained systems, have been reviewed [10, 54]; the electronic structure of derivatives has been studied by photoelectron spectroscopy [55].

Tricyclo[$2.1.0.0^{2,5}$]pentane, **3**, is stable enough to be stored at -20°C, and can be purified by gas chromatography, albeit with poor recovery [43]. Its thermal reaction, isomerization to cyclopentadiene (the reverse of the photoreaction by which it was first prepared), has been studied computationally [56, 57]. The reaction was calculated to go through a formally orbital symmetry-forbidden disrotatory transition state (see [41] Fig. 1) with high diradical character, corresponding to a barrier of about 180–200 kJ mol^{-1} (42 kcal mol^{-1} [56] and 48 kcal mol^{-1} [57]). The parent, tricyclo[$2.1.0.0^{2,5}$]pentan-3-one, can be stored for months at -5°C [58]. The tricyclopentanones corresponding to tricyclo[$2.1.0.0^{2,5}$]pentane are potential precursors of tetrahedranes by decarbonylation, and early attempts to achieve this transformation were made by Ona et al. [59]. The successful synthesis of tetra-*t*-butyltetrahedrane from the cyclopentadienone by the Maier group [60] presumably proceeds via the tricyclopentanone (Chapter 6).

Molecules 4, 5, 6, 7 (Unknown Species)

*Molecule **4**, C_5H_4* Removal of appropriate hydrogen pairs from **2** or from **3** yields **4**, tetracyclo[$2.1.0.0^{1,3}.0^{2,4}$]pentane (Fig. 13.1), unknown as of early 2007. This has so far evoked only three references in *Chemical Abstracts*, all representing theoretical work: Balaji and Michl, the inspiration for this chapter [1], and two papers in which **4** is one amongst many other molecules in a survey: a study of the limits of ring fusion [61], and a method of automatically evaluating the strain in fused- and bridged-ring molecules [62]. This tetracyclopentane is tetrahedrane with a cyclopropane ring fused on, so from the discussion of tetrahedrane in Chapter 6 one immediately suspects that it will be a synthetic challenge (it is also a propellane, and a bicyclobutane). Tetrahedrane is unambiguously predicted to lie energetically well above cyclobutadiene, its very likely isomerization sink (see Chapter 6, *The Parent Tetrahedrane, Calculations*). The calculated energy difference is 99 kJ mol^{-1} at the MP2/6-31G* level (96 kJ mol^{-1} with MP2/6-311G* [63]). What is the thermodynamic effect of fusing a cyclopropane ring onto tetrahedrane? Here we have an interesting ambiguity, because unraveling of the tetrahedrane moiety can in principle occur in two ways (Fig. 13.6), to give valence-isomeric cyclobutadienes: one that is also a cyclopropene (**9**), or one that is also a dimethylenecyclopropane (**10**). The calculations in Fig. 13.6 indicate that isomerization of **4** → **9** is very unfavorable,

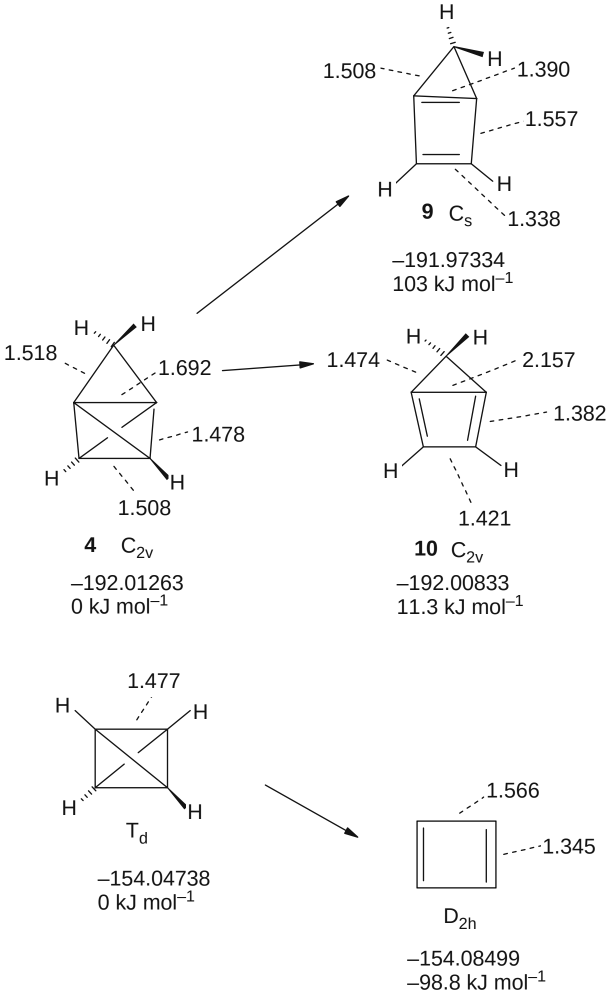


Fig. 13.6 Isomerization of the tetracyclopentane **4** to cyclobutadienes **9** and **10**, compared with isomerization of tetrahedrane to cyclobutadiene. MP2/6-31G* geometries and energies (ZPE-corrected) are shown; energies in kJ mol^{-1} are relative energies. Bond lengths are in Å. The structures have no imaginary frequencies

but isomerization to **10** is only slightly unfavorable. Actually, the peculiar structure of **10** renders the accuracy of this calculation somewhat suspect: this molecule has a rather long (formal?) C–C bond (2.157 Å) and it may thus have significant diradical character.[6] That B3LYP/6-31G* calculations gave quite similar results does lend credence to the MP2 conclusions: here **9** and **10** lie 76 kJ mol^{-1} above and 4.0 kJ mol^{-1} below **4**, respectively, and the C–C bond in question is 2.098 Å long. The calculations probably do indicate correctly that isomerization of **4** to a cyclobutadiene is thermodynamically less favorable than in the case of tetrahedrane. This reluctance to form a cyclobutadiene is likely due to the unfavorable angles demanded of the two ring-fusion, alkene, carbons, as is readily revealed by inspection of structures **9** and **10** (Fig. 13.6). Whether this would translate into increased kinetic stability of **4** compared to tetrahedrane is unclear, as some process other than cyclobutadiene formation may be possible. Nevertheless, the fact that isomerization to a cyclobutadiene appears to be thermodynamically not very favorable raises the counterintuitive possibility that **4**, although tetrahedrane with an extra cyclopropane ring fused on, will be kinetically and thermodynamically stabler than tetrahedrane. Michl and Balaji say that **4** is “a promising synthetic target, particularly since the usual plague of the efforts to synthesize the unsubstituted tetrahedrane, rearrangement to cyclobutadiene, should be prevented by the presence of the additional three-membered ring” [1].

The bonding situation in the quaternary carbons of **4** seems somewhat similar to that for the apical carbon of pyramidane (Chapter 2), a view suggested by the presence of prominent regions of electrostatic charge (electrostatic potential), approximating lone pairs, at these carbons (cf. Chapter 2, Fig. 2.5).

Molecule ***5****,* *C_5H_4* Removal of an appropriate pair of hydrogens from **3** gives, as an alternative to **4**, molecule **5**, tetracyclo[2.1.0.0^{1,3}.0^{2,5}]pentane, pyramidane. This was still unknown as of early 2007, despite having sparked a fair amount of interest (19 references in *Chemical Abstracts*) because it is the canonical molecule with a pyramidal carbon atom. Pyramidane was discussed in Chapter 2. Noteworthy are the facts that it has a lone pair at the apex (prominent electrostatic potential region), and that computations provide good evidence that it will prove to be reasonably stable, perhaps even isolable at room temperature.

Molecule ***6****,* *C_5H_2* A pair of hydrogens can be removed from either **4** or **5** to give **6**, pentacyclo[2.1.0.0^{1,3}.0^{2,4}.0^{2,5}]pentane. This is another species unknown in early 2007, with only five references in *Chemical Abstracts*: Balaji and Michl [1], the ring fusion [61] and automatic ring-strain evaluation [62] papers referred to above, and a paper on homolytic C–H bond dissociation [64] and one on ^{13}C–^{13}C coupling in strained molecules [65]. This species is also briefly mentioned in a paper on C_5H_2 isomers with acyclic and cyclopropene structures, where it is said to be “apparently considerably less stable” than those other structures [66]. The C–H bond dissociation energy for **6** was calculated to be the highest (510 kJ mol^{-1}, 122 kcal mol^{-1}) for tetracoordinate carbon among the many molecules examined; the second highest was for pyramidane (**5**, in that paper misnamed tetrahedrane; 487 kJ mol^{-1}, 116.5 kcal mol—$^{-1}$) [64]. These energies can be compared with the calculated values of 439 kJ mol^{-1} for methane and 406 kJ mol^{-1} for the tertiary C–H of 2-methylpropane, which match closely the experimental values. The authors

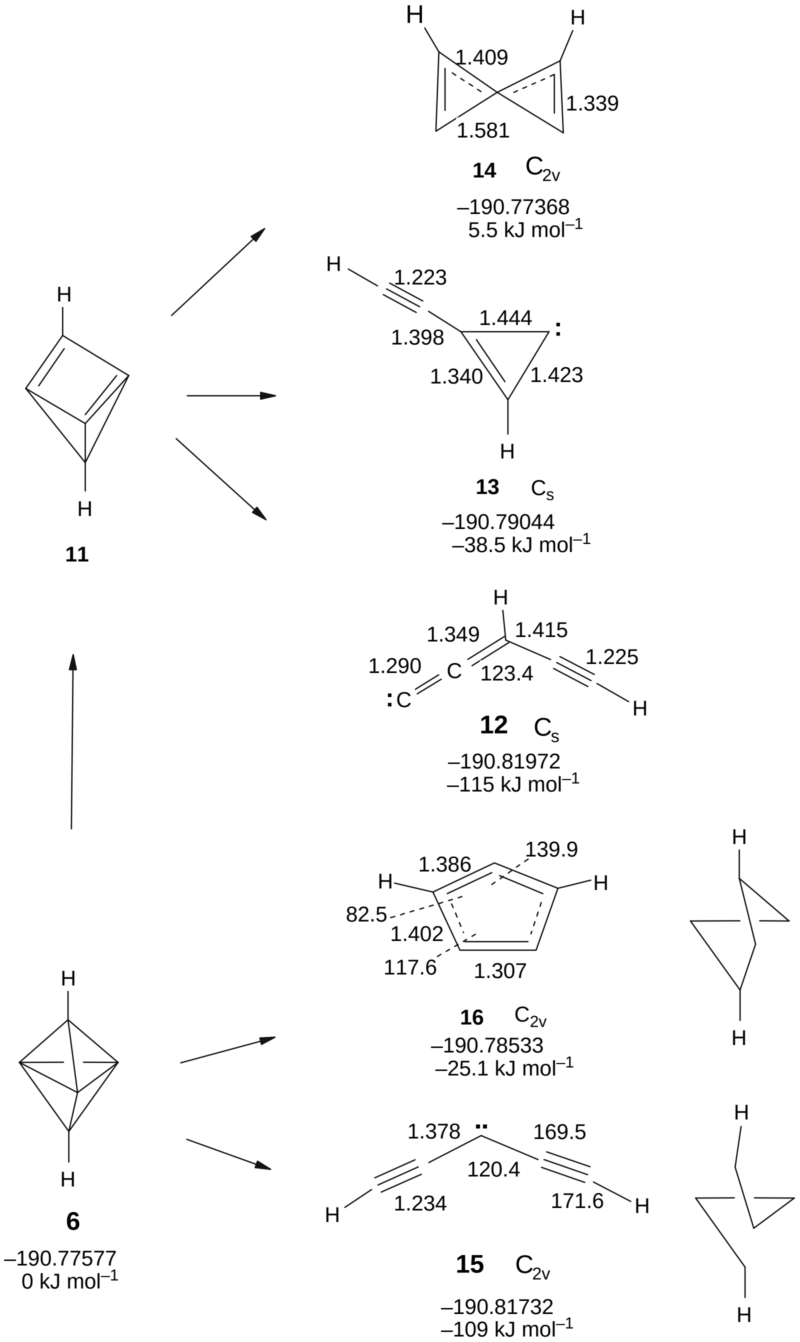
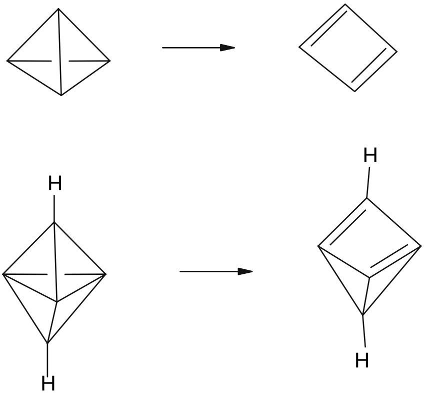


Fig. 13.7 (continued)

found a connection of C–H dissociation energies with carbon hybridization, and also with H–C–C bond angles. The spin–spin coupling study reported an abnormally low s-character for the C–C bonds [65]. Both the high C–H bond strength [64] and the low C–C s-character (by implication high C s-character for the C orbital used to bond to H) [65] are expected from the well-known fact that a "strained carbon" puts high p-character into ring C–C bonds in an attempt to make C–C–C angles approach 90°, thereby making the orbital used to bond to hydrogen relatively rich in s-character, which increases the C–H bond strength [67].

Molecule **6** is two tetrahedranes sharing a face. We saw in Chapter 6 and in connection with **4** (above) that tetrahedrane is expected to isomerize in a strongly exothermic reaction to cyclobutadiene. If we transpose this expectation unflinchingly to the case of **6**, then we are hypothesizing the isomerization of **6** to **11**:



6

11

The somewhat bizarre-looking **11** is evidently not a stationary point on a potential energy surface (not a real molecule) [68]: attempts to effect a geometry optimization that will give a molecule recognizable as **11**, even if considerably distorted, fail with quantum mechanical methods like AM1 and MP2 (molecular mechanics does permit one to create an optimized structure resembling **11**, but this is not particularly reassuring, since molecular mechanics optimizations are constrained by the inability of this method to break chemical bonds). Figure 13.7 shows how starting

Fig. 13.7 Speculative scheme for isomerization of the pentacyclopentane **6**. Structures are not arrayed in order of energy. The consequence of isomerization to **11** (see text) was examined by MP2/6-31G* optimization of structures similar to **11**; this gave **12**, **13**, or **14**. Molecules **15** and **16** were obtained by starting with structures resembling them (their connectivity cf. **6** is shown) and doing MP2/6-31G* optimizations. ZPE-corrected energies and relative energies in kJ mol^{-1} are shown. Bond lengths are in Å and angles in degrees. The structures (except for **11**, which is only a starting template for geometry optimization) are all singlets and have no imaginary frequencies from structures similar to **11**, MP2/6-31G* optimizations lead to **12**, **13** or **14**, and starting from structures which maintain some of the connectivity of **6** these optimizations yield **15** or **16**. Figure 13.7 suggests five possible isomerization products of **6** (none of which seems likely to be stable enough to be a final product under ambient conditions). Note that **14** is, at this computational level at least (B3YP/6-31G* concurs), a relative minimum with planar tetracoordinate carbon. Ions with a similar structure have been examined computationally [69]. Bearing in mind that we have not calculated activation energies, one might venture the guess that the two lowest-energy isomers **12** and **15** are the most plausible penultimate isomerization products. These are both carbenes and so would be expected to react further, possibly by dimerizing. *Triplet* (the ground state) **15** has been characterized by IR, EPR and UV spectroscopy, and **12** and other C_5H_2 carbenes have been identified by Fourier transform microwave spectroscopy [70].

