A Survey of Strained Organic Molecules

JOEL F. LIEBMAN*[1a] and ARTHUR GREENBERG*[1b]

Departments of Chemistry, University of Maryland Baltimore County, Baltimore, Maryland 21228, and Frostburg State College, Frostburg, Maryland 21532

Received January 27, 1975 (Revised Manuscript Received June 16, 1975)

Contents

I. Introduction

It is part of both the art and science of organic chemistry to ascertain the stability of any arbitrary organic compounds.[2,3] Stability is somehow a simpler concept than reactivity since we need not have to ask "reactivity with what?" However, even if a study were restricted to stability and reactivity were neglected, the resultant review would be so long as to be both unreadable and unwritable. We therefore aim to present a relatively broad treatment, neither superficial nor exhaustive. Our purpose is to bridge the gap between an individual chapter in a graduate organic textbook and the many excellent review articles concerning relatively specific topics which will be cited herein when relevant. Most sections of this review can be read independently of the others, and the reader may indulge his specific interests.

Stability is always relative: we can only speak of "stabilization energy" (e.g., resonance, conjugation, or delocalization energy; steric attraction) or "destabilization energy" (e.g., strain or steric energy; negative resonance, conjugation or delocalization energy; steric repulsion) derived through comparison of the molecule in question with appropriate reference or model compounds. We have decided to focus this article on hydrocarbons and will consider substituted and hetero analogs only when they are needed to extend or verify a concept. Comparison with the thermodynamic standard states of graphite and gaseous hydrogen (i.e., the component elements in their most stable, naturally occurring, and standard states) provides insufficient intuitive understanding of the relationships between structure and energetics. (Any other single reference state such as atomic carbon and hydrogen would be of little use.) So as not to confuse inter- and intramolecular effects, we consider the molecule in the ideal gaseous state. Since most compounds of interest are either solids or liquids under standard temperature and pressure (25 °C, 1 atm), it is necessary to determine the heat of sublimation or vaporization of these species. For many compounds of interest, these data are nonexistent, although admittedly extensive compendia for hydrocarbons are available.[4-6] Let us assume that data exist for the compound as an ideal gas at 25 °C and 1 atm.

Unfortunately, even given data there are still conceptual problems. Cyclopropane, $(CH_2)_3$ or C_3H_6, is an archetypal destabilized molecule while benzene, $(CH)_6$ or C_6H_6, is an archetypal stabilized molecule. The experimental heats of formation of cyclopropane and benzene under the above conditions

TABLE I

Compd	ΔH_f°(gas, 25 °C), kcal/mol	Increment, kcal/mol
C_2H_6	−20.24	
		−4.59
C_3H_8	−24.83	
		−5.53
C_4H_{10}	−30.36	
		−4.74
C_5H_{12}	−35.10	
		−4.82
C_6H_{14}	−39.92	
		−4.93
C_7H_{16}	−44.85	
		−5.01
C_8H_{18}	−49.86	
		−4.80
C_9H_{20}	−54.66	
		−4.96
$C_{10}H_{22}$	−59.62	

are 12.7 and 19.8 kcal/mol, respectively.[7] (We remind the reader that the heat of formation, ΔH_f°, of a compound is defined as the heat absorbed or released upon formation from the standard states of the elements composing it.) These figures naively considered suggest that cyclopropane is the more stable. Are our archetypes misleading or misassigned? In accord with our labels of stabilized and destabilized, we note benzene is the most stable C_6H_6 isomer and a fortiori, the most stable $(CH)_6$ valence isomer. (Benzene and its valence isomers will be further discussed in section IX.) Likewise, cyclopropane is less stable than its isomer propene. (Cyclopropane will also be discussed later in this article; see section III.) Must we then limit our definition of stability to a set of chemical isomers? If so, we can never compare cyclopropane and benzene. Indeed, such common compounds as methane, ethane, ethylene, acetylene, and propane would be outside our understanding as they have no isomers unless we say that propane and an equimolar mixture of methane and ethylene are isomeric.

One possible solution to this problem is to use the molecule itself as part of its own reference state. That is, we consider the molecule as composed of either a collection of bonds, say C—C, C=C, and C—H, or as a collection of groups, say CH_3–, –CH_2–, –CH< and >C<.[8–10] As such, we have two fundamental models for molecular energetics, bond energies, and group increments. Both models are customarily used, although rarely together in the same paper. We will break precedent in that we will employ both. Let us consider cyclopropane and consider a variety of simple models for it. Admittedly, more sophisticated analogs of each model exist but they will not be discussed here. The first treatment considers cyclopropane as being composed of three C–C bonds and six C–H bonds. If it were to be neither stabilized nor destabilized caused by the above-mentioned effects, the total bond energy (or atomization energy as it is more commonly called) would equal the sum of the individual bond energies.[10a] For this, we need to know the normal C–C and C–H bond energy: we must have reference states but since C–C and C–H bonds are nearly ubiquitous in organic chemistry, this is a small price to pay. Admittedly somewhat naively, we may estimate the (normal) C–C bond energy as the energy required to dissociate C_2H_6 into two CH_3 groups, i.e., D(C–C) = $2\Delta H_f^\circ(CH_3) - \Delta H_f^\circ(C_2H_6) = 2(34 - (-20)) = 84$ kcal/mol.[9] Likewise, we may estimate the (normal) C–H bond energy as the energy required to dissociate CH_4 into CH_3 and H, i.e., D(C–H) = $\Delta H_f^\circ(CH_3) + \Delta H_f^\circ(H) - \Delta H_f^\circ(CH_4) = 33 + 52 - (-18) = 103$ kcal/mol.[9] Accordingly, the atomization energy of cyclopropane is computed to be 3(84) + 6(103) = 870 kcal/mol. The heat of formation and atomization energy ΔH_a of a hydrocarbon C_cH_h are interrelated by $\Delta H_a = c\Delta H_f^\circ(C(g)) + h\Delta H_f^\circ(H(g)) - \Delta H_f^\circ(C_cH_h(g)) = 171c + 52h - \Delta H_f^\circ(C_cH_h(g))$.[9] From the experimental heat of formation of cyclopropane, we thus find $\Delta H_a(C_3H_6) = 843$ kcal/mol, a discrepancy between the calculated and experimental heat of formation of some 27 kcal/mol. That is, we find cyclopropane to be 27 kcal/mol less stable than calculated. Corresponding, but slightly more refined calculations give discrepancies less than 1 kcal/mol for propane. Clearly, there is some stabilization found in propane, not found in cyclopropane, or, equivalently, there is some destabilization found in cyclopropane not found in propane.

Alternative related analyses include heat of combustion, hydrogenation, hydrolysis, and, *in general, heat of reaction.*[2–5,8,9] For example, one may compare the amount of energy liberated on hydrogenating cyclopropane to form propane with the corresponding quantity for converting ethane into two methanes. The fact that the former is rather trivially accomplished while the latter is not does not preclude this approach. Indeed, it probably facilitates it since any experimental assembly that converts ethane to methane would probably convert propane sequentially to ethane and methane. We would then compare the cyclopropane to methane and ethane to methane conversions. From the experimental data derived in other ways, we may compare all of these possibilities. The conversion or hydrogenation of cyclopropane to propane is accompanied by a release of 38 kcal/mol while the corresponding C–C bond cleavage in ethane and propane liberates only 16 and 13 kcal/mol, respectively. Again, we conclude there is some destabilization in cyclopropane, worth either 22 or 25 kcal/mol. The reader should note that these figures of 22 and 25 kcal/mol, indeed the above 27 kcal/mol, are not contradictory. We can only say that results are model dependent and that there is no unique best C–C or C–H bond strength.

Despite the above assertion, we now define a method that purports to give such a value, the method of group increments.[3–5,8,9] Carbons and hydrogens may be put together to form groups such as CH_3, CH_2, CH, and C as noted before. No claim is made that the C–H bond in each of these groups is equivalent to that of another, and indeed in more complicated versions of what follows corrections exist for what is bonded to what. Let us consider a particularly simple example, cyclopropane again. It is made of three CH_2 groups or fragments. The heat of one such methylene fragment (not to be confused with the triatomic molecule CH_2 itself) may be obtained from the series of straight-chain alkanes (see Table I). Somehow, we associate these species with being normal, and we hope for more reliable reasons than the prefix "*n*-" that is so often used. What value is to be chosen for the CH_2 increment? The increments all vary, and the heats of formation themselves are uncertain to a few tenths of a kcal/mol. The preferred value is clearly around −5 kcal/mol where the exact value depends on the exact literature reference used. The set of values that we will use gives −5.13 kcal/mol; the corresponding values for CH_3, CH, and C are −10.05, −2.16, and −0.30 kcal/mol.[11,12] These values should be viewed as qualitatively correct as the differences in the quoted values[12–14] are usually of little consequence. We thus predict the heat of formation of cyclopropane to be about 3 × (−5) kcal/mol. This calculated value of −15 kcal/mol is in contrast to the experimental value of +12.7 kcal/mol. This calculation thus shows cyclopropane to be destabilized by 28 kcal/mol. Again, the precise number should not be relied upon as group increment methods of varying complexity give somewhat different numbers. However, note that all of our methods of estimating heats of formation suggest cyclopropane is highly destabilized relative to our model compounds.

Qualitatively, organic chemists usually recognize a strained molecule when they see one. When structural features of the molecule (bond angles, bond lengths, torsional angles, nonbonded distances) depart from their optimal values, the molecule is said to be strained. Often, functional units are the standards of choice and, for example, nonlinear carbon–carbon triple bonds, twisted olefinic linkages, and nonplanar benzene rings are features indicating molecular strain. While strain is qualitatively an intuitively simple subject, a good deal of complexity (and confusion) enters when quantitative results are desired or when comparison between formally unrelated molecules is attempted. For example:

(1) Are there unstrained molecules? Alternatively, must one simply attempt to define molecules, bonds, or group increments of minimum strain?

(2) Is ethylene an unstrained olefin or highly strained "cycloalkane"?

(3) Is tetrafluoroethylene a strained or an unstrained olefin?

(4) To what extent is benzene strained? The strain is, of course, hidden in the apparent stability of the molecule.

(5) In a molecule in which there are several features connoting strain, what are the relative contributions to the destabilization energy (and are these contributions additive)? Again, only a single number representing the total destabilization energy is available, although molecular mechanics is useful here.

(6) In a molecule such as bicyclobutane, how should one apportion a measured strain energy between different types of bonds and/or atoms?

(7) How should one compare the strain in the central bond in bicyclobutane to the bridgehead–bridgehead bond in a small propellane?

(8) The strain per carbon and the strain per bond in tetrahedrane are quite different. Which value best allows understanding of its instability?

Thus, we do not expect to introduce the reader to any unknown molecular features of strain. We intend to point out some of the complexities inherent in their careful analysis and in interrelating them. In the above discussion, data have been cited for the unremarkable purpose of establishing that cyclopropane is destabilized. To say that cyclopropane is "strained" is not the end of the problem; indeed it marks the beginning of our study.

II. Nature of Strain in Organic Molecules

A. Thermodynamics and Symmetry

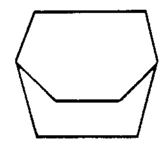
In this article, we will consider only those compounds that are destabilized relative to the model compounds. Moreover, we will disregard those species characterized by negative resonance, conjugation, or delocalization energy. Thus we will consider aromaticity and antiaromaticity only in very special circumstances. With the scope of our article accordingly delineated, we label all destabilization effects as molecular "strain" although strain has neither a single origin nor a single effect.

The reader may have noted that we spoke of energies but wrote ΔH or enthalpies. The former is more intuitively convenient while the latter is more experimentally thermodynamically convenient. Interrelated by $P\Delta V$ terms, usually the errors involved in these terms are small under the conditions of interest: 25 °C (298 K) and 1 atm pressure. We do not claim accuracy better than 1 kcal/mol or so; both the data and our concepts are usually too ill-defined to do any more than this. We omit discussion of zeropoint vibrational energies. These corrections are generally small and nonconstant but are otherwise usually unknown. We admit we are not rigorous thermodynamicists. As such, emphasis in this article will be placed on differences in strain energy as measured by differences in enthalpies. The reader should realize that it is the free energy (ΔG) which truly determines relative stability:

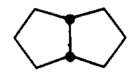
$$\Delta G = \Delta H - T\Delta S = -RT \ln K_p \qquad (1)$$

From this equation, it is evident that the free energy is composed of an enthalpy (or energy) term as well as an entropy term. Whereas ΔH is essentially temperature independent, increasing the temperature increases the entropy term. In most cases near ambient temperature, the enthalpy term dominates. As such, it is usually safe to consider differences in ΔH and consider this equivalent to the differences in ΔG. In any case, it is ΔH differences that define strain energy and ΔG differences that define relative thermodynamic stability.

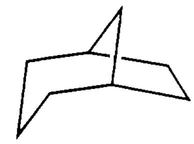
However, some interesting phenomena may be noted when the magnitudes of the enthalpy and entropy among a set of compounds are nearly equal. Two examples should suffice. Consider the set of isomeric bicyclooctanes, **1**, **2**, and **3**. It may



1



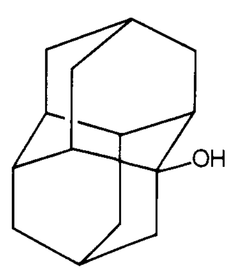
2



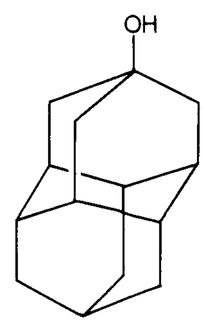
3

be shown that **2** has the greatest strain energy while **1** and **3** have essentially equal strain energies.[15] However, at 298 K,[16] **2** is more stable than **1** while **3** is the most stable of the three isomers. At this temperature, compound **2** gains stability from the entropy advantages of molecular flexibility. Both the cis ring junction and the two five-membered rings are unique to this isomer, and indeed at temperatures greater than 378 K isomer **2** becomes the most stable of the three isomers. Analogously, isomer **3** is more stable than **1** because of the low entropy of the latter. This may be attributed to the symmetry of both species: compound **3** has only one plane of symmetry, i.e., C_s, while compound **1** has both threefold and mirror symmetry, D_{3h}.[17] (This obvious symmetry assignment is admittedly simplistic; the structure of this and related compounds will be discussed later in section IV of this article.[18]) The lowering of the entropy of **1** relative to **3** is quantitatable in terms of their respective symmetry numbers.[19,20] Compound **1** has a symmetry number σ of 6 while **3** has $\sigma = 1$. The entropy difference is $R \ln (6) - R \ln (1)$ or 3.6 eu (gibbs), which equals approximately 1.1 kcal/mol at 298 K. The reader should note that this number is absolutely known to the extent that our symmetry assignments are valid and the numerical constant R is determined.