The electronic structure of **6** as indicated by NBO analysis [41] is shown in Fig. 13.8. The main features to emerge from this are that each of these carbons has a lone pair (this is supported by the visualization of an electrostatic potential region near each; cf. Chapter 2, Fig. 2.5) and that there is no bonding between the equatorial

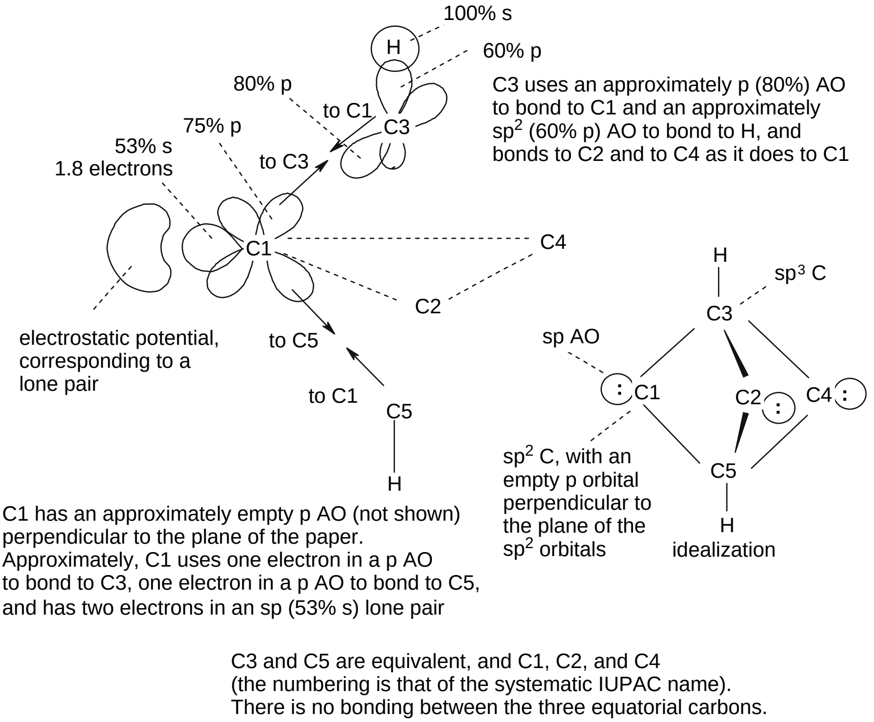
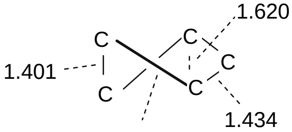


Fig. 13.8 Bonding in molecule **6**, from an NBO [41] STO-3 G analysis on the MP2/6-31G* geometry. One can go from the simple idealization of the bonding to the more complex picture revealed by NBO analysis by adjusting the s/p ratio in the various atomic orbitals

carbons (C1, C2, C4 in Fig. 13.8). The latter point is apparently at variance with the Löwdin bond order [30, 31, 32] of 0.60 between these atoms, but the possible limitations of this algorithm, the problem of defining a bond, and the consonance of the analysis in Fig. 13.8 with features calculated from the wavefunction, in particular the three electrostatic charge (electrostatic potential) lobes, suggest that the structure shown with six, rather than nine, C–C bonds is the better representation of **6**. The bonding-or-not conundrum is revisited below for **7**. This tricarbene structure with "missing" C–C bonds is essentially the one suggested by Michl and Balaji [1].

Molecule 7, C_5 Removal of the hydrogens from **6** gives **7**, hexacyclo[2.1.0.0^{1,3}.0^{2,4}.0^{2,5}.0^{3,5}]pentane, ending our incremental investing of **1** with increasing formal unsaturation. We now have a molecule which represents an allotrope of carbon. This was unknown in early 2007. Queried via the structural formula **7** in Fig. 13.1, *Chemical Abstracts* returned only the references to the same five theoretical papers as for **6**, above: [1, 61, 62, 64, 65]. Reference [1] brought **7** the attention of the chemical world, [61] catalogs it in exploring the limits of ring fusion, [62] estimates a strain energy, [64] does not, in fact, seem to mention **7** (which is not surprising, since it deals with C–H bond energies), and [65], concerned with ^{13}C–^{13}C spin–spin coupling, reported, as expected, abnormally low s-character for the C–C bonds (cf. **6** above). A *formula* search for C_5, however, unearthed many publications, mostly for charged species, but one combined experimental and computational study of C_5 molecules in which **7** is considered in passing, with the conclusion that *linear* C_5 undergoes a scrambling process that does not involve **7** [71]. From several studies, the linear isomer is concluded to be the stablest neutral C_5 species [71, 72, 73, 74] (a potential energy search routine using a "lower-level" empirical potential indicated that a cyclic structure was the lowest-energy species [75]) and it is open-chain C_n that has attracted the most attention, e.g. [72, 73, 74]; among these are species that have been identified in stellar media [76].

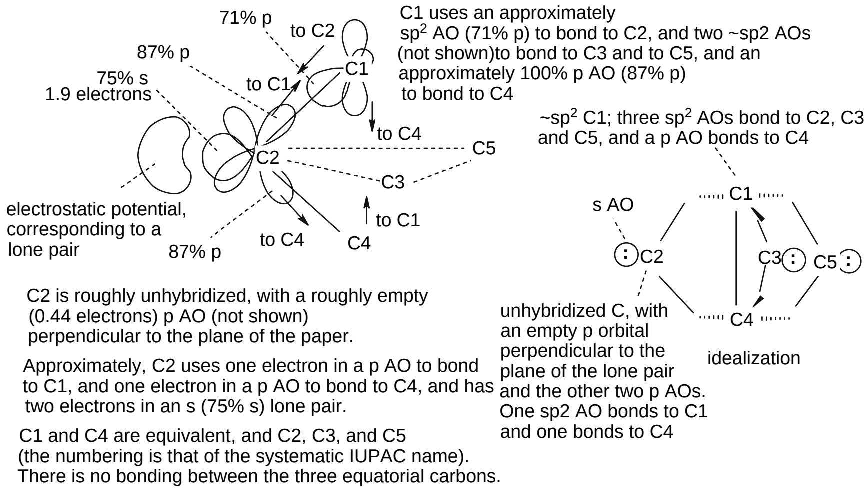
Our MP2/6-31G* calculations located a cyclic (bicyclic, if one counts the 1.620 Å bond) C_5 molecule **17** of C_2 symmetry (planar cyclic C_5 of D_{5h} symmetry has two imaginary frequencies at this level) that seems not to be among the eleven shown by Dua et al. [71]:



17 C_2

The MP2/6-31G* energies with ZPE corrections for **7**, the C_2-symmetry molecule **17**, and linear C_5 are: **7**, −189.47783, relative energy 312 kJ mol^{-1}; **17**, −189.48652, relative energy 289 kJ mol^{-1}; linear, −189.59662, relative energy 0 kJ mol^{-1}.

In conceptualizing the formation of **7** from **6**, we create a new C–C bond between the apical carbons (Fig. 13.1). These atoms are calculated (MP2/6-31G*) to be



C1 uses an approximately sp^2 AO (71% p) to bond to C2, and two ~sp2 AOs (not shown)to bond to C3 and to C5, and an approximately 100% p AO (87% p) to bond to C4

~sp^2 C1; three sp^2 AOs bond to C2, C3 and C5, and a p AO bonds to C4

C2 is roughly unhybridized, with a roughly empty (0.44 electrons) p AO (not shown) perpendicular to the plane of the paper.

Approximately, C2 uses one electron in a p AO to bond to C1, and one electron in a p AO to bond to C4, and has two electrons in an s (75% s) lone pair.

C1 and C4 are equivalent, and C2, C3, and C5 (the numbering is that of the systematic IUPAC name). There is no bonding between the three equatorial carbons.

unhybridized C, with an empty p orbital perpendicular to the plane of the lone pair and the other two p AOs. One sp2 AO bonds to C1 and one bonds to C4

Fig. 13.9 Bonding in molecule **7**, from an NBO [41] STO-3 G analysis on the MP2/6-31G* geometry. One can go from the simple idealization of the bonding to the more complex picture revealed by NBO analysis by adjusting the s/p ratio in the various atomic orbitals

2.111 Å apart in **6**, and the rigid framework does not permit much geometric relaxation: the corresponding distance in **7** is 2.005 Å. Is this merely a formal bond? Although it is considerably longer than the maximum C–C bond length of 1.748 adjudicated by the intriguing bond-length/strength formula discovered by Zavitsas [77], it can reasonably be argued that this is a real bond: it would be naive not to realize that bond order algorithms may be up against limitations in dealing with exotic species, but the Löwdin bond order [30, 31, 32] of 0.81 is well above what might be considered borderline bonding. Interestingly, the three *shorter* equatorial bonds, 1.911 Å, have orders of only 0.51, suggesting that they are weaker than the ostensibly problematic, longer, apical bond. This preliminary analysis gains credence from an NBO [41] assay (Fig. 13.9), the most salient point to emerge from which is that there is bonding between the apical carbons but not between the equatorial ones. The depiction of **7** in Fig. 13.1 thus appears to be formal in showing nine or ten, rather than seven (Fig. 13.9) bonds. However, the whole question of the definition and the existence of bonds in molecules is not simple,[7] and a more sophisticated analysis might (or might not) reveal some bonding between the equatorial atoms. In discussing bonding in these molecules I tacitly assume, without condoning any definition, that the bond concept is meaningful and that it can have chemical consequences: thus partitioning electrons into bonding and nonbonding pairs can help to rationalize the prominent electrostatic charge (electrostatic potential) regions, diagnostic of lone pairs (cf. Chapter 2, Fig. 2.5), visualized from the wavefunction in **2**, **4**, **5**, **6**, and **7**. Like **6**, molecule **7** is here assigned a tricarbene structure.

A Comparative Survey of some Salient Characteristics of 1–7: Geometry, Strain, Ionization Energies, and IR and Electronic Spectra

Geometries In Fig. 13.10 the calculated geometries of **1–7** are shown, with (for the known **1–3**) experimental parameters. The very limited experimental data on parent molecules in the gas phase represent geometries that are essentially the same as the calculated ones, and from general studies of the accuracy of MP2/6-31G* and B3LYP/6-31G* geometries one can be confident that the computed structures are

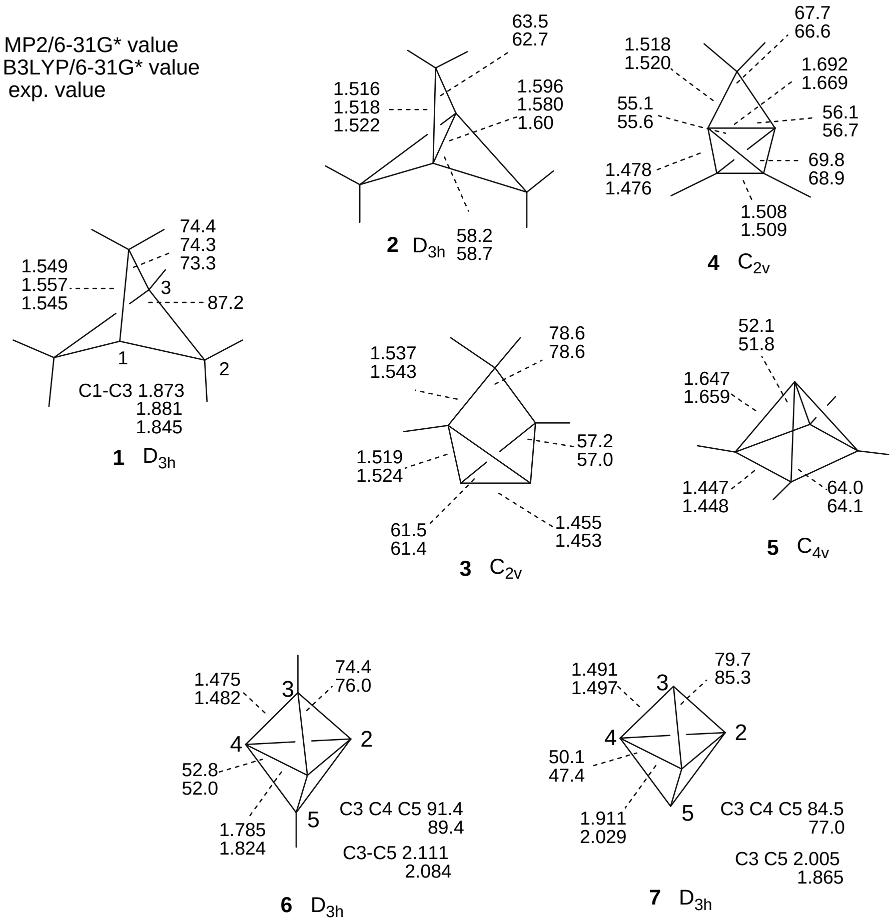


Fig. 13.10 Carbon framework geometries (for clarity C–H bonds are indicated) of **1**-**7** by MP2/6-31G* and B3LYP/6-3G* calculations, and where available some gas phase electron diffraction measurements [10]; experimental geometries of derivatives of **1**, **2**, and **3** are given in [10]. Bond lengths are in Å and angles in degrees. The numbering of **6** and **7** is according to the IUPAC rules

reliable [78]. Bond lengths of more than 1.7 Å arouse suspicion, and we have seen that for **6** and **7** the "normal" Kekulé structures with all carbons tetracoordinate could more realistically be replaced by tricarbene structures (Figs. 13.8 and 13.9).

Strain Anticipated excessive strain is probably the factor responsible for the skepticism likely to be ignited by the unknown and more outré structures in this series, **4**, **5**, **6**, and **7** (that these have carbons with bonds pointing "the wrong way" ceased to be very disturbing with the demonstration that **2** is reasonably stable). Figure 13.11 gives strain energies calculated by isodesmic-type reactions (homodesmotic reactions) [26, 27, 28] (cf. the propellane calculations of Fig. 13.3); Fig. 13.11a shows model homodesmotic reactions, to provide strain energies of cyclobutane, bicyclobutane, and cubane for perspective, and Fig. 13.11b shows homodesmotic reactions for molecules **1**–**7**. In Table 13.2 these results are summarized with some values from the literature. Not unexpectedly, the pairs **2**/**3** and **4**/**5**, with the same numbers of C–C bonds, have somewhat similar strain energies.

Reasonable stability is exhibited by cyclobutane [79] and bicyclobutane [80, 81, 82] ([80]: it could be kept at room temperature, and [81] reported that it decomposed in a few days "well below 0^{o}, presumably as a result of radical polymerization or autooxidation" implying that oxygen was not excluded, and in 4 minutes at 110° decomposition was only slight). Cubane is kinetically very stable: "despite the considerable degree of strain...this molecule is extraordinarily stable,