The second example involves equilibration[21] of the two diamantanols **4** and **5**.[22] Although discussion of this type of

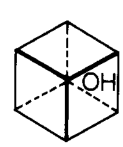


4



5

compound is deferred until section V, it should be clear that the carbocyclic framework of both enforces molecular rigidity and differences in flexibility should be negligible. If we neglect the asymmetry induced by the bent C–O–H group,[23] then the higher symmetry of **5** (C_{3v}, symmetry number of 3) should result in a lower entropy than that of **4** (C_s, symmetry number of 1) by R ln (3) or 2.2 eu. Drawing **6** is an alternate representation of the



6

diamantane structure where both the darkened and dotted lines are C–CH_2–C "bonds" while the normal lines are C–C bonds. The HO and the arrow point to the symmetry axis, thereby "synthesizing" compound **5** and justifying the C_{3v} symmetry.

B. Components of Molecular Strain

We now return to the normal case where the entropy effects are small compared to the enthalpy or energy effects. As such, we will refer to strain (or steric) energy and not strain free energy and tacitly assume that information about ΔH is conceptually equivalent to that about ΔG. Let us now turn to a discussion of the origin and nature of strain in organic molecules. We initially partition strain into three components,[12,24] all expressible in terms of classical, i.e., not quantum, chemical language. The first component is torsional: ideally (for lowest energy and thus a logical reference state), all C–C–C–C fragments will be trans or zig-zag.[24] This constitutes the idealized "strain-free" alkane geometry, although at room temperature alkane molecules also occupy other conformations or geometries. We may attribute those to an entropic effect. Although the differences are relatively small for alkanes, this choice of reference state is of both numerical and conceptual importance in the understanding of polycyclic hydrocarbons.[11,12] Considerable experimental interest has been shown in torsional and rotational barriers.[25] Theory far from mute is filled with apparent conceptual conflicts.[26] It may be argued that the preference for trans or staggered geometry is a special case of nonbonded repulsion.[27] (Literature mention of this usually treats torsional effects separately when quantitation is desired.) That is, two groups not attached to each other will usually repel each other. Nyholm–Gillespie or valence shell electron pair repulsion theory[28] similarly appears to be a special case.[29] Although intuitively understandable and visualizable from space-filling models, quantitation of the torsional component remains a major computational problem in predicting molecular structures.[12–14,23,29,30] We wish to note that nonbonded attractions have also been recently discussed in the literature.[31–35] Conformational applications are, however, rarely made.

The second contribution to strain is bond angle distortion, a concept long labeled as Baeyer strain. One may argue there are "natural" bond angles such as tetrahedral (109.5°) for tetracoordinate (T_d) carbon[28] or trigonal planar (120°) for tricoordinate (D_{3h}) carbon,[28] and indeed suggest that these angles minimize nonbonded repulsions.[28,29] Although it was originally applied to $-CH_2-$ angles in cycloalkanes,[12,36] application to >CH– and >C< angles is a logical consequence of our understanding. In one form or another, angle distortion and resultant strain energy will be found throughout all of our subsequent sections since angle opening and/or compression seems unavoidable in molecules.

The third contribution to strain to be discussed is linear bond stretching or compression. Intuitively, a chemical bond may be envisioned as a spring, and thus there is a "natural" bond length. Whereas bond angle variation is common, there is surprisingly little variation in bond length.[12] As such, little mention of this type of strain appears in the literature. We cannot immediately conclude that bond stretching or compression is disfavored because of the high-energy expense. From the bond stretching expression in Engler, Andose, and Schleyer's "molecular mechanics" calculations,[12] one finds a 10% or 0.15 Å C–C bond stretch from 1.54 to 1.7 Å is accompanied by an energy increase of only 3.1 kcal/mol.[37] Alternate bond stretching expressions in the literature give different, but similarly small, distortion energies. We note that angle strain for distorting a C–C–C, C–C–H, or H–C–H molecular "fragment" is usually less energetically disfavored than bond stretching. This result supports the earlier mentioned conclusion, but it is also important to note that "merely" stretching bonds hardly lessens most other molecular destabilization such as torsional or nonbonded repulsions.[38,39]

We wish to emphasize that the various contributions to molecular strain are essentially inseparable and interdependent and indeed model dependent.[12] One molecule that exemplifies this is tri-*tert*-butylmethane, $((CH_3)_3)_3CH$ (2,2,4,4-tetramethyl-3-(2-methyl-2-propyl)pentane).[40,41] Enormous nonbonded interactions in the "undistorted" hypothetical compound are relieved by a compression of the H–C–C(*t*-Bu) angle to 101.6° and an outward stretching of the C–C(*t*-Bu) single bond to 1.611 Å, the longest single bond recorded for an acyclic hydrocarbon. The strain energy was computed by Engler, Andose, and Schleyer[12] using the "force fields" of Allinger[13] and Boyd[14] as well as their own. The results were 31.48, 40.40, and 49.61 kcal/mol for the Allinger, Boyd, and Engler–Andose–Schleyer force fields, respectively. Significantly different partitioning of the molecular strain was also found. Owing to different group increment schemes, the calculated heats of formation are in considerably better agreement, −57.07, −55.80, and −53.08 kcal/mol, respectively. Two points need to be made. First of all, "it would *not* be expected that the different blends of strain components and group contributions would always balance out when tested over a wide range of molecules".[42] As such, careful experimental determination of the heat of formation of this compound would be of great interest. Secondly, we should compare the heat of formation of tri-*tert*-butylmethane, presumably ca. −55 kcal/mol, with that of the straight-chain isomer.[12] This value is computed to be −76.53 kcal/mol, resulting in apparent strain energy of only 20 kcal/mol or so. Molecular crowding and stability relative to the straight-chain isomer do not directly correlate as the experimental heats of formation of pentane, isopentane, and neopentane decrease in that order. This may be related to our assertion that there is no normal C–C and C–H bond. Indeed we note the energy for two CH_2 group increments is more than that of one CH_3 and one CH. That is, we would expect $R-CH_2-CH_2-R'$ to be less stable than $R-CH(CH_3)-R'$ no matter what R and R′ are. The greater the number of CH and C groups, the greater the "strain-free" stability but also the greater the strain. These clearly are in opposition but quantitation is indeed possible.[11–14,30] Unfortunately, both intuition and understanding are harder to acquire.

We now describe two more types of strain in molecules. The first arises from rotation or twisting of double bonds and will be further discussed in sections X through XIII. The final type is "electrostatic strain",[43] found in such species as 1,4-bicyclo[2.2.2]octyl dication[43] (**42**), and cyclooctatetraene dianion, $C_8H_8^{2-}$.[44] Much as the first three types of strain have their analogs in classical mechanics, this type relates to electrostatics. Two positive (or negative) charges repel each other, and hence the aromaticity gain on formation of the dication[43] or dianion[44] must be balanced against this repulsion.[45] This type of strain is sufficiently rare that intuition is absent as to its magnitude. For example, no gas-phase thermochemistry data are available on either diion. Even given these data, one could not delineate the contribution. For example, the C–C–C angle in cyclooctatetraene is 127°,[46] while in the dianion it is opened to 135°.[47] The hardest term to disentangle is the aromaticity of the diions and the resultant molecular stabilization. We will rarely consider aromatic systems (except in sections VIII.B, IX, XII, and XIII) and so are largely absolved from the problem. Nonetheless, it remains a major lesson that theoretical and thermochemical quantitations seem more achievable than qualitative intuition and understanding.

In the next section we rediscuss cyclopropane, the simplest strained system. The introductory section of this article introduced the reader to this molecule and easily demonstrated that cyclopropane is destabilized or strained. In our return to it, we take what is essentially a theoretical diversion into fundamental organic chemical bonding theory. Many conceptual problems and paradoxes arise, most of which are indubitably parallelled in larger molecules. However, since neither the data nor understanding extends to these systems in general, we may take an "ignorance is bliss" attitude. We have thus written the remainder of this review article in such a way that the forthcoming section may be disregarded by the reader with no loss of continuity or intelligibility.

III. Cyclopropane

A. Propane vs. Cyclopropane

Let us briefly compare propane and cyclopropane in an effort to understand the origin of the strain energy in the latter. What molecular properties reflect this destabilization? The answer is of both theoretical and experimental interest. One would like to estimate molecular strain energy without burning and/or hydrogenating the compound as this is not only wasteful but also often impossible for lack of the necessary sample. In Ferguson's[48] review of cyclopropane, he presents a comparison of the properties of the C–H bond in cyclopropane and in the unstrained alkanes. The former C–H bond is shown to be shorter, of higher force constant in stretching frequency, and has a higher ^{13}C–H NMR coupling constant. These results are consistent with the thermochemical observation that the C–H bond in cyclopropane is indeed stronger than either the primary or secondary C–H bond in propane.[49] We note that all of the hydrogens are in an eclipsed conformation. Energetically, this costs approximately $\frac{2}{3}\cdot\frac{3}{1}\cdot 2.6$ kcal/mol: the 2.6 is the rotational barrier of ethane while the $\frac{2}{3}$ arises from considering only two hydrogens per carbon rather than three, and the 3 corresponds to three sets of CH_2–CH_2 repulsions rather than one. Admittedly, the carbons contribute to the torsional strain, but the quantitative contribution is harder to intuit. This 5-kcal/mol effect, although relevant, is clearly not responsible for all of the strain in cyclopropane. Thus, intuitively one suspects that the destabilization of cyclopropane is to be found in the C–C bond framework. The C–C bonds in cyclopropane[50,51] are shorter than in propane,[52] and the vibrational frequencies for the former are higher than the corresponding ones in the latter.[53] Analogous to the above analysis we would conclude that the cyclopropane C–C bonds are stronger and we deduce that cyclopropane should be more stable than propane! While there is no reason to expect that bond strengths will correlate with vibrational frequencies, this logic appears implicit in numerous published studies. We may also in part rationalize this contradiction by citing that the C–C bonds in cyclopropane are bent and thus r(C–C) is not the measured internuclear distance. We will discuss bent bonds later but merely note that quantitative thermochemistry or stability does not arise from this argument. Additionally, the C–C stretching modes considered above should also be considered as, or at least coupled strongly to, angle compression. If we argue cyclopropane is strained, then the angle compression will be more energetically unfavored than in propane since the angle is already abnormally compressed; i.e., we are worsening a bad molecular situation. We may assume that the energy of angle bending is quadratic, i.e., $E = \frac{1}{2}K_\theta(109.5 - \theta)^2$. It may then be shown a vibration that corresponds to a 5° variation in a normal compound; i.e., 105–115°, is less energetically "expensive" than 5° in cyclopropane (60°), i.e., 55–65°. However, this argument is somewhat cyclic and in any case does not give us the numerical data we need.

Let us see what chemical bonding theory says about cyclopropane. We know not to ask for quantitative results (see the computational complexities of ref 54 through 57). Instead we want qualitative indications of molecular strain. Cyclopropane has been actively studied via molecular orbital calculations, and indeed no less than 18 ab initio calculations have been reported.[58] One interesting qualitative finding is that d orbitals seem to stabilize strained compounds over open-chain analogs.[59]

B. d Orbitals and Hybridization

Bonding in organic compounds, in particular hydrocarbons, is usually implicitly assumed to involve only 2s and 2p orbitals on carbon and 1s orbitals on hydrogen. When numerical agreement with experiment is desired, higher orbitals such as the carbon 3d are unavoidable.[54–57] Qualitatively the use of carbon 3d orbitals in SN2 reactions[60] and carbonium ion rearrangements[61] has been suggested, but for the case of the former there is quantitatively little effect.[62] Carbon 3d and 4f orbitals have also been invoked as the origin of rotational barriers in ethane-like molecules.[63] (Part B of section II provides relevant discussion of this phenomenon.) However, we will maintain the

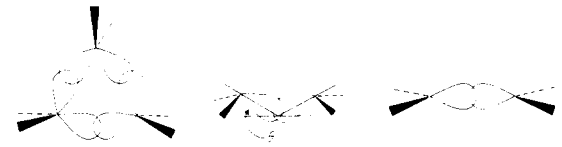


Figure 1. (a) A bent bond picture of cyclopropane, (b) bent bond connecting two CH_2 fragments where θ is the angle of bending, and (c) a normal bond.

chemical "myth" of the total irrelevance of these higher orbitals.