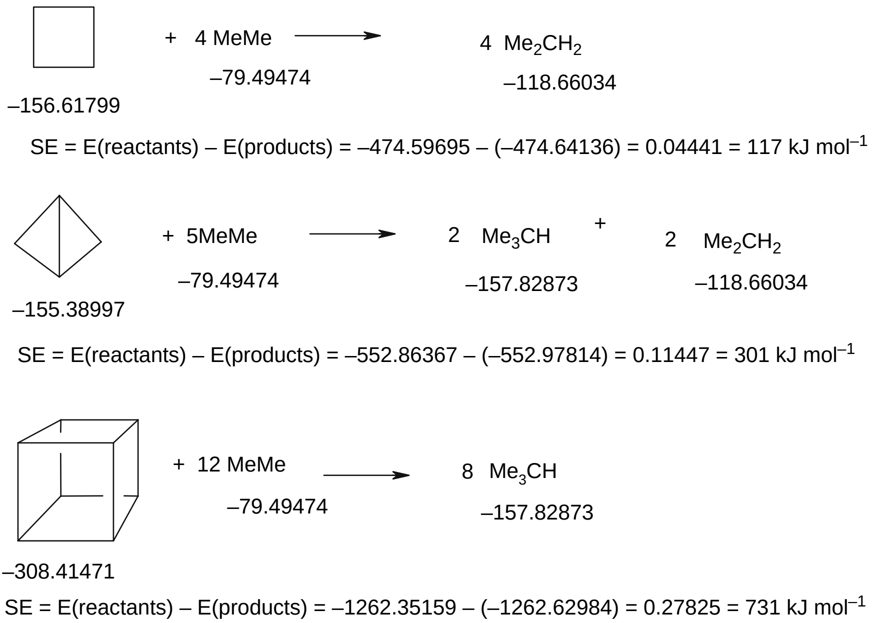
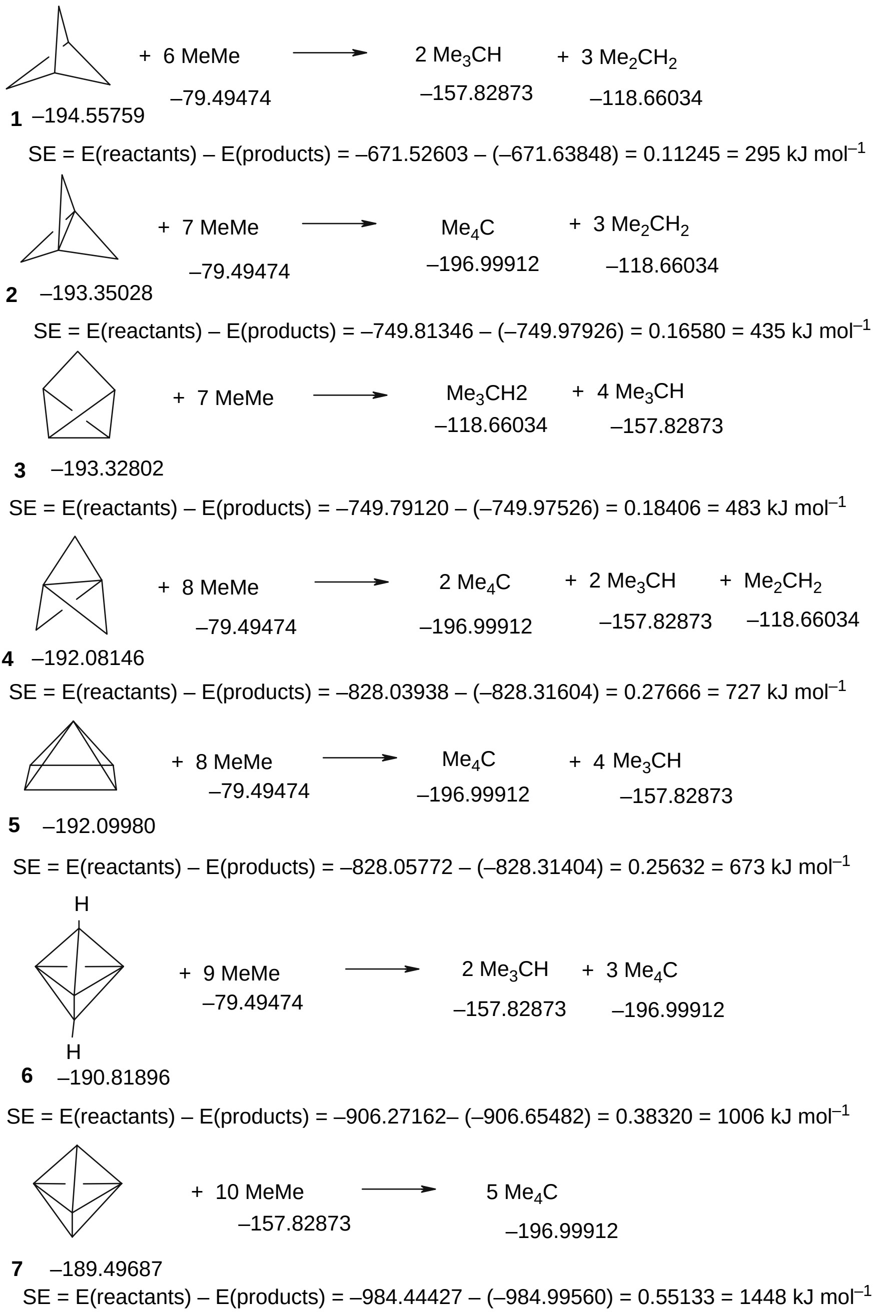


Fig. 13.11a Strain energies (SEs) of some model compounds from homodesmotic reactions [26, 27, 28] at the MP2/6-31G* level, without ZPE. Quantities are atomic units (hartrees) and kJ mol^{-1}. Cf. Table 13.2



1 –194.55759 + 6 MeMe → 2 Me_3CH + 3 Me_2CH_2

–79.49474 –157.82873 –118.66034

SE = E(reactants) – E(products) = –671.52603 – (–671.63848) = 0.11245 = 295 kJ mol^{-1}

2 –193.35028 + 7 MeMe → Me_4C + 3 Me_2CH_2

–79.49474 –196.99912 –118.66034

SE = E(reactants) – E(products) = –749.81346 – (–749.97926) = 0.16580 = 435 kJ mol^{-1}

3 –193.32802 + 7 MeMe → Me_3CH2 + 4 Me_3CH

–118.66034 –157.82873

SE = E(reactants) – E(products) = –749.79120 – (–749.97526) = 0.18406 = 483 kJ mol^{-1}

4 –192.08146 + 8 MeMe → 2 Me_4C + 2 Me_3CH + Me_2CH_2

–79.49474 –196.99912 –157.82873 –118.66034

SE = E(reactants) – E(products) = –828.03938 – (–828.31604) = 0.27666 = 727 kJ mol^{-1}

5 –192.09980 + 8 MeMe → Me_4C + 4 Me_3CH

–79.49474 –196.99912 –157.82873

SE = E(reactants) – E(products) = –828.05772 – (–828.31404) = 0.25632 = 673 kJ mol^{-1}

6 –190.81896 + 9 MeMe → 2 Me_3CH + 3 Me_4C

–79.49474 –157.82873 –196.99912

SE = E(reactants) – E(products) = –906.27162– (–906.65482) = 0.38320 = 1006 kJ mol^{-1}

7 –189.49687 + 10 MeMe → 5 Me_4C

–157.82873 –196.99912

SE = E(reactants) – E(products) = –984.44427 – (–984.99560) = 0.55133 = 1448 kJ mol^{-1}

Fig. 13.11b Strain energies (SEs) of molecules **1**x2013;**7** from homodesmotic reactions [26, 27, 28] at the MP2/6-31G* level, without ZPE. Quantities are atomic units (hartrees) and kJ mol^{-1}. Cf. Table 13.2

Table 13.2 Strain energies (SEs) of molecules **1**–**7** and three comparison molecules, from the homodesmotic reactions of Figs. 11a and 11b (MP2/6-31G* level, without ZPE). The SE/C–C values utilize the formal bonds of the Kekulé structures (e.g. Fig. 13.1). Reference [28] gives references to other (very similar) published values. Energies are in kJ mol^{-1}

Molecule	SE	SE/C–C	SE from other sources
cyclobutane	117	117/4 29.3	110 [28], B3LYP/6-31G* homodesmotic.
bicyclobutane	301	301/5 60.2	277 [28], B3LYP/6-31G* homodesmotic.
cubane	731	731/12 60.9	643 [28], B3LYP/6-31G* homodesmotic.
1	295	296/6 49.2	280 [28], B3LYP/6-31G* homodesmotic. 293 [1], HF/6-31G* + group equivalents
2	435	435/7 62.1	411 [28],B3LYP/6-31G* homodesmotic. 437 [1], HF/6-31G* + group equivalents
3	483	483/7 69.0	459 [1], HF/6-31G* + group equivalents
4	727	727/8 90.9	728 [1], HF/6-31G* + group equivalents
5	673	673/8 84.1	639 [1], HF/6-31G* + group equivalents
6	1006	1006/9 112	954 [1], HF/6-31G* + group equivalents
7	1448	1448/10 145	Not calc. in [1]: “unstable at this approximation”.

surviving essentially unchanged at temperatures up to 200°C” [83]. As stated above, molecules **1** and **2** are quite stable, and **3** is stable enough to be stored at −20°C and to be purified by gas chromatography. The other compounds **4**–**7** are unknown. From this look at these six compounds what can we draw about the connection between strain energy and stability? Cyclobutane, bicyclobutane, and cubane are all more or less stable, and their strain varies from 117 to 731 kJ mol^{-1}; the most highly-strained one, cubane, could with little meaningful exaggeration be said to be perfectly stable. If strain is a chemically useful index, the strain energy per C–C bond (SE/C–C) should be a more meaningful index of the ability of strain to express itself in reactivity; after all, other things being the same, a bigger molecule will, trivially, have more total strain than a smaller one. The SE/C–C of the six known compounds varies from 29 to 69 kJ mol^{-1}; the very stable cubane has a SE/C–C only a little smaller than that of the more reactive **3** (61 cf. 69 kJ mol^{-1}). It thus seems, purely empirically, that there is no particular connection between SE/C–C and kinetic stability, at least for cycloalkane-type molecules in this range of SE/C–C. Perhaps well beyond ca. 70 kJ mol^{-1} there is some correlation, and **6** and **7**, with values of 112 and 145 kJ mol^{-1}, could turn out to exhibit a fragility well beyond that of the three known C_5 polycycles. The strain energy of **6** was described as “awesome”, and “little hope” was seen for **7** as a synthetic target [1].

Ionization energies We will consider the vertical ionization energies(IEs; ionization potentials) of **1**–**7** and, for perspective, of the prosaic pentane and cyclopentane. The vertical ionization energy of a neutral molecule is the energy of the radical cation at the equilibrium geometry of the *neutral*, minus the energy of the neutral;

the adiabatic ionization energy is the energy of the radical cation at *its* equilibrium geometry, minus the energy of the neutral at its equilibrium geometry [84]. Both IEs can in principle be calculated straightforwardly by computing the energies of the appropriate species and subtracting [85]. Here I choose to use vertical ionization energies, because these seem to be more an inherent property of the neutral molecule, since here the radical cation intrudes only as a ghostly "ionized neutral"; an attempt to optimize the radical cation will not necessarily even lead to a stationary point on the potential energy surface. Table 13.3 shows calculated IEs at the MP2/6-31G* and AM1//MP2/6-31G* (AM1 single-point at the MP2/6-31G* geometry) levels, IEs from Koopmans' theorem (as the negative of the HOMO [85]), and available experimental values. These IEs of pentane and cyclopentane [86], **1** [87], and **2** [88] are vertical IEs, measured by photoelectron spectroscopy [89, 90]. Judging by the first four entries, none of the three the computational methods is systematically particularly accurate. One might very tentatively suggest that the "AM1 Koopmans" method (single point AM1 calculation of MO energies using the MP2/6-31G* geometry) consistently overestimates the IE by ca. 0.6 eV, and in Table 13.3 the IEs calculated by subtracting 0.6 from these values are shown in brackets. If we consider pentane and cyclopentane (experimental IEs ca. 11 eV) to be normal saturated hydrocarbons, and if the assumption of a systematic overestimation of about 0.6 eV by "AM1 Koopmans" is true, then **1** (experimental IE 10.6 eV) and **7** (estimated IE ca. 11 eV) are normal, and **2**–**6** (estimated IEs ca. 10 eV) have slightly unusually low IEs. This very tentative suggestion is not contradicted by the evidently more erratic MP2/6-31G* and MP2 Koopmans results. Of **1**–**7** the only ones lacking prominent electrostatic potential regions are **1** and **3**, i.e. **2** and **4**–**7** have lone pairs, so unlike what might have been expected there is no obvious correlation here between low IE and the presence of nonbonding electrons.

Note that the popular high-accuracy Gaussian [91] and complete-basis-set (CBS) [92] methods cannot be used for the calculation of *vertical* IEs, as by definition they

Table 13.3 Vertical ionization energies (eV) by various methods. Numbers in parentheses are deviations from experimental and numbers in brackets are AM1 Koopmans minus 0.6 (see text). Regarding the three *Calculated* columns: MP2/6-31G* refers to the difference in energy of the radical cation (at the geometry of the neutral) and the neutral at the MP2/6-31G* level, AM1 Koopmans refers to the negative of the HOMO energy from an AM1 calculation on the MP2/6-31G* geometry, and MP2 Koopmans refers to the negative of the HOMO energy from an MP2/6-31G*//MP2/6-31G* calculation (MP2/6-31G* energy at the MP2/6-31G* geometry)

Molecule	Calculated			Experimental
	MP2/6-31G*	AM1 Koopmans	MP2 Koopmans'	
Pentane	10.0 (−0.9)	11.3 (0.4)[10.7]	12.15 (1.25)	10.9±0.1 [86]
cyclopentane	11.2 (0.5)	11.3 (0.6)[10.7]	12.2 (1.5)	10.7±0.1 [86]
1	10.5 (−0.1)	11.4 (0.8)[10.8]	11.8 (1.2)	10.6 [87]
2	9.7 (0.0)	10.2 (0.5)[9.6]	9.8 (0.1)	9.74 [8]
3	8.9	10.6 [10.0]	9.6	not available
4	9.8	10.3 [9.7]	10.0	not available
5	8.9	10.4 [9.8]	9.9	not available
6	9.9	10.9 [10.3]	10.2	not available
7	12.7	11.4 [10.8]	11.4	not available

Table 13.4 MP2/6-31G* IR stretching frequencies (cm^{-1}). Multiplication by 0.9434, not done here, has been recommended to bring frequencies calculated at this level into better agreement with experimental values [87]

Molecule	Lowest frequency	Highest C–H stretch
1	562	3182
2	552	3280
3	479	3350
4	450	3376
5	327	3343
6	417	3391
7	508	no C–H present

incorporate geometry optimizations, and we want to keep the radical cation at the geometry of the neutral.

IR spectra The lowest frequencies and the highest C–H stretching frequencies of **1**–**7** are given in Table 13.4 (multiplication of MP2(fc)/6-31G* frequencies by 0.9434 has been recommended to bring them into better agreement with experiment [93], but this has not been done in the table). All the molecules **1**–**7** are relative minima (no imaginary frequencies) at the MP2/6-31G* and B3LYP/6-31G* levels, and all but **7** are also relative minima at the HF/6-31G* level (here **7** is a second-order saddle point, i.e. it has two imaginary frequencies). This agreement between the three levels gives reasonable assurance that these species can exist, i.e. represent real molecules. A lowest-frequency vibration not too far above zero, say 100–200 cm^{-1}, at a reasonably high computational level, and corresponding to a reaction mode rather than just torsional motion, is cause to fear that the species may in reality not be able to exist [68]. This is nicely illustrated in inquiries into the existence of oxirene by Vacek et al. [94, 95]. The lowest frequencies of **1**–**7** are all well above zero.

In Table 13.5 strain energies/C–C (SE/C–C) and the highest C–H stretching frequencies for **1**–**7**, cyclobutane, bicyclobutane and cubane have been tabulated in order of increasing angle strain/C–C. There is a rough positive correlation of the highest C–H stretching frequency with SE/C–C. A positive correlation is expected

Table 13.5 Strain energies/CC (kJ mol^{-1}) (cf. Table 2) and IR stretching frequencies (cm^{-1}) from MP2/6-31G* calculations, tabulated in order of increasing strain energies/CC

Molecule	Strain energy/CC	Highest C–H stretch
cyclobutane	29.3	3199
cyclopropane	42.2	3312
1	49.2	3182
bicyclobutane	60.2	3312
cubane	60.9	3187
2	62.1	3280
3	69.0	3350
5	84.1	3343
4	90.9	3376
6	112	3391
7	145	no C–H present

Table 13.6 Electronic spectra bands calculated by TDDFT [96], using the B3P86/6-311++G** functional/basis on MP2/6-31G* geometries, and HOMO–LUMO gap from MP2/6-31G*

Molecule	eV/nm, intensity	exp nm	H–L gap, eV
Propane	8.28/150, f=0.0026	Below 180 nm [97]	19.03
cyclopropane	7.66/162, f=0.0013	182–189 and lower [98]	17.99
cyclopropylidene	2.20/563, f=0.0061	Not available	12.19
1	7.86/158, f=0.0386	"at ... high energies" [10]	18.62
2	6.92/179, f=0.0000	"transparent in the near UV" [10] (7.26 eV, electron impact [105])	14.27
3	6.42/193, f=0.0187	Not available	16.80
4	4.92/252, f=0.0008	Not available	13.24
5	6.46/192, f=0.0000	Not available	15.61
6	4.66/266, f=0.0000	Not available	13.27
7	1.78/696, f=0.0000	Not available	10.02

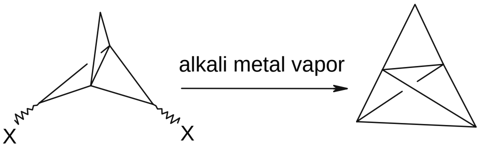
since increasing strain implies, in a general way, stronger C–H bonds, with bigger force constants, due to increasing s character in the atomic orbitals carbon uses to bond to hydrogen [67]. If the somewhat extraneous C_3, C_4 and C_8 compounds are removed from Table 13.5, the increase of highest C–H stretch with SE/C–C is monotonic except for the fact that **5** has a slightly lower frequency than **3**. By comparison with cyclopropane, none of the compounds **1**–**7** has a particularly extraordinarily high C–H stretching frequency.