As such, we will consider the idea of hybridization of orbitals and assume that tetrahedral carbon arises from sp^3 hybrid orbitals. (Although extensive use of hybrid orbitals will be made, a general discussion is deferred to part G of this section.) We nonetheless feel obligated to acquaint the reader with a recent quantum mechanical study of CH_4[64] that showed that the presence of s orbitals was unnecessary to acquire a tetrahedral geometry for this species. Numerical values of total energy and energy differences upon molecular distortion or strain were, however, dependent on the presence of carbon 2s orbitals. It is also often implicitly assumed that hybrid orbitals derived from carbon 2s and 2p atomic orbitals may not have an interorbital angle of less than 90°. One may argue that the natural angle for p orbitals is 90° while s admixture merely increases the angle. We wish to note this assertion is false if we are allowed to use the most general form of hybridization or linear combination of atomic orbitals, i.e., the use of complex coefficients.[65,66] However, it may be shown that these more general orbitals cannot be pictorialized and that there is ambiguity as to their "directionality".[67] Using the definition preferred by Coulson and White,[67] the need of complex orbitals for strained compounds vanishes: the ideal complex orbitals for cyclopropane are almost identical with the real (not complex) orbitals suggested by the conventional bonding picture to be described below in part C of this section. In any case, since we believe organic chemistry is essentially a pictorial and not mathematical science, we will consider solely the normally used real orbital.

Let us now return to the conventionally simplest unavoidably strained molecule, cyclopropane. (We use the term "unavoidably" to denote there is no mode of bond rotation or stretching that stabilizes the molecule. As such, the eclipsed rotamer of ethane is thus not unavoidably strained.) Cyclopropane, $(CH_2)_3$, has a C–C–C angle of precisely 60° as the molecule has the geometry of an equilateral triangle.[50,51] This seems self-evident that three identical groups would combine in such an arrangement. However, ozone, O_3 (isoelectronic to cyclopropane) has an O–O–O angle of 117°.[68] A cyclic form of O_3 with an equilateral triangle geometry has been discussed,[59,69–71] and reasons for the preference of the acyclic or open form given. Extension to general three-membered rings was given,[69–71] for these results appear to be of insufficient extrapolative or predictive value for rings not discussed. We seemingly must content ourselves with the experimental geometry for cyclopropane.

C. Bent Bonds

A particularly simple model for cyclopropane uses methane-like sp^3 hybrids.[72] Three such units are joined cyclically and the orbitals overlap outside the ring, i.e., nuclear perimeter (see Figure 1). That is, the maximum overlap is not along the line connecting the two nuclei, and so the term "bent" bonds has been introduced.[72–74] The molecule chooses a compromise between the maximum nuclear–electron attraction which suggests high electron density along the bond and maximum conformity with the intrinsic shell structure or natural hybridization which suggests a tetrahedral interorbital angle.[75] As such, molecular geometry is a sensitive quantity to small changes and the earlier noted complexities[69–71] become understandable.

By considering hybridization other than sp^3 (ref 76), we may quantitate the intuitive notions of "bent" bonds by valence

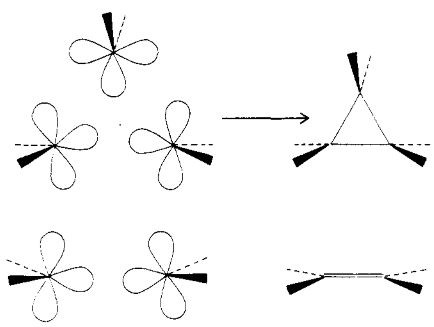


Figure 2. (a) Synthesis of cyclopropane form three CH_2 groups and (b) corresponding synthesis of ethylene from two CH_2 groups.

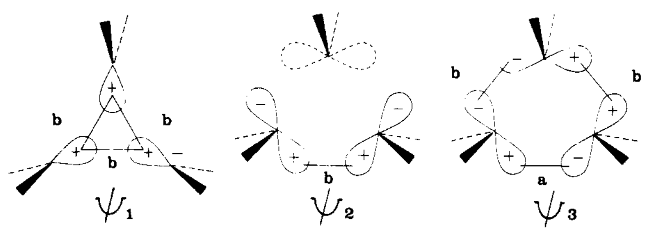


Figure 3. The three Walsh orbitals for cyclopropane: b means bonding; a means antibonding. ψ_1 comes from the σ "pool" while the degenerate pair ψ_2 and ψ_3 come from the π "pool".

bond,[67,72] molecular orbital (e.g., ref 77 and 78), or maximum overlap[79-81] calculations. All of these calculations yield an interorbital angle of approximately 104° for cyclopropane and a corresponding angle of bending of 21°. This is to be contrasted with methane where the interorbital and internuclear angles are equal to the natural 109.5° ($\cos^{-1}(-1/3)$) for strictly tetrahedral carbon. We remind the reader that the internuclear angle in propane is 112° (ref 50 and 51), but we admit ignorance as to the interorbital angle. Maximum overlap criterion calculations probably are the simplest conceptually of the computational approaches to understanding molecular strain. The greater the overlap between two orbitals,[82] the greater the bond strength[83-85] and the more stable the compound. Little work has been done on compounds that do not contain only carbon and hydrogen,[86] but this provides few problems for the authors in our survey of strained compounds.

We do note, however, an interesting complexity in the literature. We cited above the reason for molecular strain of cyclopropane in the current model. This is compatible with the strain in ethylene, i.e., cycloethane. Two bent or banana bonds are drawn and analogous logic[87,88] may be given. However, whenever C–C double bonds appear in any of the compounds discussed in this approach, they are always drawn as conventional σ and π bonds. We personally prefer the σ and π bond formulation of double bonds although the pictures are quantum mechanically interconvertible. Perhaps, there are essentially invariant units or collections of bent bonds other than C–C double bonds. Connection with "superstrain" discussed in our later section XV seems apparent, although the mathematical details are involved enough for the authors to merely mention but not ascertain the validity of our assertion. We will return to bent bonds and maximum overlap considerations when discussing other strained species in depth.

D. Walsh Picture

Another picture for cyclopropane is the so-called Walsh model.[89-91] Analogous to the formal synthesis of ethylene from two CH_2 groups,[92] cyclopropane is "synthesized" from three CH_2 groups. These, with their accompanying sp^2 hybridization

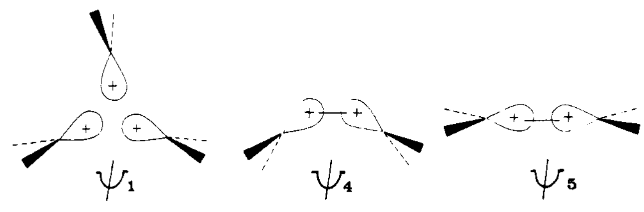


Figure 4. A closer examination of the lowest lying Walsh orbital of cyclopropane, ψ_1. ψ_4 is the corresponding two-center orbital, a bent sp^2–sp^2 σ bond, while ψ_5 is the normal sp^2–sp^2 σ bond.