A correlation between *uncoupled* C–C stretch and bond strength was found by Zavitsas [77] , but the lack of truly uncoupled vibrations of this kind in **1**–**7** makes this inapplicable here; all these molecules show calculated (MP2/6-31G*) C–C stretch at roughly 800–900 cm^{-1} and breathing modes at roughly 1300–1400 cm^{-1}.

Electronic spectra Table 13.6 shows UV absorptions of **1**–**7** and some reference compounds, calculated by time-dependent DFT (TDDFT) [96]; for simplicity, only the longest-wavelength bands are shown. Calculated and experimental values are compared for the reference compounds propane and cyclopropane [97, 98] and for **1** and **2** [10]. Comparison with experiment for several compounds suggests that the TDDFT data are probably reliable to within about 30 nm, giving a semiquantitative prediction of the positions of these longest-wavelength bands. There is a rough correlation of the energies of these bands with the HOMO–LUMO gaps, but, as expected, the gap is by no means equal to the transition energy. This is essentially because the calculated LUMO energy is not a good measure of the ionization energy of the excited state [99].

Synthesis

Michl and Balaji implied [1] that the still-unknown molecules **4**–**7** might be accessible by dehalogenation of appropriate precursors followed by trapping in a cryogenic matrix. This would be analogous to the conceptual progression from **1** to **7**, with elision of halogen atoms taking the place of removal of hydrogens, for example:



4

It was feared that **5** and **6** might abstract electrons from the alkali metal, because of their calculated low-level LUMOs (3.7 and 2.7 eV), although this was recognized as only a crude indication of the electron affinity. The synthesis of the dihalo (or polyhalo, for possible multistep one-pot syntheses) compounds was considered to be a major hurdle with this demetallation approach. We sketch below some possible synthetic alternatives to the above dehalogenation route.

Molecule **4** (Fig. 13.12). One fairly obvious suggestion arises from the relationship between cyclobutadienes and tetrahedranes, and the fact that **4** is a tetrahedrane.

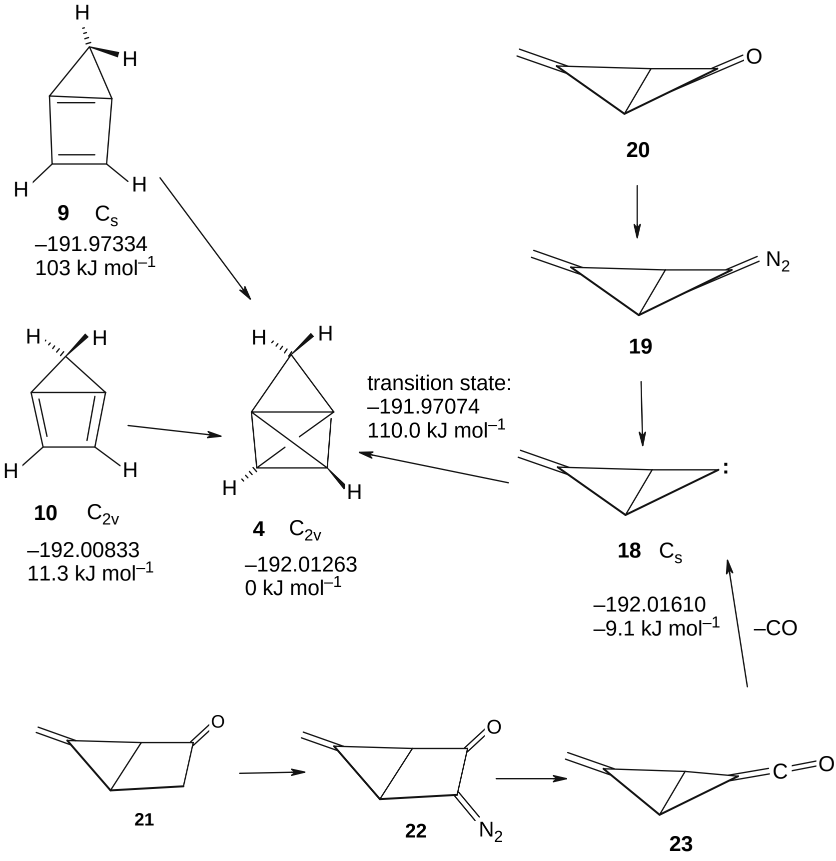
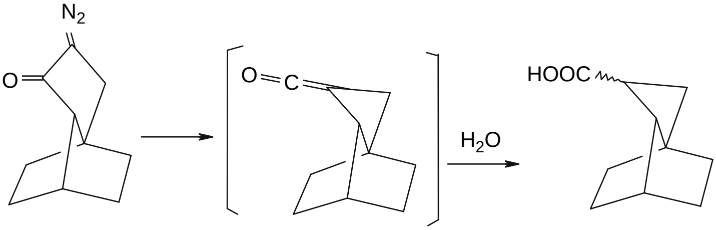


Fig. 13.12 Suggested syntheses of **4**. MP2/6-31G* ZPE-corrected energies and relative energies in kJ mol^{-1} are shown

We saw in Chapter 6 that tetrakis(trimethylsilyl)tetrahedrane can be made by photochemical isomerization of the corresponding cyclobutadiene, so **4** might be similarly accessible, and thermal reversion to **9**, at least, is not expected. However, the synthesis of **9** or **10** poses challenges of its own. Another approach is to recognize that **4** is a bicyclobutane and to construct the cyclopropane ring by carbene insertion into a CC double bond (cf. the synthesis of bicyclobutane by intramolecular carbene addition to a CC double bond [100]). The MP2/6-31G* energies of the reaction profile (Fig. 13.12) indicate that this may work, provided the calculations have erred in placing the carbene **18** (slightly) below **4**, rather than above it. The carbene precursor might be synthesized from a diazomethylenebicyclobutane **19**, which may be preparable from the corresponding methylenebicyclobutanone **20**. However, the bicyclobutanes will almost certainly be unstable compounds (the dimethylene analogue of **20** is very unstable [101]) and the synthetic manipulations needed to convert **20** to **19** may not be feasible in practice. More promising is the synthesis of 5-methylenebicyclo[2.1.0]-2-one, **21**, and its conversion to a diazo ketone **22**; these molecules have a cyclobutanone ring in lieu of the cyclopropanone ring of **20** and the cyclopropanone-like ring of **19**, and so may be more tractable. Photolysis of **22**, if necessary under matrix isolation conditions, might result in ring contraction to the ketene **23** followed by extrusion of carbon monoxide and formation of the carbene **18**. These are standard organic chemistry reactions, but there is no guarantee that they would work in this particular case. An example of the synthesis of a strained molecule by ring contraction of a diazo ketone to a ketene is [102]:



Molecule **5** (Fig. 13.13). A possible synthesis of this, suggested in Chapter 2, is recapitulated here. The carbene-bridged bicyclobutane **25**, possibly accessible from

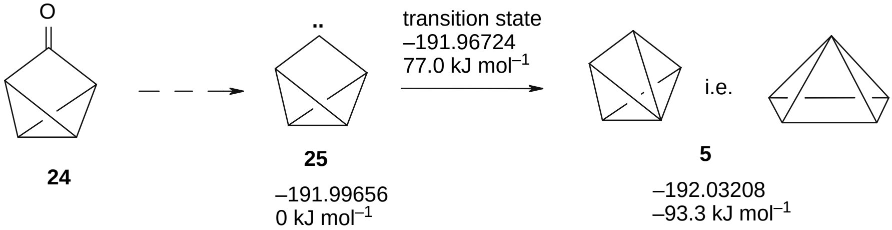
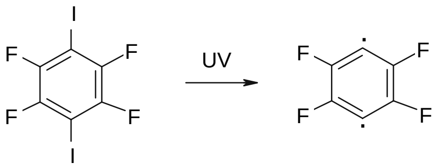


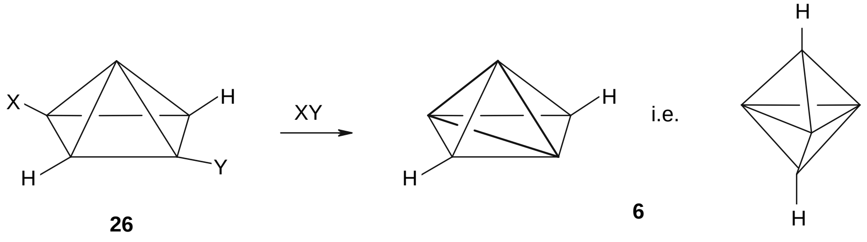
Fig. 13.13 A suggested synthesis of **5** (Chapter 2). MP2/6-31G* ZPE-corrected energies and relative energies in kJ mol^{-1} are shown

the known ketone **24** [103], is calculated to insert into a C–H bond with a fairly low barrier of 77 kJ mol^{-1}, forming **5**, which lies 93 kJ mol^{-1} below **25**. Because of its predicted stability (Chapter 5) and the promising availability and reactivity of the carbene **25** (which may be available from several precursors), of the unknowns **4**–**7**, molecule **5** is the most promising candidate for synthesis.

Molecule **6** (Fig. 13.14). The most feasible route to **6** seems to be via **26**, some derivative of pyramidane, because of the predicted stability of pyramidane. If X and Y (Fig. 13.14) are halogens, then this could correspond to the metal-promoted approach suggested by Michl and Balaji for these molecules, but alternatives are conceivable. It might be possible to make a pyramidane with groups X and Y which can be photochemically removed under matrix isolation conditions with concomitant (formal?) C–C bond formation. One possibility is X = Y = I, by analogy with the preparation of tetrafluoro-*p*-benzyne [104]:



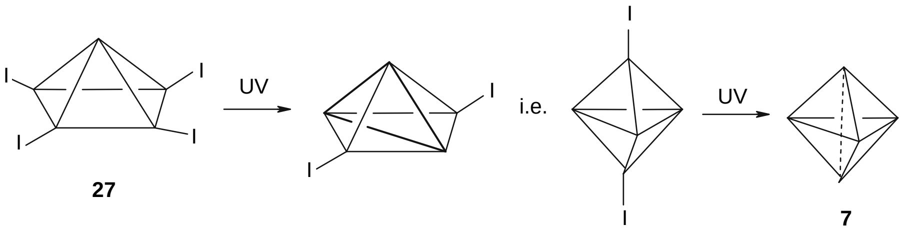
Molecule **7** (Fig. 13.15). A trivial extension of the approach suggested above for the synthesis of **6** leads to a putative route to 7, illustrated in Fig. 13.15 using specifically iodide as the photolabile group. Tetraiodopyramidane **27** is shown forming



26

6

Fig. 13.14 A suggested synthesis of **6**



27

7

Fig. 13.15 A suggested synthesis of **7**

diiodo-**6**, which in turn affords **7**. Of course these suggested syntheses of **6** and **7** are predicated on the hope that suitably substituted pyramidanes can be made.

Conclusions

The conceptual progression from **1** to **7** generates a series of exotic-looking molecules which are challenges to synthesis and theory. With the exception of the somewhat prosaic **1**, all exhibit unorthodox umbrella or pyramidal tetracoordinate bonding and are highly strained (taking bicyclobutane and cubane as examples of highly strained molecules). Calculations at the MP2/6-31G* and B3LYP/6-31G* levels predict that all seven can exist (are potential energy surface relative minima, real molecules), and experience indicates that these calculations are probably reliable as “existence theorems”. Of the known **1**, **2**, and **3**, compounds **1** and **2** are easily handled at room temperature and **3** appears to be stable in solution at ca. −25°C. Regarding the molecules **4**–**7**, the still-unknown members of the series, **4**, **6** and **7**, and perhaps **5**, may require matrix isolation techniques for their study. These further conclusions seem reasonable:

(1) Fusion of a cyclopropane ring onto tetrahedrane may render **4** kinetically and thermodynamically stabler than tetrahedrane (unfortunately we do not know how stable the parent tetrahedrane will be). Recognizing **4** as a bicyclobutane with an extra cyclopropane ring evokes the possibility of its synthesis from a methylenebicyclobutane carbene.

(2) Pyramidane, **5** (Chapter 2) is a very promising synthetic goal because of its likely fairly high kinetic stability. A plausible route to it is insertion into a C–H bond by a carbene-bridged bicyclobutane.

(3) The “bitetrahedrane” **6** probably has a tricarbene electronic nature (the three equatorial C–C bonds may be only formal), which may render it very reactive (probably limited to matrix isolation studies). It may be accessible from a pyramidane by 1,3-elimination of two groups from basal carbons.

(4) The bipyramidal carbon cluster **7** is electronically similar to **6**; here however the two apical carbons are approximately sp^2 rather than sp^3, with the two apical p atomic orbitals probably forming a long C–C bond. This molecule is likely to be particularly reactive and may be limited to matrix isolation studies. Also like **6**, molecule **7** may be preparable from a substituted pyramidane (via an intermediate disubstituted derivative of **6**).

Notes

1. A note on the correct application of the naming rules: J. Meinwald, J. K. Crandall, J. Am. Chem. Soc., 1966, *88*, 1292.
2. Chem. Rev., 1989, *89*(5), whole issue.

3. Cf. bicyclobutanes: M. R. Rifi, J. Am. Chem. Soc., 1967, *89*, 4442.
4. “The bonds are all pointing in the same direction”: remark with a dismissive gesture by R. B. Woodward to the author at a seminar, Harvard University, 1970.
5. The standard way of handling singlet diradicals like **8** is by complete active space self-consistent-field calculations (CASSCF), occasionally by generalized valence bond calculations (GVB), both of which methods require from the chemist careful selection of certain parameters and the execution and examination of multistep procedures: e.g. I. N. Levine, “Quantum Chemistry”, Fifth Edn., Prentice Hall, Engelwood Cliffs, NJ, 2000; pp. 448–449 (CASSCF), pp. 612–613 (GVB). Attempts to use DFT to make calculations on singlet diradicals more purely algorithmic, i.e. “model chemistries” (J. A. Pople, Acc. Chem. Res., 1970, *3*, 217) are in the development stage: (a) J. Gräfenstein, E. Kraka, M. Filatov, D. Cremer., Int. J. Mol. Sci., 2002, *3*, 360. (b) D. Cremer, M. Filatov, V. Polo, E. Kraka, S. Shaik, Int. J. Mol. Sci., 2002, *3*, 604. (c) D. Cremer, Mol. Phys., 2001, *99*, 1899. (d) J. Gräfenstein, D. Cremer, Mol. Phys., 2001, *99*, 981. (e) J. Gräfenstein, A. M. Hjerpe, E. Kraka, D. Cremer, J. Phys. Chem., 2000, *104*, 1748. (f) A. Krylov, Acc. Chem. Res., 2006, *39*, 83.
6. The zero-bridge C–C bond length in bicyclo[2.2.0] hexane and the corresponding C/C distance in the 1,4-singlet diradical were calculated (CASSCF) to be 1.596 Å and 2.830 Å, respectively: D. A. Hrovat, W. T. Borden, J. AM. Chem. Soc., 2001, *123*, 4069 (from the coordinates in the Supporting Information).
7. (a) A supposedly foolproof test for bonding is based on the quantum theory of atoms in molecules: R. F. W. Bader, J. Phys. Chem. A, 1998, *102*, 7314, and references therein. (b) An illustrative application of the methods of ref. (a): R. F. W. Bader, C. F. Matta, Inorg. Chem., 2001, 20, 5603. (c) A claimed case of failure of the methods of ref. (a): J. Poater, M. Solà, F. M. Bickelhaupt, Chem. Eur. J. , 2006, *12*, 2889. (d) A polemic in defense of the methods of ref (a) against the assault of ref. (c): R. F. W. Bader, Chem. Eur. J. , 2006, *12*, 2896. (e) A rebuttal of ref. (d): J. Poater, M. Solà, F. M. Bickelhaupt, Chem. Eur. J. , 2006, *12*, 2902. (f) S. Ritter, Chem. Eng. News, 2007, *January 29*, 37; letter: J. S. Miller, Chem. Eng. News, 2007, *March 19*, 8. (g) Issue devoted to bonding: J. Comp. Chem., 2007, *28*(1), whole issue.

References

1. V. Balaji, J. Michl, Pure and Appl. Chem., 1988, *60*, 189.
2. D. Hellwinkel, “Systematic Nomenclature of Organic Chemistry”, Springer, New York, 2001.
3. K. B. Wiberg, Angew. Chem. Int. Ed. Engl., 1986, *25*, 312.
4. J. F. Liebman, A. Greenberg, Chem. Rev., 1976, *76*, 311.
5. K. B. Wiberg, D. S. Connor, Tetrahedron Lett., 1964, *9–10*, 531.
6. K. B. Wiberg, D. S. Connor, J. Am. Chem. Soc., 1966, *88*, 4437.
7. M. R. Rifi, Tetrahedron Lett., 1969, *13*, 1043.
8. J. Meinwald, W. Szkrybalo, D. R. Dimmel, Tetrahedron Lett., 1967, *8*, 731.
9. R. Srinivasan, K. H. Carlough, J. Am. Chem. Soc., 1967, *89*, 4932.
10. M. D. Levin, P. Kaszynski, J. Michl, Chem. Rev., 2000, *100*, 169.
11. U. Bunz, G. Szeimies, Tetrahedron Lett., 1990, *31*, 651.
12. K. B. Wiberg, H. H. Walker, J. Am. Chem. Soc., 1982, *104*, 5239.
13. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; section 6.1, and refs. 20, 21.
14. P. Kaszynski, J. Michl, J. Org. Chem., 1988, *53*, 4593.
15. P. Kaszynski, A. C. Friedli, J. Michl, J. Am. Chem. Soc., 1992, *114*, 601.
16. P. E. Eaton, G. H. Temme, J. Am. Chem. Soc., 1973, *95*, 7508.
17. D. P. G. Hamon, V. C. Trenerry, J. Am. Chem. Soc., 1981, *103*, 4962, and refs. therein.
18. P. G. Gassman, G. S. Proehl, J. Am. Chem. Soc., 1980, *102*, 6862.

19. K. Mlinaric-Majerski, Z. Majerski, J. Am. Chem. Soc., 1980, *102*, 1418.
20. K. B. Wiberg, H. H. Walker, J. Michl, J. Am. Chem. Soc., 1982, *104*, 2056.
21. J. F. Liebman, A. Greenberg, "Strained Organic Molecules", Academic Press, New York, 1978; p. 344.
22. M. L. Herr, Tetrahedron, 1977, *33*, 1897.
23. F. A. Carey, R. J. Sundberg, "Advanced Organic Chemistry", Fourth Ed., Kluwer, Boston, 2000; Part A, p. 14.
24. E. Lewars, "Computational Chemistry", Kluwer, Boston, 2003; Chapters 5 and 7.
25. K. B. Wiberg, J. Wendoloski, J. Am. Chem. Soc., 1982, *104*, 5679.
26. P. George, M. Trachtman, C. W. Bock, A. M. Brett, Tetrahedron, 1976, *32*, 317.
27. P. R. Khoury, J. D. Goddard, W. Tam, Tetrahedron, 2004, *60*, 8103.
28. P. R. Khoury, J. D. Goddard, W. Tam, Tetrahedron, 2004, *60*, 8103.
29. K. B. Wiberg, J. Am. Chem. Soc., 1983, *105*, 1227.
30. M. A. Natiello, J. A. Medrano, Chem. Phys., 1984, *105*, 180.
31. M. A. Natiello, J. A. Medrano, Chem. Phys., 1984, *110*, 445.
32. L. C. Cusachs, P. Politzer, Chem. Phys., 1968, *1*, 529.
33. H. Hopf, "Classics in Hydrocarbon Chemistry", Wiley-VCH, Weinheim, New York, 2000; section 6.1.
34. A. B. Pierini, H. F. Reale, J. A. Medrano, J. Mol. Struct. (Theochem), 1986, *33*, 109.
35. J. E. Jackson, L. C. Allen, J. Am. Chem. Soc., 1984, *106*, 591.
36. R. F. W. Bader, T. H. Tang, Y. Tal, F. W. Ziegler-Koenig, J. Am. Chem. Soc., 1982, *104*, 940.
37. V. Polo, J. Andrés, B. Silva, J. Comp. Chem., 2007, *28*, 857.
38. T. Bar, K. Jug, Chem. Phys. Lett., 1996, *256*, 201.
39. D. Feller, E. R. Davidson, J. Am. Chem. Soc., 1987, *109*, 4133.
40. P. Politzer, K. Gesture, J. Mol. Struct. (Theochem), 1986, *28*, 245.
41. A. E. Reed, L. A. Curtis, F. Weinhold, Chem. Rev., 1988, *88*, 899.
42. F. A. Carey, R. J. Sundberg, "Advanced Organic Chemistry", Fourth Ed., Kluwer, New York, 2000; Part A, section 1.1.1.
43. G. D. Andrews, J. E. Baldwin, J. Am. Chem. Soc., 1977, *99*, 4851.
44. J. I. Brahman, L. E. Ellis, E. E. van Tamelen, J. Am. Chem. Soc., 1966, *88*, 846.
45. E. E. van Tamelen, L. E. Ellis, J. I. Brahman, J. Am. Chem. Soc., 1967, *89*, 5073.
46. E. E. van Tamelen, J. I. Brahman, L. E. Ellis, J. Am. Chem. Soc., 1971, *93*, 6145.
47. E. E. van Tamelen, S. P. Pappas, J. Am. Chem. Soc., 1963, *85*, 3297.
48. K. E. Wilzbach, J. S. Ritscher, L. Kaplan, J. Am. Chem. Soc., 1967, *89*, 1031.
49. S. Masamune, J. Am. Chem. Soc., 1964, *86*, 735.
50. J. Trotter, C. S. Gibbons, N. Nakatsuka, S. Masamune, J. Am. Chem. Soc., 1967, *89*, 2792.
51. C. S. Gibbons, J. Trotter, J. Chem. Soc., 1967, *12*, 2027.
52. G. L. Closs, R. B. Larrabee, Tetrahedron Lett., 1965, *4*, 287.
53. J. Meinwald, J. K. Crandall, J. Am. Chem. Soc., 1966, *88*, 1292.
54. P. Dowd, H. Irmgartinger, Chem. Rev., 1989, *89*, 985.
55. R. Gleiter, R. Haider, P. Bischof, S. Zefirov, A. M. Boganov, J. Org. Chem., 1984, *49*, 375.
56. S. R. Davis, C. Qin, Z. Zhao, Int. J. Quantum Chem., 2004, *96*, 411.
57. I. Oezkan, A. Kinal, M. Balci, J. Phys. Chem. A, 2004, *108*, 507.
58. D. W. Kohn, P. Chen, J. Am. Chem. Soc., 1993, *115*, 2844.
59. H. Ona, H. Yamaguchi, S. Masamune, J. Am. Chem. Soc., 1970, *92*, 7495.
60. G. Maier, S. Pfriem, U. Schäfer, K.-D. Malsch, R. Matusch, Chem. Ber., 1981, *114*, 3965.
61. P. Gund, T. M. Gund, J. Am. Chem. Soc., 1981, *103*, 4458.
62. M. Ekholm, V. Nevalainen, P. Pyykko, Finnish Chem. Lett., 1989, *16*, 107.
63. G. Maier, J. Neudert, O. Wolf, D. Pappusch, A. Sekiguchi, M. Tanaka, T. Matsuo, J. Am. Chem. Soc., 2002, *124*, 13819.
64. Y. Feng, L. Liu, J.-T. Wang, S.-W. Zhao, Q.-X. Guo, J. Org. Chem., 2004, *69*, 3129.
65. E. A. Chirkina, O. R. Sergeeva, L. B. Krivdin, Russian J. Org. Chem., 2000, *36*, 509.
66. R. A. Seburg, R. J. McMahon, J. F. Stanton, J. Gauss, J. Am. Chem. Soc., 1997, *119*, 10838.

67. R. D. Bach, O. Dmitrenko, J. Am. Chem. Soc., 2004, *126*, 4444.
68. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 2.
69. M. R. Siebert, D. J. Tantillo, J. Org. Chem., 2006, *71*, 645.
70. N. P. Bowling, R. J. Halter, J. A. Hodges, R. A. Seburg, P. S. Thomas, C. S. Simmons, J. F. Stanton, R. J. McMahon, J. Am. Chem. Soc., 2006, *128*, 3291, and refs. therein.
71. S. Dua, J. H. Bowie, J. Phys. Chem. A, 2002, *106*, 1374.
72. J. M. L. Martin, J. El-Yazal, J.-P. Francois, Chem. Phys. Lett., 1996, *252*, 9.
73. D. W. Ewing, G. V. Pfeiffer, Chem. Phys. Lett., 1987, *134*, 413.
74. E. E. Pasqualini, M. López, Chem. Phys. Lett., 2000, *320*, 415.
75. S. Hobday, R. Smith, J. Chem. Soc., Faraday Trans., 1997, *93*, 3919.
76. P. F. Bernath, K. H. Hinkle, J. J. Keady, Science, 1989, *244*, 562.
77. A. A. Zavitsas, J. Phys. Chem. A, 2003, *107*, 897.
78. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; sections 5.5.1 and 7.3.1.
79. J. Cason, R. L. Way, J. Org. Chem., 1949, *14*, 31, and refs. therein.
80. K. B. Wiberg, G. M. Lampman, Tetrahedron Lett., 1963, *30*, 2173.
81. R. Srinivasan, J. Am. Chem. Soc., 1963, *85*, 4045.
82. D. M. Lemal, F. Menger, G. W. Clark, J. Am. Chem. Soc., 1963, *85*, 2529.
83. G. W. Griffen, A. P. Marchand, Chem. Rev., 1989, *89*,997.
84. S. G. Lias, J. E. Bartmess, J. F. L. Holmes, R. D. Levin, W. G. Mallard, J. Phys. Chem. Ref. Data, 1988, *17*, Suppl. 1., American Chemical Society and American Institute of Physics.
85. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 315–316.
86. G. Bieri, F. Burger, E. Heilbronner, J. P. Maier, Helv. Chim. Acta., 1977, *60*, 2213.
87. R. Gleiter, K.-H. Pfeifer, G. Szeimies, U. Bunz, Angew. Chem. Int. Ed. Engl., 1990, *29*, 413.
88. E. Honegger, H. Huber, E. Heilbronner, W. P. Dailey, K. B. Wiberg, J. Am. Chem. Soc., 1985, *107*, 7172.
89. T. Bajorek, N. H. Werstiuk, Can. J. Chem., 2005, *83*, 1352.
90. H. M. Muchall, N. H. Werstiuk, B. Choudhury, Can. J. Chem., 1998, *76*, 221.
91. L. A. Curtiss, K. Raghavachari, Theor. Chem. Acc., 2002, *108*, 61.
92. G. A. Petersson, “Computational Thermochemistry”, K. K. Irikura, D. J. Frirup, eds., American Chemical Society, Washington, DC, 1998.
93. A. P. Scott, L. Radom, J. Phys. Chem., 1996, *100*, 16502.
94. G. Vacek, J. M. Galbraith, Y. Yamaguchi, H. F. Schaefer, R. H. Nobes, A. P. Scott, L. Radom, J. Phys. Chem., 1994, *98*, 8660.
95. G. Vacek, B. T. Colegrove, H. F. Schaefer, Chem. Phys. Lett., 1991, *177*, 468.
96. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 419–421.
97. E. V. Anslyn, D. A. Dougherty, “Modern Physical Organic Chemistry”, University Science Books, Sausalto, CA, 2006; p. 943.
98. P. Wagner, A. B. F. Duncan, J. Chem. Phys., 1953, *21*, 516.
99. M. Klessinger, J. Michl, “Light Absorption and Photochemistry of Organic Molecules”, VCH, New York, 1993.
100. D. M. Lemal, F. Menger, G. W. Clark, J. Am. Chem. Soc., 1963, *85*, 2529.
101. G. J. Snyder, D. A. Dougherty, J. Am. Chem. Soc., 1989, *111*, 3942.
102. P. E. Eaton, P. G. Jobe, I. D. Reingold, J. Am. Chem. Soc., 1984, *106*, 6437.
103. P. Dowd, H. Irngartinger, Chem. Rev., 1989, *89*, 885.
104. H. H. Wenk, A. Balster, W. Sander, D. A. Hrovat, W. T. Borden, Angew. Chem. Int. Ed. Engl., 2001, *40*, 2295.
105. O. Schafer, M. Allan, G. Szeimies, M. Sanktjohanser, J. Am. Chem. Soc., 1992, *114*, 8180.

Chapter 14
Summary

Introduction

In Chapters 1–13 we examined the theoretical and experimental consensus on a medley of molecules. These were presented in no obvious order, the better, one hopes, to conjure a feeling of surprise and fascination, engendered by the protean possibilities dormant in the chemistry of common elements like carbon, oxygen, nitrogen, and the aloof helium. In this chapter we shall retrospectively assess the thirteen computational interrogations, ordering them more soberly according to five unifying themes:

(1) A tetracoordinate carbon atom with a planar or pyramidal disposition of its bonds (Chapters 1 and 2), or the butterfly stereochemistry of the scaffolding carbons of polyprismanes (Chapter 12), represents an assault on stereochemical orthodoxy. We would like to know if molecules harboring such entities can exist, and what their properties would be.

(2) Some molecules assault valence orthodoxy. Nitrogen pentafluoride and helium compounds (Chapters 4 and 5) require, if they exist, that the the bonding power of the key atom exceed that shown in any of its known compounds (for helium the known bonding power and number of its combinatorial progeny is in fact zero).

(3) A molecule may show no obvious “existence flaws”, and indeed, by analogy with known relatives, may be expected to be capable of existence. Such a species is oxirene (Chapter 3), which embodies the structural features of the well-known oxirane (with a CC single bond) and cyclopropene (with a CH_2 in place of an O). Yet oxirenes remain elusive.

(4) Strain of various kinds challenges the existence of tetrahedrane (Chapter 6), orthogonene (Chapter 7), hexaphenylethane (Chapter 8), and the menagerie of Michl and Balaji (Chapter 13).

(5) The oligomeric (using the term to include even dimers) molecules of Chapters 9, 10, and 11 have in common that, intuitively, they should all decompose to small, stable, familiar molecules: CO, N_2, and CO_2 or, mainly, $CO_2 + N_2$.

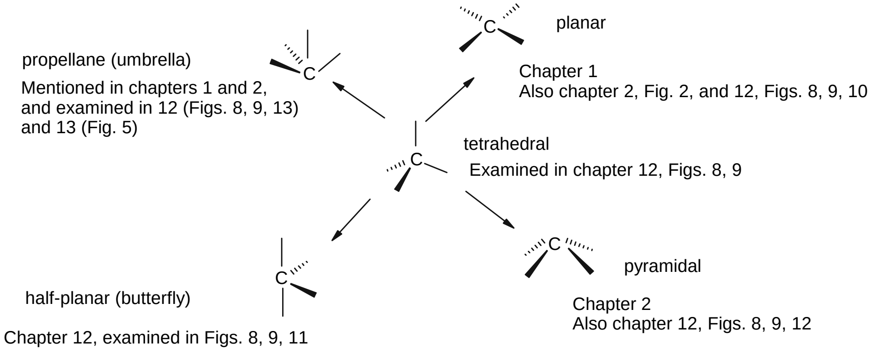
E.G. Lewars, *Modeling Marvels*, DOI: 10.1007/978-1-4020-6973-4_14,

For each of the above species which appears capable of existence we would of course also welcome plausible suggestions as to how it might be synthesized, and in the preceding chapters such suggestions were proffered. Here we will see if any unifying synthesis themes can be found.

Our Medley of Molecules, Arranged by Common Themes

Theme 1. Chapters 1, 2, and 12: planes, pyramids, butterflies and umbrellas: assaults on stereochemical orthodoxy.