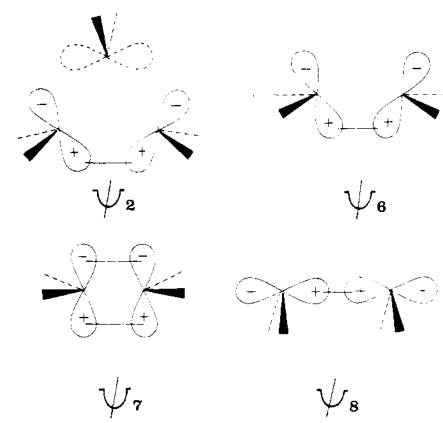


Figure 5. A closer examination of one of the degenerate pair of Walsh orbitals, in particular ψ_2. ψ_6 is the corresponding two-center orbital, *strictly* ψ_7, the π bond of an undistorted olefin, and ψ_8, the σ bond formed from two unhybridized carbon 2p orbitals.

and σ and π orbitals are combined to form six molecular (supermolecular) orbitals[93] (see Figure 2). Not surprisingly, these six orbitals consist of two sets of three. The molecule "chooses" the lowest energy three which in fact consist of one from the σ and two from the π "pool" (see Figure 3). We note that in studies of general ring systems, the terms σ and π have not been used particularly.[94-99] Few applications to polycyclic ring systems have been made,[100-102] and indeed a unique Walsh orbital set is not always constructible.[103]

Let us now consider the Walsh model and try to understand where the strain in cyclopropane arises. The lowest lying orbital corresponds to a closed three-center bond[104] and thus contributes to increasing the molecular stability.[105] One may immediately recall the increased π orbital resonance energy of cyclopropenyl cation over the open-chain allyl cation.[106] This, however, is somewhat deceiving and overestimates the stabilizing influence of this orbital. In both the cyclopropenyl and allyl cations, all of the π orbital overlaps are essentially normal, i.e., unchanged from ethylene. For cyclopropane, the individual C–C σ orbital overlaps are reduced from the normal ethane-like situation since they are severly bent (see Figure 4). Admittedly, ψ is a relatively low-energy molecular orbital and some restabilization is found so that the C–C bonds involve sp^2-hybridized carbons[107] and so are relatively strong. However, it is doubtful that this compensates. (We may generalize this model to use other than sp^2 hybridization and so form a model[76] equivalent to that of the bent bonds treatment.) Quantitation can be attempted, but we feel meaningful numerical results are unlikely to arise. Let us now consider the next and indeed highest occupied molecular orbitals, a pair of degenerate ones. The first one can be viewed either as the π bond of a highly distorted olefin or as the highly distorted σ bond formed from two unhybridized carbon 2p orbitals (see Figure 5). In either case, little stabilization arises. The second orbital can be viewed as having two of the above weakened σ or π bonds but also a corresponding antibonding σ^* or π^* bond. Again, little stabilization arises.

TABLE II

Label of hybrid	No. of equiv orbitals	Angle	Example	Geometry
sp^3	$4 = 3 + 1$	$109.5° = \cos(-1/3)$	$CH_4 = CH_{3+1}$	Tetrahedral
sp^2	$3 = 2 + 1$	$120° = \cos(-1/2)$	$BF_3 = BF_{2+1}$	Trigonal
sp (sp^1)	$2 = 1 + 1$	$90° = \cos(-1/1)$	$CO_2 = CO_{1+1}$	Digonal

E. Delocalized Molecular Orbitals from Group Orbitals

Another model for describing cyclopropane entails the formation of delocalized molecular orbitals from group orbitals.[108] Both the C–H and C–C bonds have been so treated, but as we are interested primarily in the strain energy of the carbocyclic framework (or ring), we will consider only the latter. Three C–C bond orbitals are combined to form three new orbitals. Not surprisingly, these three orbitals have the same symmetry or + sign and − sign arrangement as the three Walsh orbitals. After all, two essentially correct descriptions of a molecule should be conceptually interrelatable. In the current model it is perhaps easier to locate some of the origin of molecular strain. All three orbitals are bonding in a localized or two-center C–C bonding description. However, only the lowest lying orbital has no nodes, or sign changes, between all three atoms. The small internuclear or C–C–C angle markedly increases the antibonding character of the next two orbitals and so the molecular is destabilized. This situation is analogous to the σ and π where the former has one fewer node in the bonding region. Although this approach is useful for cyclopropane, we feel in general it will be difficult to apply as considerable complexities arise in systems of lower symmetry such as substituted derivatives of polycyclic systems in general. (This charge may also be leveled at the other conceptual models in this section.)

F. Cyclopropane vs. Ethylene

Many of the models we presented for the understanding of the bonding and energetics of cyclopropane interrelated this species with ethylene. Extensive chemical documentation of the validity of this comparison exists,[48,109] and the reader is referred to these compendia just cited. We will concentrate here on physical characteristics: we tacitly assume that what is true of cyclopropane and ethylene likewise applies to their substituted derivatives although corresponding data are usually absent. The archetypal, i.e., unsubstituted, species have comparable C–H bonds as manifest by bond length, force constant, and ir stretching frequency and ^{13}C–H coupling constant.[48] While the C–H bond strength of cyclopropane is less than ethylene, the C–H bond strengths of both species are significantly greater than those of propane.[49] The reader may be wary of such comparisons from the earlier discussion of cyclopropane and propane. Comparing the C–C bonds of cyclopropane and ethylene, we find no surprise that the C–C bond of the latter is considerably shorter.[48,110] Comparison of bond strengths is a little subtle since each CH_2 in ethylene is bonded to only one other CH_2 while in cyclopropane it is bonded to two: however, classical chemical formulas draw a double bond between the CH_2's in ethylene but only a single bond in cyclopropane. It appears simplest to give the bond strength per CH_2. That is, set it equal to $(1/n)(n\Delta H_f°(CH_2) - \Delta H_f°(CH_2)_n)$. Using this definition, we find that cyclopropane is more bound than ethylene. Though initially surprising, this may be simply explained by recalling our description of ethylene as cycloethane. One might also say that while cyclopropane contains normal but distorted single bonds, ethylene contains one normal and perhaps strengthened single (σ) bond and another weaker (π) bond. Indeed, the total bond strength has been partitioned into 106 kcal/mol for the σ bond and 60 kcal/mol for the π bond.[111] As apparent support for this, we find removal of a π electron in ethylene costs less energy than a σ electron in ethane (10.51[112] vs. 11.54 eV,[113] respectively.) Furthermore, the bond strength in ethane is nearly halved in the radical cation as measured by $D(CH_3-CH_3) = 2\Delta H_f°(CH_3) - \Delta H_f°(C_2H_6)$ and $D(CH_3{}^+-CH_3) = \Delta H_f°(CH_3{}^+) + \Delta H_f°(CH_3) - \Delta H_f°(C_2H_6{}^+)$. We may recast these expressions as

$$D(CH_3-CH_3) - D(CH_3{}^+-CH_3) = IP(CH_3-CH_3) - IP(CH_3) \quad (2)$$

where IP is simply the ionization potential. Using analogous expressions for ethylene and acetylene and the experimental ionization potentials of C_2H_4,[114,115] CH_2,[116] C_2H_2,[115,117] and CH,[118] we find the surprising result that ionization of a π electron is without effect as to the binding of C_2H_4 and is of relatively little importance for C_2H_2. We may argue that the molecular geometry of the radical cations formed by ionization and the more normal neutral species are quite different.[119] As such, our earlier comparisons and our attempts at partitioning σ and π energies are perhaps futile. We thus are thwarted in our attempts to understand why cyclopropane radical cation is more bound than the neutral.[120] Indeed, we pessimistically conclude that while, qualitatively, intuition may be used in an estimation of strain energy, only experimentally determined or rigorously computed heats of formation or reaction allow its quantitation.