The common theme here is distortion of orthodox tetrahedral tetracoordinate carbon toward four novel stereochemistries:



First, note that of these five kinds of geometry, manifested in CH_4, only tetrahedral CH_4 is a “real” molecule, i.e. a relative minimum on the potential energy surface. Reproducing here Fig. 9 from Chapter 12 as Fig. 14.1, we see that apart from tetrahedral methane, which is of course a minimum, only two of the five (two specific geometries of propellane CH_4 are shown) are stationary points on the CH_4 potential energy surface, and these are higher-order saddle points, with four and three imaginary frequencies. A transition state is a first-order saddle point, with one imaginary frequency, and higher-order saddle points are rarely chemically significant: only minima and transition states play a part in chemical reactions [1]. Nevertheless, examination of the structures in Fig. 14.1 provides some indication of the energetic demands of the four kinds of distortions; this is shown explicitly in Fig. 14.2. The ordering bears some resemblance to the experimental situation, but a good correspondence cannot be expected because the CH_4 structures are idealizations of possible actual molecules, and furthermore the reactivity of a particular species depends on its kinetic and thermodynamic relationship to proximate reaction products; this is particularly clear for [2.2.2]- and [1.1.1]propellane, below (a structure may be bad, but can it readily go to something better?).

The canonical tetrahedral carbon is lowest, and the structure which can be regarded as borderline tetrahedral/propellane is next. This lies only 103 kJ mol^{-1} above tetrahedral CH_4, and molecules with this kind of carbon atom might have

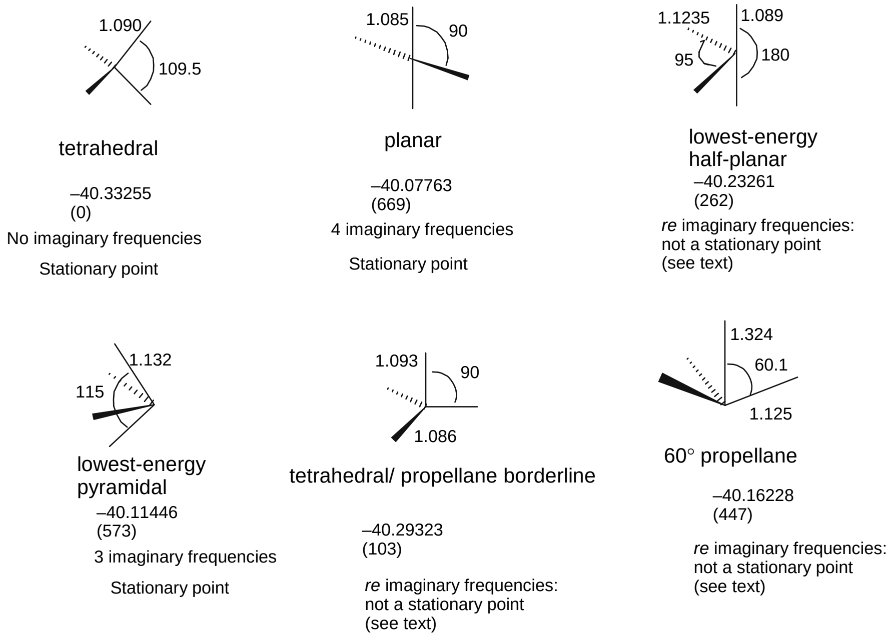
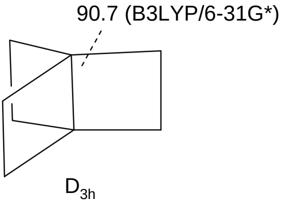


Fig. 14.1 (= Fig. 9 in Chapter 12). The five notable CH_4 structures (two explicit geometries are shown for propellane CH_4), MP2/6-31G* geometries (cf. Fig. 8 in Chapter 12). Tetrahedral CH_4 is the only "real" molecule here and the standard with which the others are compared. Planar and pyramidal CH_4 are stationary points. The half-planar structure shown is a minimum along its distortion curve but is not a stationary point. No propellane structure is a distortion minimum or a stationary point; the 60° structure shown has an HCH angle similar to the corresponding CCC angle calculated for [1.1.1]propellane. The MP2/6-31G* energies in hartrees (atomic units) and relative energies (kJ mol^{-1}, in parentheses) are given

been expected to be reasonably stable. However, [2.2.2]propellane, which has two such carbons, is highly reactive [2, 3]:[1]



This is not so surprising in view of the discussion centered on Fig. 13.2 in Chapter 13, where we saw that the reactivity of small-ring propellanes is influenced by their strain relative to the diradical resulting from central bond cleavage, a fact responsible for the remarkable stability of [1.1.1]propellane.

Lying next above tetrahedral/propellane CH_4 is the half-planar arrangement with a CCC angle of 95°. Molecules with truly half-planar carbons appear to be unknown,

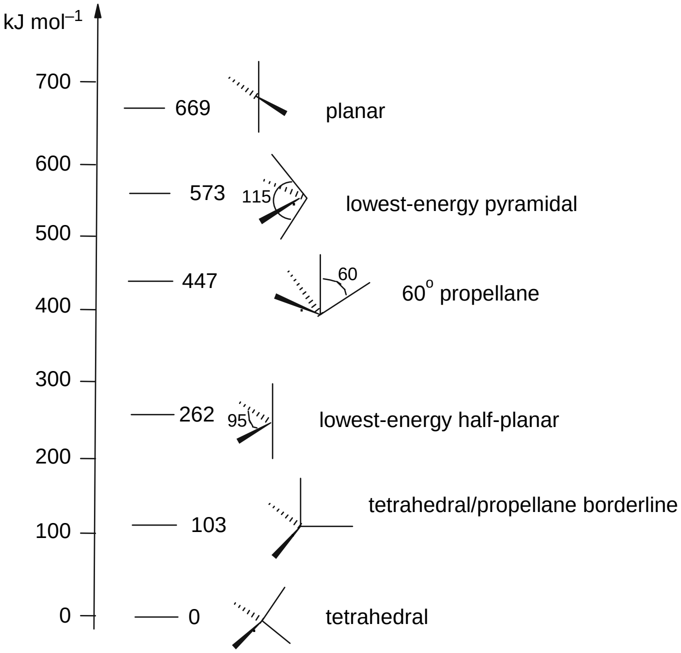


Fig. 14.2 The structures of Fig. 1 arrayed by relative energy; cf. Chapter 12, Fig. 12.9

although a highly reactive system with a nearly linear CCC angle (but with this bond line not perpendicular to the appropriate plane) has been made [4] (see Chapter 12, *Other Candidates for Half-Planar or Linear C-C-C Carbons*).

Well above half-planar CH_4 is 60^o propellane CH_4, with a geometry corresponding to the bridgehead carbons of the stable compound [1.1.1]propellane [5, 6] (discussed in Chapter 12, *The energetics and electronic structure of the characteristic polyprismane, and other distorted, carbons*, and in Chapter 13; see Fig. 14.2 and Table 14.1). Wiberg's anticipation of the stability of this contorted molecule came from the realization that the energy needed to break the central bond is higher for this propellane than for its homologues, due to the high energy of the product diradical.

Above the 60° propellane structure we find the lowest-energy pyramidal CH_4, with CCC = 115°. The canonical pyramidal hydrocarbon pyramidane (Chapter 2) is calculated to have an apical CCC angle of only 76.0^o, which must correspond to minimization of the pyramidal C_5H_4 energy with respect to all geometric parameters (a C_{4v} pyramidane structure with an apical CCC angle of 115° is not geometrically absurd; for example, a molecular mechanics structure with this angle had basal CC lengths of 1.673 Å and base-apex lengths of 1.403 Å). Pyramidane is predicted to be surprisingly stable, with a barrier to isomerization of about 100 kJ mol^{-1}, which may allow it to be isolated at room temperature [7, 8, 9]. The relatively high barrier may be because the lowest-energy pathway leads to a carbene in which a CC bond has been lost (Chapter 2, Fig. 2.3).

Table 14.1 Strain energies (SEs) of molecules from homodesmotic reactions (cf. Table 13.2, Chapter 13), MP2/6-31G* level, without ZPE; kJ mol^{-1}

Molecule	SE	SE/formal C–C	No. and kind of rings; sum of SE of rings	Ratio[a]
cyclopropane	127	127/3 42.3	1 ring, C_3; 1(127) = 127	127/127 = 1
cyclobutane	117	117/4 29.3	1 ring, C_4; 1(117) = 117	117/117 = 1
tetrahedrane	627	627/6 105	3 rings, 3 C_3; 3(127) = 381	627/381 = 1.6
1	295	296/6 49.2	2 rings, 2 C_4; 2(117) = 234	295/234 = 1.3
2	435	435/7 62.1	3 rings, 3 C_3; 3(127) = 381	435/381 = 1.1
3	483	483/7 69.0	3 rings, 2 C_3 + 1 C_4; 2(127) + 1(117) = 371	483/371 = 1.3
4	727	727/8 90.9	4 rings, 4 C_3; 4(127) = 508	727/508 = 1.4
5	673	673/8 84.1	4 rings, 4 C_3; 4(127) = 508	673/508 = 1.3
6	1006	1006/9 112	5 rings, 5 C_3; 5(127) = 635	1006/635 = 1.6
7	1448	1448/10 145	6 rings, 6 C_3; 6(127) = 762	1448/762 = 1.9

[a] Ratio of SE to sum of SEs of component rings in isolation.

The highest-energy CH_4 stereochemistry is the planar one, and indeed planar carbon, without the electronic assistance of elements like lithium or boron, is unknown, and an elaborate scaffolding may be needed to constrain the maverick atom (Chapter 1).

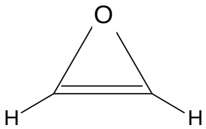
Theme 2. Chapters 4 and 5: how sociable can nitrogen be? And is helium really absolutely aloof? Assaults on valence orthodoxy.

The common theme here is really, and to the point, abnormal coordination number. As discussed in Chapter 4 (*Nitrogen Pentafluoride, the Octet Rule, and Hypervalency*), correct assignment of valence implies that we know how many electrons are really involved in bonding, while the coordination number of an atom simply denotes the number of atoms or groups that that atom is bonded to. The valence conundrum is tied to the question of hypervalency, and while this is interesting, our focus is on the question of how many atoms or groups nitrogen or helium can bond to, i.e. coordinate with. Current investigations ask specifically whether nitrogen can be pentacoordinate and helium dicoordinate (or monocoordinate, as in e.g. $HeCCH^+$). Since plausible electron-deficient bonding models exist for pentacoordinate nitrogen and dicoordinate helium (Chapter 4, Fig. 4.5; Chapter 5, Fig. 5.2) the octet and duplet rules, even if they were sacrosanct, are not necessarily violated. There appears to be no experimental evidence for species with nitrogen bonded to more than four atoms or groups, although quite high-level computations indicate that NF_5 can exist (e.g. [19] in Chapter 4). Helium bonded to a proton (HHe^+) has long been known, and the analogous $HeCCH^+$ cation seems to be a very realistic synthetic target. There is reasonable computational evidence for the possibility of a handful of helium compounds: the $FHeO^-$ ion (Chapter 5, *Overview of the Chemistry of Neon, Argon, Krypton, Xenon, (Radon)*), and the molecules HeBeO and HHeF, the latter perhaps requiring confinement in solid helium (Chapter 5, *Helium Compounds*). The factor obstructing the ability of nitrogen and helium to be hypercoordinate is atomic size. This manifests itself in different ways for the two atoms: for nitrogen, the problem is physical crowding, and for helium it is orbital size.

In the case of nitrogen the question is whether five fluorine atoms can be squeezed on to a nitrogen atom. Although calculations predict NF_5 to be a potential energy surface minimum, there is enough doubt about the ability of ab initio calculations to accurately handle molecular size (related somewhat to nonbonded interactions [10]) for one to be less than fully confident that this compound will be synthesized.

For helium the size problem is subtler than for nitrogen. For HHeF, for example, a favored bonding model requires a 1s atomic orbital (AO) on helium to mix with a 1s AO on hydrogen and a 2p AO on fluorine, forming the 3-center-2-electron bond (Chapter 5, Fig. 5.2). However, the helium 1s AO is much smaller than the fluorine 2p AO, and this difference in size results in poor overlap; the disparity in energy also limits the extent to which the wavefunctions can mix [11].

The denouement of these considerations is that at present it is not possible to be confident that nitrogen pentafluoride can exist, because of the difficulty of reliably taking into account the steric requirements of accommodating the fluorines. Helium, however, can likely form compounds, albeit fragile ones, such as HeBeO and HHeF.
Theme 3. Chapter 3: oxirene, subtly but fatally flawed?



This molecule has been put in a class by itself because it is the only one we have discussed for which the conventional structural formula (its Kekulé structure) looks quite normal, yet extensive computational study has failed to convincingly show that it can exist, and careful experimental studies have failed to provide convincing evidence for its synthesis (in fact, there is no definitive experimental evidence for the preparation of any oxirene). Let us review the essential relevant conclusions from the best calculations on oxirene, then look for a generalization and an analogy. In a 1994 publication, Scott et al. [12] concluded from what would still be regarded as quite high-level calculations that the potential energy surface in the region of oxirene and its ring-opened oxo carbene ("ketocarbene") isomer methanoylcarbene (formylcarbene) is very flat (the lows and highs in this region are no more than a few $kJ\ mol^{-1}$). Several calculations at good correlational levels with reasonably big basis sets led to similar results. Their best calculations showed oxirene and methanoylcarbene to lie in very shallow minima separated by a very small barrier of only $2\ kJ\ mol^{-1}$; the carbene rearranged to the far lower-energy ketene with a low barrier of $24\ kJ\ mol^{-1}$. This is shown in Fig. 14.3, which also illustrates how an isotopically

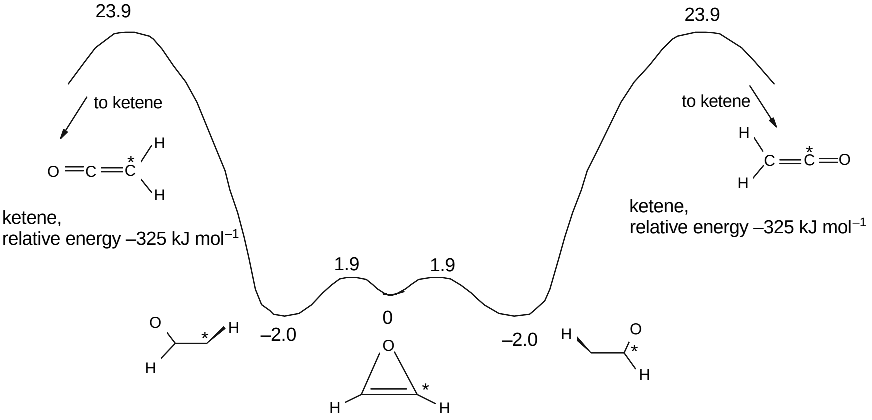
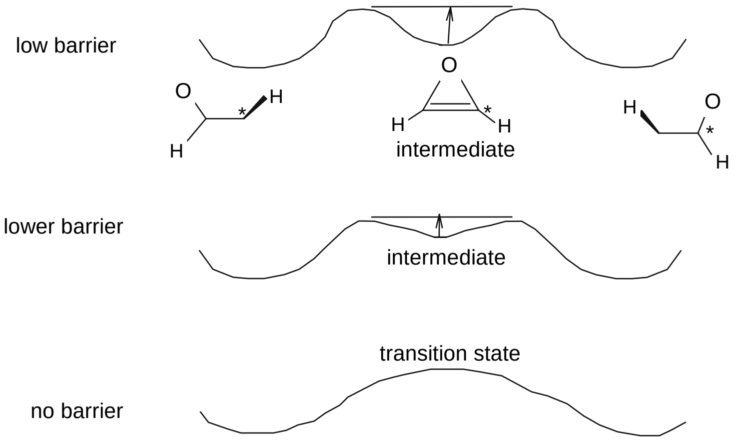


Fig. 14.3 (cf. Fig. 3.12) Calculated potential energy surface for the oxirene-methanoylcarbene (formylcarbene) interconversion and isomerization of the carbene to ketene. Based on the best CCSD(T) calculations of Scott et al. [12]. ZPE corrections are omitted here; the only significant effect of their inclusion is to raise the relative energy of the carbene slightly above that of oxirene

labeled carbene (or its diazo ketone precursor H–C*(N_2)–CHO or H–C(N_2)–C*HO) gives a ketene in which the label has been scrambled. This scrambling is the main evidence that the carbenes are interconverted through a species with the symmetry of oxirene, but it does not distinguish between an oxirene intermediate and an oxirene transition state.

If we could somehow continuously decrease the oxirene-to-carbene barrier, eventually an oxirene intermediate would lose its hold on reality and the carbenes would be connected not by an intermediate, but by a transition state:



If oxirene is a transition state there is no barrier separating it from the carbene (more precisely, the barrier is negative, because the curvature of the potential energy surface at a transition state is negative along the reaction coordinate [1]). The calculations of Scott et al. [12] do not settle whether oxirene and substituted oxirenes are intermediates with very low barriers to isomerization, or mere transition states; this question has been specifically addressed in other publications, without final resolution.[2]

We might conclude from this that whether a normal Kekulé structure represents a genuine molecule or just a transition state depends on whether there is a barrier to its isomerization. However, Nature offers another possibility. Consider cyclohexatriene (not benzene, but the hypothetical molecule with genuine single and double bonds). The situation here is that shown in Fig. 14.4, where we contrast benzene with cyclobutadiene. Benzene is a relative minimum and does not interconvert cyclohexatriene minima: the less symmetrical cyclohexatriene is not a stationary point on the PES, but represents only vibrational extremes [13, 14]. In contrast, square cyclobutadiene is a transition state connecting the symmetrical rectangular cyclobutadiene molecules, which are relative minima [15] (the different behavior of benzene and cyclobutadiene has been ascribed to differences in the distorting and symmetrizing effects of the σ and π electrons [13, 14]). We thus see that there are two ways in which a Kekulé structure might not correspond to a real molecule (a local minimum): it could be a transition state, or it may be a cross between two (or more) Kekulé structures – it may be a resonance hybrid (actually, benzene is a resonance hybrid not of the vibrationally distorted cyclohexatriene structures in Fig. 14.4, but of even more hypothetical bond-fixed cyclohexatriene structures with localized single and double bonds and the same

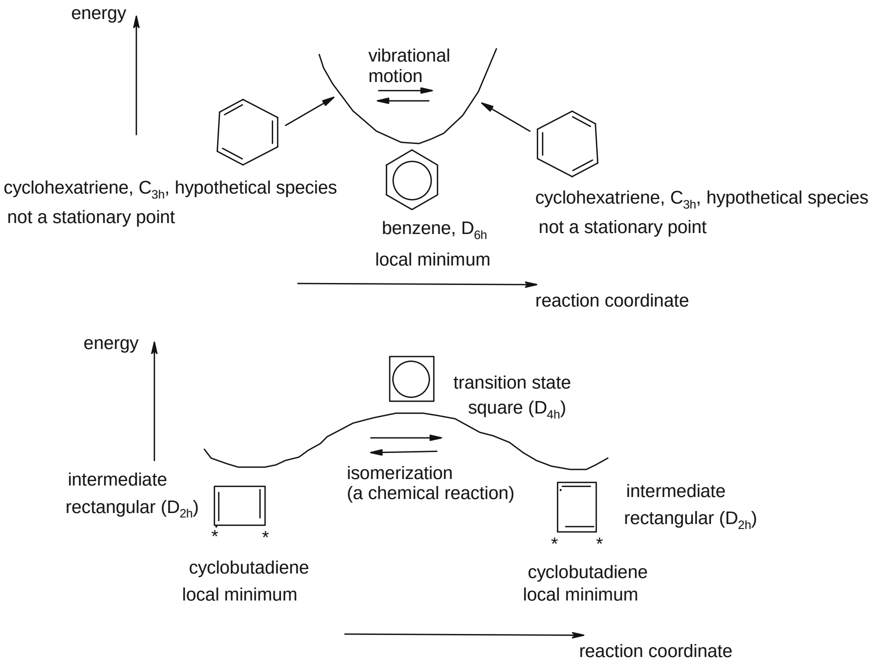


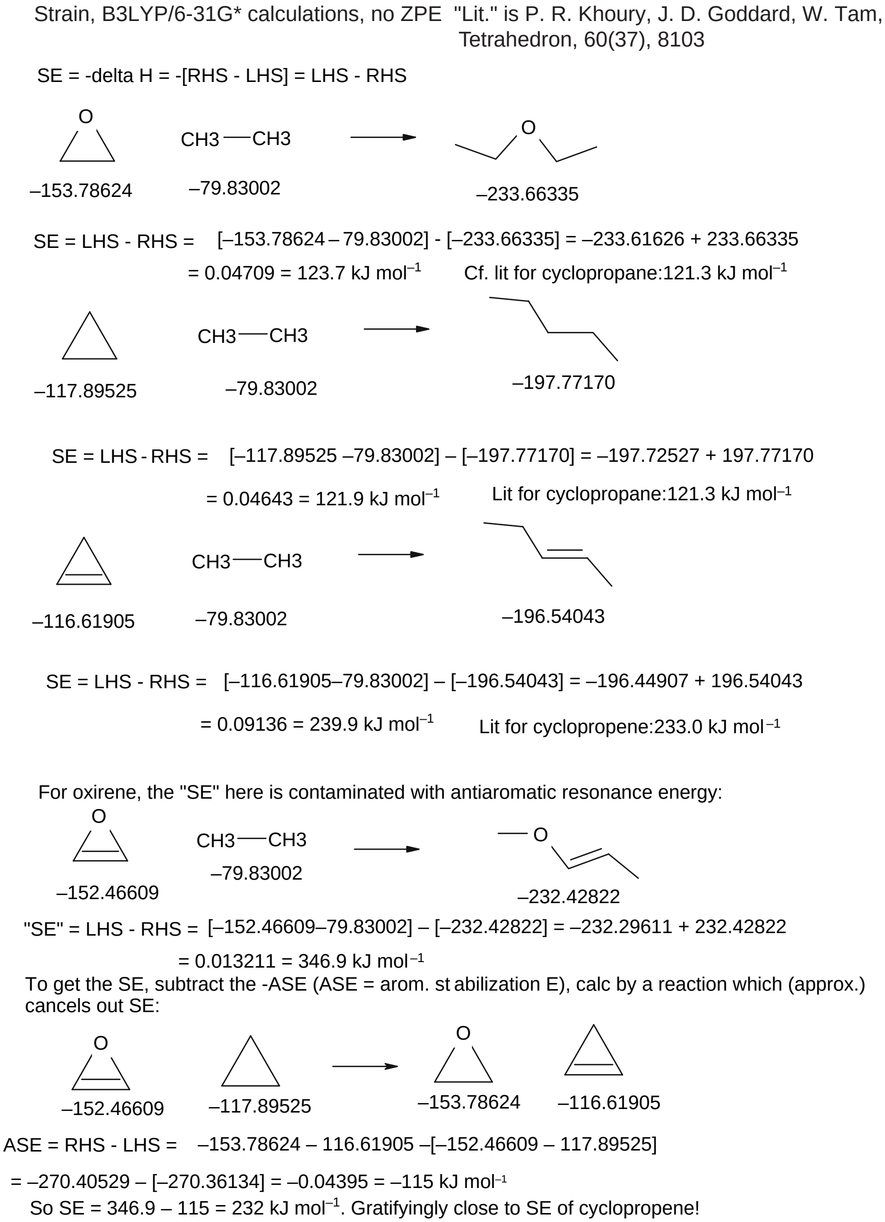
Fig. 14.4 Benzene/cyclohexatriene and square/rectangular cyclobutadiene on their potential energy surfaces (PESs), contrasted. See text

geometry as benzene [16]). The second possibility, a resonance hybrid, is not open to the oxirene/oxo carbene system, because oxirene and the carbene have distinctly different geometries. If oxirene is one of those molecules which cannot exist although a Kekulé structure can be drawn, then it is, like square cyclobutadiene, a transition state. Why might this be so? We expect oxirene to be destabilized by ring strain and antiaromaticity.

Like any three-membered carbocyclic or heterocyclic ring, oxirene should be a victim of ring strain or angle strain (Baeyer strain) caused by squeezing in bond angles from ca. 109° (sp^3 atoms) or ca. 120° (sp^2 atoms) to the geometric angle of ca. 60° [17]. Of course, the 60° interbond angle is only formal, since the bond paths lie outside the triangle defined by the three nuclei.[3] For molecules like oxirane, cyclopropane, and cyclopropene, ring strain energy (SE) can be readily calculated by a homodesmotic reaction (cf. e.g. Chapter 12, *Strain*) [18, 19], whose exothermicity is a measure of the SE of the molecule. In Fig. 14.5 the rings are opened with CH_3–CH_3; the results here for cyclopropane and cyclopropene are close to those reported by Khoury et al. using a slightly different method in their extensive compilation for hydrocarbons [19]. The "strain energy" of oxirene calculated in this way includes destabilizing antiaromaticity, because oxirene is a 4-π-electron ring system [20, 21], and could be called total cyclic destabilization. To obtain the SE one subtracts the destabilizing antiaromaticity. The aromatic stabilization energy, ASE, can be estimated from an isodesmic reaction in which the reactants and products have approximately equal total strain but only the molecule of interest has the cyclic conjugation associated with aromaticity or antiaromaticity [22]. In the convention we use here, ASE is positive for an aromatic molecule and negative for an antiaromatic one. In Fig. 14.5 the ring-opening energy release from oxirene (total cyclic destabilization, strain energy plus antiaromatic destabilization) is calculated as 347 kJ mol^{-1}; subtracting the antiaromatic destabilization (−ASE, 115 kJ mol^{-1}) gives a ring strain of 232 kJ mol^{-1}, comfortingly close to that obtained here for cyclopropene, 239.9 kJ mol^{-1}. These calculations thus indicate that oxirene is fairly strongly destabilized by ring strain and by antiaromaticity: its total cyclic destabilization, SE, and ASE (347 kJ mol^{-1}, 232 kJ mol^{-1}, and −115 kJ mol^{-1}) can be compared with those calculated by the same methods for say, cyclobutadiene, which is widely regarded as the canonical antiaromatic molecule [23]: total cyclic destabilization 332 kJ mol^{-1}, SE 180 kJ mol^{-1}, ASE −152 kJ mol^{-1} (by combining an experiment in which cyclobutadiene was generated with isodesmic reactions, Deniz et al. estimated for cyclobutadiene a total cyclic destabilization of 364 kJ mol^{-1}, which they dissected into 163–134 kJ mol^{-1} due to strain and 201–230 kJ mol^{-1} due to antiaromaticity [24]).

Theme 4. Chapters 6, 7, 8, and 13: tetrahedrane, orthogonene, hexaphenylethane, and the C_5 menagerie of Michl and Balaji. The challenge of strain.

These four molecules exhibit three different kinds of strain: tetrahedrane has ring strain or angle strain (Baeyer strain), which we saw as one of the destabilizing features of oxirene, orthogonene has what we might call twist strain, hexaphenylethane has steric strain, and the C_5 molecules derived from bicyclo[1.1.1] pentane have, again, angle strain.



Strain, B3LYP/6-31G* calculations, no ZPE "Lit." is P. R. Khoury, J. D. Goddard, W. Tam, Tetrahedron, 60(37), 8103

SE = -delta H = -[RHS - LHS] = LHS - RHS

SE = LHS - RHS = [–153.78624 – 79.83002] - [–233.66335] = –233.61626 + 233.66335

= 0.04709 = 123.7 kJ mol^{-1} Cf. lit for cyclopropane:121.3 kJ mol^{-1}

SE = LHS - RHS = [–117.89525 –79.83002] – [–197.77170] = –197.72527 + 197.77170

= 0.04643 = 121.9 kJ mol^{-1} Lit for cyclopropane:121.3 kJ mol^{-1}

SE = LHS - RHS = [–116.61905–79.83002] – [–196.54043] = –196.44907 + 196.54043

= 0.09136 = 239.9 kJ mol^{-1} Lit for cyclopropene:233.0 kJ mol^{-1}

For oxirene, the "SE" here is contaminated with antiaromatic resonance energy:

"SE" = LHS - RHS = [–152.46609–79.83002] – [–232.42822] = –232.29611 + 232.42822

= 0.013211 = 346.9 kJ mol^{-1}

To get the SE, subtract the -ASE (ASE = arom. stabilization E), calc by a reaction which (approx.) cancels out SE:

ASE = RHS - LHS = –153.78624 – 116.61905 –[–152.46609 – 117.89525]

= –270.40529 – [–270.36134] = –0.04395 = –115 kJ mol^{-1}

So SE = 346.9 – 115 = 232 kJ mol^{-1}. Gratifyingly close to SE of cyclopropene!

Fig. 14.5 Isodesmic reactions used to calculate strain energy and the aromatic stabilization energy of oxirene. See text

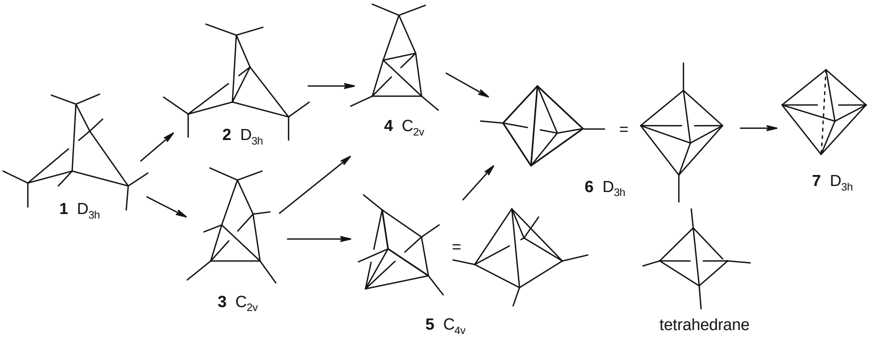
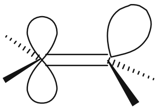


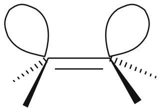
Fig. 14.6 The seven strained C_5 molecules and tetrahedrane. The structures are drawn from MP2/6-31G* geometries. The C–H bonds are indicated for clarity

Let us consider once again ring strain, focusing on tetrahedrane and the C_5 molecules (Chapters 6 and 13), which have in common that they are concatenations of small rings (Fig. 14.6). Except for bicyclo[1.1.1]pentane (**1**), tetrahedrane and the molecules **1**–**7** all have two or more fused three-membered rings, as shown in Table 14.1. For each of them the total ring strain exceeds the sum of the strain of the isolated component rings, the ratio being particularly high for tetrahedrane (1.6), **6** (1.6) and **7** (1.9). This is expected, since in conceptually building up a polycyclic molecule each new ring is geometrically constrained by those already in place.

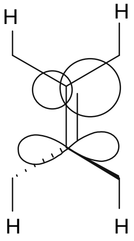
Moving on to orthogonene (Chapter 7): whereas the usual way a small ring can be destabilized is by angle distortion strain (above), an alkene can suffer strain from either pyramidal distortion or torsional (twisting) distortion (Fig. 14.7). Rings as well as alkanes and alkenes can also experience steric strain, caused by the mutual proximity of nonbonded groups – see below for hexaphenylethane. Pyramidal distortion or pyramidalization of an alkene is seen when the molecular framework constrains one or both alkene carbons to dispose its three σ bonds in a pyramidal rather than a planar manner [25]. Torsional distortion is the result of twisting around a CC double bond, so that the planes defined by the three groups at each end of the bond are not mutually coplanar, i.e. the alkene moiety is not flat. Like pyramidalization, this raises the energy of alkene compared to some similar but planar comparison molecule because p orbital overlap is reduced:



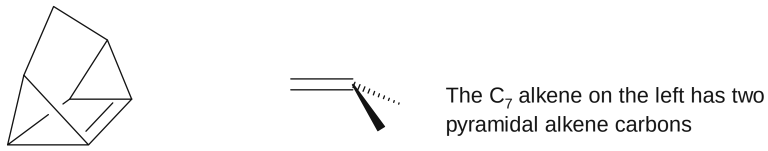
single pyramidal C=C



double pyramidal C=C

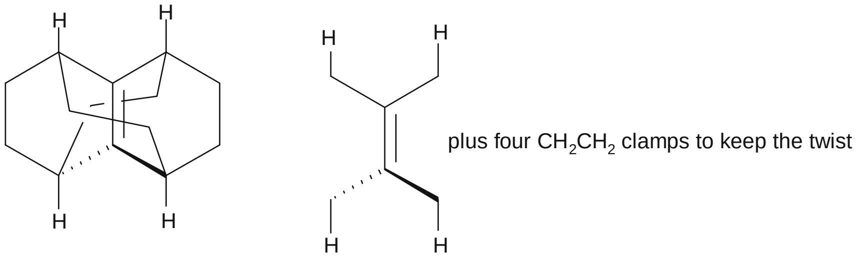


twisted C=C



5-dehydroquadricyclane

C_7H_6



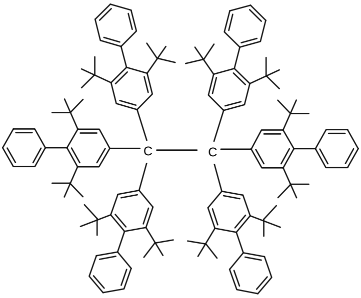
orthogonene

$C_{14}H_{20}$

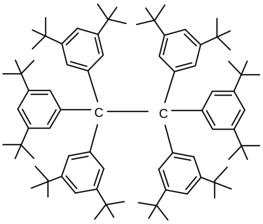
Fig. 14.7 A pyramidalized alkene and a twisted and alkene

In energy cost, how do these two modes of contorting an alkene compare? Figure 14.8 shows graphs for the rise in energy on going from normal, planar $H_2C{=}CH_2$ to $H_2C{=}CH_2$ distorted by twisting and by pyramidalization. Because of problems with optimizing the constrained geometries with the same quantum-mechanical method (MP2/6-31G* [26]) used to calculate the energies, the geometries were obtained by constrained (to force the desired degree of twisting or pyramidalization) molecular mechanics optimizations [27] and the energies calculated at those geometries (single-point energies [28]). Because we are dealing with different kinds of geometric distortion it is unclear how the extent of one should be compared with that of the other, but the impression from Fig. 14.8 is that the energy of an alkene rises very rapidly with twisting or with pyramidalization.