G. Orbital Hybridization

We now turn to the general question of orbital hybridization in cyclopropane and in other strained compounds. Depending on the model discussed for cyclopropane, the orbital hybridization explicitly considered was either sp^2 or sp^3 although sp^5 has also been enthusiatically suggested.[76] Before discussing general hybridization, we wish first to define our terms. Historically, at least in the organic chemical literature and tradition, hybridization referred to atoms and not individual orbitals per se. In this context, sp^n was limited to $n = 1$, 2, and 3. Table II presents this outlook. There is no meaning to sp^5 in this approach. From the additional awareness that sp^3 hybrids are "synthesized" from one "part" s orbital and three "parts" p, we may conclude sp^5 hybrid may be likewise "synthesized" from one "part" s and five "parts" p. With this assignment, the n in sp^n may take on any value between 0 and ∞, where $n = 0$ is a pure s orbital and $n = \infty$ is a pure p orbital. (Equivalently, an orbital is said to be an sp^n hybrid if it is $100(1/n + 1))$ % s, synonymously $100(n/n + 1)$ % p.) From the above discussion, it might appear that orbital hybridization would be solely of interest to theoretical chemists, and indeed the theoretical literature contains many references to it (see, for example, ref 80, 81, 121, and 122 as well as the later citations in this review). However, there are additionally extensive experimental correlations of hybridization, or, as usually expressed, % s character, with ^{13}C NMR coupling constants.[123] In general, good qualitative correlations of % s character and bond strengths were found: the more s character in the C–H bond, the stronger; the more p character in the C–C bond, the more acetylenic or olefinic.

It should be noted that there is not always agreement between theory and experiment. For example, for cyclopropane, the ^{13}C–H coupling constant value suggests 32% s character.[124] Quantitative theoretical studies of this species give values between 30 and 45% s character with the more rigorous calculations[121,122] giving the higher values. In contrast, the C–H bond in ethane has been calculated[121,122] to have between 20 and

TABLE III

Ring size	Total ring size, kcal/mol	Strain per carbon, kcal/mol
2	22.6	11.3
3	27.6	9.2
4	26.2	6.5
5	6.5	1.3
6	0.0	0.0
7	6.3	0.9
8	9.6	1.2
9	12.6	1.4
10	12.0	1.2
11	11.0	1.0
12	3.6	0.3
13	5.2	0.4
14	0.0	0.0
15	1.5	0.1
16	1.6	0.1
17	−3.4	−0.2

27% s character of the C–C bonds for either compound since all of the carbons are equivalent. This would seem to be irrelevant since it would appear that the sum of the % s character for all bonds to a given carbon is 100% or an average of 25% in a closed-shell compound. That is, all octets are filled and there are two 2s and six 2p electrons occupying the single s and three p orbitals. We wish to emphasize that this assumption is false as shown by chemical theory,[126–129] quantum chemical calculations,[126–129] and seemingly experiment.[41,130,131]

From all of our paradoxes, we suggest that we are much more ignorant as to the origin and indeed nature of molecular strain than we thought.

IV. Cycloalkanes

A. Cyclobutane

We will now discuss cyclobutane having described cyclopropane in the previous section. Our current treatment need not be as extensive since our earlier conceptual models are applicable to both species.[132] Not surprisingly, cyclobutane is considerably less reactive and thus more "saturated" than cyclopropane,[133] although olefinic features such as conjugation with carbocationic or other unsaturated centers remain.[96,134]

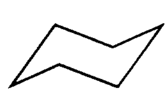
Let us sequentially consider the C–H bonds and the carbon skeleton of cyclobutane. It is instructive to compare the relative C–H strengths of ethylene, cyclopropane, cyclobutane, and the acyclic and saturated propane. Using hydrocarbon data from ref 4 and free radical data from ref 49, we find the numerical values to be 109, 100, 97, and 95 kcal/mol, respectively. This trend in decreasing methylene >CH–H bond strengths is systematic: "highly strained rings have a proclivity commensurate with the degree of internal stresses present for acidity, . . . [the] resistance to H-atom abstraction, and large $J(^{13}C\text{–}H)$ coupling constants".[135] Turning to structural considerations of the carbon skeleton, intuitively, cyclobutane and its derivatives would appear to be simple. Any deviation from planarity would further compress the already small C–C–C angle away from the idealized tetrahedral, 109.5° geometry. We remind the reader that the C–C–C angle in propane and other alkanes is 112°.[36] However, planar cyclobutane has considerable 1,2 and 1,3 nonbonded repulsion.[136] As such, cyclobutane is definitively nonplanar,[137] but the inversion barrier is only ca. 1 kcal/mol due in part to residual nonbonded repulsions.[138] Substituted derivatives are clearly more complicated, and a variety of geometries have been cataloged.[138]

We wish to note a recent quantitative regularity,[139] "the principle of minimum bond tortuosity", that interrelates the flexing of the ring, orientations of the hydrogens or other nonring atoms, and the directions of the bonding orbitals. Qualitatively employed by Stewart and Eyring[75b] for a large number of general chemical problems and labeled "the principle of minimum bending of orbitals", applications remain surprisingly rare.[139,140]

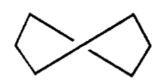
B. Cycloalkanes in General

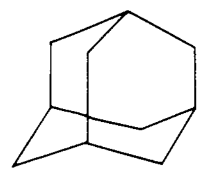
We now proceed from cyclobutane to cyclopentane and so find a classically nearly strain-free molecule. Planar cyclopentane has an angle of 108°, nearly identical with the idealized tetrahedral geometry. However, as with cyclobutane, the presence of 1,2 and 1,3 C–C and H–H nonbonded repulsion causes nonplanarity.[141,142] Strain is not eliminated, merely lessened, and the strain energy is 6.5 kcal/mol.[143] Table III presents the experimental strain energy of the lower cycloalkanes, where for completeness we have also included ethylene or cycloethane.

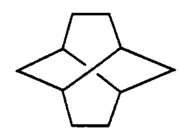
The next cycloalkane, cyclohexane, is essentially strainless[143] in its natural chair conformation.[144] However, it has numerous alternative structures, and thus even more numerous studies have been made on cyclohexane and its derivatives.[145] Besides their inherent interest, six-membered rings are a very common component of polycyclic hydrocarbons. For example, the most common conformers of cyclohexane, the chair (**7**), boat (**8**), and twist boat (**9**), are amply found in adamantane (4 × chair) (**10**), bicyclo[2.2.2]octane (3 × boat) (**1**), and twistane (4 × twist boat) (**11**). Although the relationships between the strain energy of the


7


8


9


10


11

polycyclic hydrocarbon and its component rings will be largely deferred until section XV, the reader is not to be dissuaded from seeking these rings. This mental exercise provides pictorial, organizational,[13,14,146] and even synthetic[146] frameworks for the compounds of interest.