Finally on the subject of strain, consider hexaphenylethane (Chapter 8). The dimerization of the corresponding triarylmethyl radicals to give the isolable, well-characterized hexaarylethanes **8** and **9**, as well as computational studies, strongly indicate that hexaphenylethane can exist (Chapter 8, *Hexaphenylethane: The Modern Period*). So although the calculations of the groups of Mislow [29, 30, 31, 32] and Morokuma [33] indicate a long, weak central bond, due presumably to nonbonded steric interactions, which we could call steric strain [34, 35], hexaphenylethane is likely to be capable of existence. I argued in Chapter 8 that this incipient steric strain in the transition state for dimerization of the triphenylmethyl radical favors, or rather disfavors less, the alternative dimerization mode, which leads to a methylenecyclohexadiene.



8



9

Theme 5. Chapters 9, 10, and 11: $(CO)_2$, N_x, $(CO_2)_x$ and $(CO_2)_x(N_2)_y$. Dimers, oligomers, polymers on the edge.

The carbon monoxide dimer O=C=C=O, ethenedione, appears to differ fundamentally from dimers etc. (oligomers and polymers) based on nitrogen, on carbon

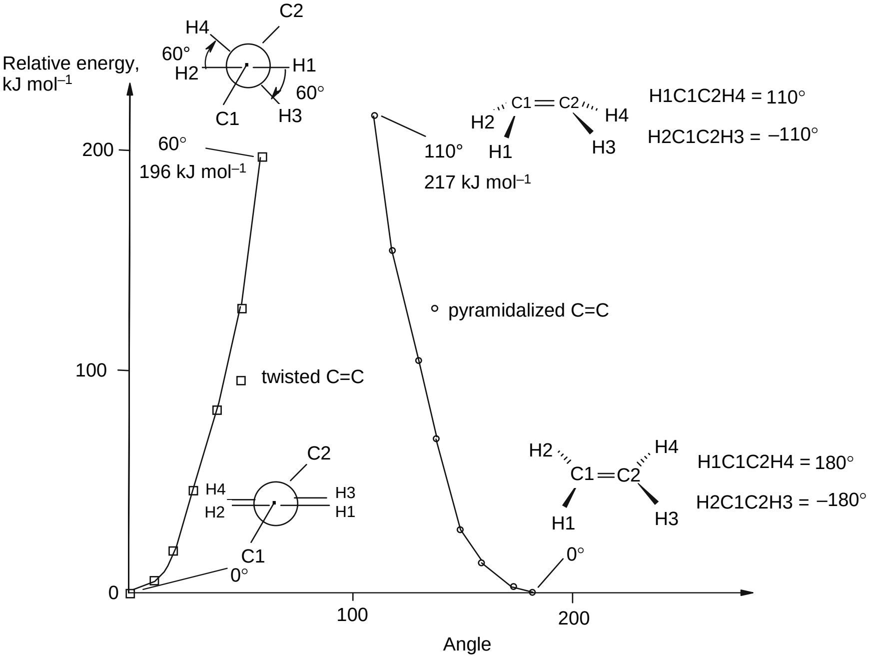


Fig. 14.8 The change in energy on going from a normal, planar CC double bond by twisting, and by pyramidalization. The energies are based on MP2/6-31G* single-point calculations on constrained molecular mechanics geometries and are only approximate. Here the extent of twisting is defined by dihedral angles which begin with 0°/0° in the planar structure and increase with the twist. The degree of pyramidalization is defined here by dihedral angles which begin with 180°/−180° in the planar structure and become less positive/less negative with increasing pyramidalization

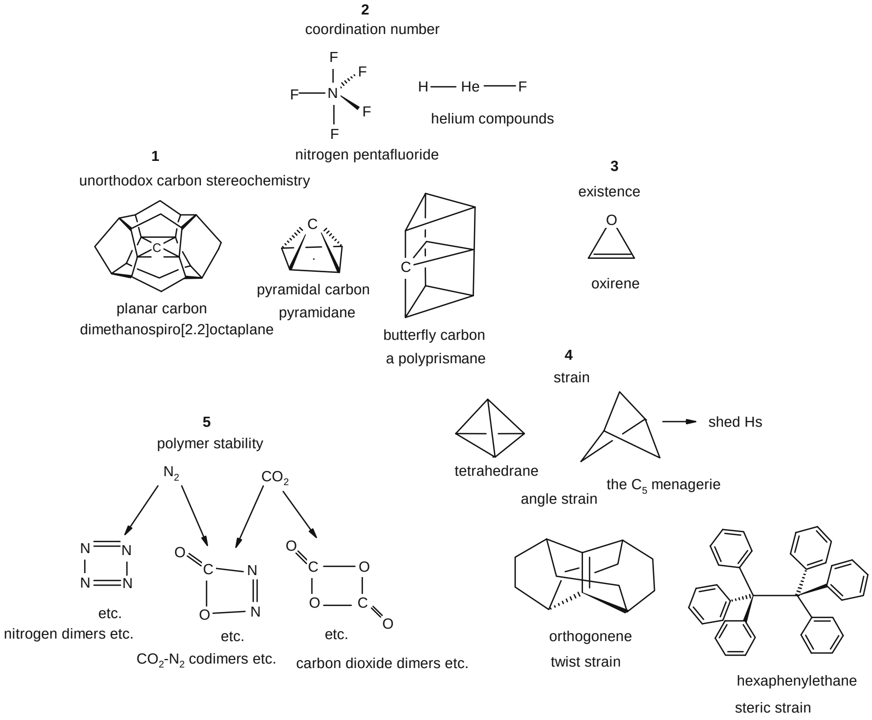
dioxide, and on nitrogen plus carbon dioxide. Whereas many of these latter species appear to be able to exist, although they may be fragile and require low temperatures for observation, O=C=C=O may be incapable of existence for fundamental theoretical reasons. As stated in Chapter 9, *Electronic Structure and Stability of Ethenedione*, the ground state of O=C=C=O corresponds to a triplet rather than the normal closed-shell singlet implied by the Kekulé structure. The singlet potential energy surface is apparently dissociative, with no ethenedione relative minimum. The triplet, in contrast, was thought to be stable (a relative minimum, isolable in principle). However, the work of Schröder et al. indicates that crossing of the two potential energy surfaces would cause the triplet to convert rapidly to the singlet, which would be expected to dissociate, giving the molecule a halflife of about 0.5 nanosecond [36]. This is enough the time for about 10^4 molecular vibrations (10^{-9} s cf. 10^{-13} s), so the existence of ethenedione is not absolutely ruled out, and as suggested in Chapter 9, its detection by femtosecond spectroscopy may be possible.

Nitrogen dimers, oligomers, and polymers have been the most thoroughly studied (computationally!) of the hypothetical polymers based on small, stable molecules (we do not exclude from consideration species with an odd number of atoms, or a few nonnitrogens, e.g. hydrogen). As we saw in Chapter 10, with the possible exception of the more baroque, polycyclic structures (for which calculation of accurate decomposition barriers is not yet feasible), few polynitrogens seem to hold promise for isolation at room temperature. The N_5^+ and of course the N_3^- ions are known. Among the neutrals we find a very few compounds which just might lend themselves to room-temperature isolation: compound/calculated decomposition barrier, kJ mol^{-1} – azidopentazole/ca. 80–100, octaazacubane/ca. 60–90, tetraazatetrahedrane/250 (but with the strong caveat that crossing to an excited potential energy surface may lead to facile decomposition), acyclic N_6/105–126. Compounds with calculated barriers of about 100 kJ mol^{-1} or lower are only borderline possibilities for handling at room temperature. Although polynitrogens are unpromising as kinetically stable high-energy-density materials, computational chemistry indicates that several of them should be isolable at low temperatures. Some, like octaazacubane, are likely to be synthetically intractable, but the acyclic chains, particularly N_6 (because of its structural relationship to azide ion), are attractive goals.

Dimers etc. of carbon dioxide, and codimers etc. of carbon dioxide and nitrogen, represent a problem somewhat similar to that of polynitrogens: what kinetic stability can we expect from these species (we do not expect them to be *thermodynamically* stable)? As they did for the polynitrogens, computations predict the potential existence of a large family of molecules based on CO_2 and on CO_2 plus N_2, and as was the case for the polynitrogens, none of these compounds seems to be particularly stable.

Metamedley

We come to the end of our foray into the realm of the exotic molecules, a realm represented by five themes:



In a sense the first question concerning any of these molecules is: can it exist? In principle this can be answered by performing a (sufficiently high-level!) calculation and seeing if it remains bound and shows no imaginary frequencies. A novel structure may simply dissociate on attempted geometry optimization, indicating that atomic configuration does not represent a stationary point on the potential energy surface; this will be the case for covalently bonded dihelium, which will optimize at best to two atoms in van der Waals contact. Or a novel structure may indeed optimize to a reasonable-looking covalently bound species, but among its vibrational frequencies may lurk one or more imaginary vibrations, showing that we have (at this level of calculation, anyway) a transition state or a higher-order saddle point. Such a straightforward attack on a molecular existence problem will in many cases yield a trustworthy answer, but a satisfying interpretation of the result may take us back to the reason we asked the question: our interest in the putative molecule likely arose because we suspected it to hold some unorthodox feature. Such a feature may have been (Themes 1–5) odd stereochemistry, an unprecedentedly high coordination number, a recalcitrance to synthesis out of keeping with an evidently orthodox structure, extraordinary strain, or intriguing potential metastability relative to stable subunits. These qualitative concepts, which can be intuitively apprehended, rescue our exotic molecule from dry contemplation as a point on a potential energy surface and allow us to ascribe to it a kind of personality.

Notes

1. The 2-carboxamide of [2.2.2]propellane: P. E. Eaton, G. H. Temme III, J. Am. Chem. Soc., 1973, *95*, 7508.
2. (a) Oxirene: G. Vacek, J. M. Galbraith, Y. Yamaguchi, H. F. Schaefer, R. H. Nobes, A. P. Scott, L. Radom, J. Phys. Chem., 1994, *98*, 8660. (b) Substituted oxirenes: G. Vacek, B. T. Colegrove, H. F. Schaefer, Chem. Phys. Lett., 1991, *177*, 468.
3. Review of strain: K. Wiberg, Angew. Chem. Int. Ed. Engl., 1986, *25*, 312.

References

1. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 2.
2. K. B. Wiberg, G. A. Epling, M. Jason, J. Am. Chem. Soc., 1974, *96*, 912.
3. J. J. Dannenberg, T. M. Provic, C. Hutt, J. Am. Chem. Soc., 1974, *96*, 913.
4. K. B. Wiberg, J. R. Snoonian, J. Org. Chem., 1998, *63*, 1390.
5. K. B. Wiberg, F. H. Walker, J. Am. Chem. Soc., 1982, *104*, 5239.
6. H. Hopf, “Classics in Hydrocarbon Chemistry”, Wiley-VCH, Weinheim, New York, 2000; section 6.1.
7. E. Lewars, J. Mol. Struct. (Theochem), 2000, *507*, 165.
8. E. Lewars, J. Mol. Struct. (Theochem), 1998, *423*, 173.
9. J. P. Kenny, K. M. Krueger, J. C. Rienstra-Kiracofe, H. F. Schaefer, J. Phys. Chem. A, 2001, *105*, 7745.
10. A. K. Rappé, E. R. Bernstein, J. Phys. Chem. A, 2000, *104*, 6117.
11. Y. Jean, F. Volatron, J. Burdett, “An Introduction to Molecular Orbitals”, Oxford University Press, New York, 1993; Section 3.2.2.
12. A. P. Scott, R. H. Nobes, H. F. Schaefer, L. Radom, J. Am. Chem. Soc., 1994, *116*, 10159.
13. P. C. Hiberty, D. Danovich, A. Shurki, S. Shaik, J. Am. Chem. Soc., 1995, *117*, 7760.
14. S. C. A. H. Pierrefixe, F. M. Bickelhaupt, Chem. Eur. J., 2007, *13*, 6321.
15. J. C. Santo-García, A. J. Pérez-Jiménez, F. Moscardó, Chem. Phys. Lett., 2000, *317*, 245.
16. J. H. van Lenthe, R. W. A. Havenith, F. Dijkstra, L. W. Jenneskens, Chem. Phys. Lett., 2002, *361*, 203–208.
17. A. Baeyer, Berichte, 1885, *18*, 2269.
18. P. George, M. Trachtman, C. W. Bock, A. M. Brett, Tetrahedron, 1976, *32*, 317.
19. P. R. Khoury, J. D. Goddard, W. Tam, Tetrahedron, 2004, *60*, 8103.
20. P. v. R. Schleyer, Chem. Rev., 2001, *101*, 1115, and refs. therein.
21. P. v. R. Schleyer, Chem. Rev., 2005, *105*, 3433, and refs. therein.
22. M. K. Cyrañski, T. M. Krygowski, A. R. Katritzky, P. v. R. Schleyer, J. Org. Chem., 2002, *67*, 1333.
23. T. Bally, Angew. Chem. Int. Ed. Engl., 2006, *45*, 6616.
24. A. A. Deniz, K. S. Peters, G. J. Snyder, Science, 1999, *286*, 1119.
25. R. N. Hoenigman, S. Kato, V. M. Bierbaum, W. T. Borden, J. Am. Chem. Soc., 2005, *127*, 17772, and refs. therein.
26. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; section 5.4.2.
27. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; Chapter 3.
28. E. Lewars, “Computational Chemistry”, Kluwer, Boston, 2003; pp. 241–242.

29. W. D. Hounshell, D. A. Dougherty, J. P. Hummel, K. Mislow, J. Am. Chem. Soc., 1977, *99*, 1916.
30. E. Osawa, Y. Onuki, K. Mislow, J. Am. Chem. Soc., 1981, *103*, 7475.
31. B. Kahr, D. van Engen, K. Mislow, J. Am. Chem. Soc., 1986, *108*, 8305.
32. N. Yannoni, B. Kahr, K. Mislow, J. Am. Chem. Soc., 1988, *110*, 6670.
33. T. Vreven, K. Morokuma, J. Phys. Chem. A, 2002, *106*, 6167.
34. T. T. Tidwell, Tetrahedron, 1978, *34*, 1855.
35. D. P. White, J. C. Anthony, O. Oyefeso, J. Org. Chem., 1999, *64*, 7707.
36. D. Schröder, C. Heinemann, H. Schwarz, J. N. Harvey, S. Dua, S. J. Blanksby, J. H. Bowie, Chem. Eur. J., 1998, *4*, 2550.

Index