Analogous considerations apply to aromatic or polynuclear hydrocarbons although we will largely neglect this class of compounds (see section XIII). We briefly note that the strain energy of benzene, the building block analogous to cyclohexane, is surprisingly nonzero. Benzene may be visualized as a resonating cyclohexatriene. Although resonance contributes considerable molecular stabilization, the three formal double bonds still are strained as in ethylene or cycloethane. Another source of strain is due to stretching the three double bonds and compressing the three C–C single bonds to the uniform distance found in benzene.[147,148] Finally, the equilateral, equiangular, planar geometry[148] forces all of the C–C–C and C–C–H angles to be 120°. However, there is no reason why the unstrained angles in a C–C(H)–C fragment should have these values. Indeed, the C–C–C angle in propylene is 124°.[149] (Allyl radical is an even better reference compound, but no experimental structural data are known.) We will, however, usually consider the benzene ring as a unit and consider it without strain. Deformations of the ring will be considered (section XIII) but whether the benzene ring mimics chair, boat, or twist-boat cyclohexane is immaterial now.

We now turn briefly to the higher cycloalkanes. Not surprisingly, these species are nonplanar. The "conflicts" between angle distortions of the C–C framework and C–C–H and H–C–H angles, torsional barriers, and nonbonded repulsions result in apparently random strain energies (see Table III.) There are also a plethora of conformations[150,151] and intriguing transannular, i.e., intra-ring,[152] interactions. Although further mention will rarely be made on cycloalkanes per se, derivatives such as cycloalkenes (sections VIII, IX, X, and XI), allenes (section XI), alkynes (section XII), cumulenes (section XII), and polycyclic analogs (most sections subsequent to this) will be actively discussed. While we note all of these species are dehydrocycloalkanes, we feel little is to be gained by noting cyclodecyne and adamantane (or twistane) are isomers.

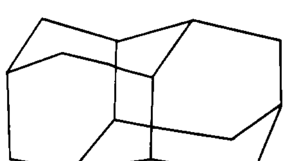
The strain energy of ethylene or cycloethane was found by setting it equal to the difference of twice the strain free energy of a CH_2 group and the heat of formation of C_2H_4. All of the strain energy values were taken from E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison "Conformational Analysis", Interscience, New York, N.Y., 1965, p 193. We note that other references give different but comparable numbers.

V. Adamantane and Adamantoids

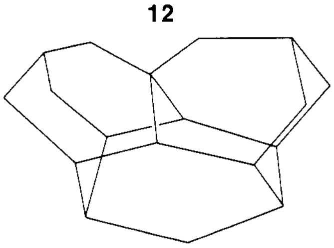
The ideal tetrahedral angle is perfect only for CX_4 molecules such as methane and carbon tetrachloride and virtually perfect for diamond [there is no cental carbon in adamantane (**10**), neopentamantane (five fused adamantane units having T_d symmetry), or diamond]. One of the sources of strain in adamantane[153] is the occurrence of near-tetrahedral geometry at carbons of lower symmetry.

Adamantane was discovered in petroleum in 1933,[154] synthesized in a low-yield, multistep sequence in 1941,[155] and obtained in quantity in 1960 through rearrangement of isomeric hydrocarbons.[156] It possesses tetrahedral symmetry with bond angles around 109.5° and bond lengths of 1.54 Å.[157–159] Originally considered to be strainless because of its "perfect" geometry, adamantane is currently estimated to be destabilized by 8.8 kcal/mol relative to strain-free increments.[153] In addition to producing the bond angle strain which is noted above, the rigid cage structure of adamantane forces the presence of significant nonbonded repulsions which are much less prominent in more flexible molecules such as cyclohexane. These nonbonded repulsions have been primarily attributed to carbon–carbon interactions[11] or to hydrogen–hydrogen interactions;[160] the assignment is dependent upon the particular repulsion potential functions employed.[12]

Adamantane may be regarded as (1) a structure composed of four rather rigid fused cyclohexane chair faces (the total strain of four separate cyclohexane molecules is 5.7 kcal/mol;[12] the strain in the isomeric molecule twistane (**11**),[161] which has four cyclohexane twist-boat faces, is about 33.3 kcal/mol[12]); (2) the unsubstituted central unit of diamond (termed the "infinite adamantylogue of adamantane" [162]); (3) the methane analogue in an homologous series of adamantoids in which diamantane ("congressane") (**12**)[162] and triamantane (**13**)[163] are analogues



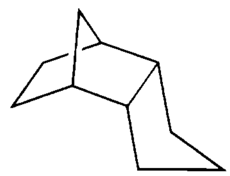
12



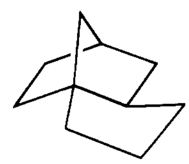
13

of ethane and propane; the three isomeric tetramantanes have yet to be observed.[164]

The ubiquitous appearance of adamantane in acid-catalyzed rearrangement reactions is, at least in part, explained by its relatively low strain energy which is fairly uniformly distributed throughout its symmetric skeleton. (Obviously, high symmetry introduces an unfavorable entropy component to the free energy of this molecule.) Diamantane[162] and triamantane[163] are also obtained by acid-catalyzed rearrangement of isomeric hydrocarbons. The mechanisms of rearrangements leading to adamantane have been examined,[165–167] and the importance of relative energies on the corresponding carbonium ion manifold has been stressed.[167] Rearrangement manifolds for even relatively small hydrocarbons such as adamantane are enormously complex. The crucial importance of the particular pathway traversed on such surfaces (i.e., the choice of starting material) is emphasized by (1) difficulties in detecting intermediates en route to adamantane when **14** is the starting material, in contrast to the identification of intermediates when **15** is the starting



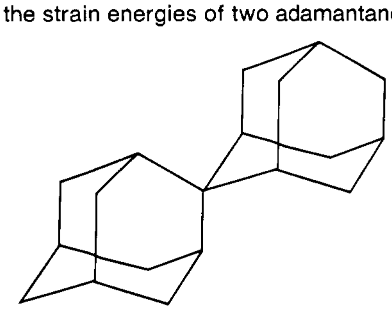
14



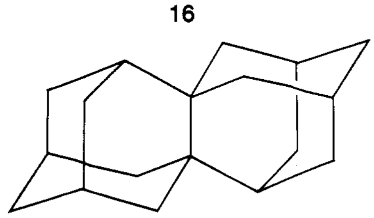
15

material;[167] (2) isolation of the isomer bastardane rather than the more stable compound tetramantane when another $C_{22}H_{28}$ isomer is rearranged;[164] (3) difficulties in approaching iceane (section XIV) from the $C_{12}H_{18}$ manifold, on which ethanoadamantane occupies the energy minimum for the tetracyclic series. The diamantane rearrangement manifold (hydrocarbons and cations) has also been calculated, providing likely pathways to the most stable species.[167a]

The strain energies of adamantane (8.8 kcal/mol[153]), diamantane (10.69,[12] 11.9 kcal/mol[168]), and triamantane (13.45 kcal/mol[12]) suggest that the strain energy per carbon in these three is about equal. The calculated strain energies[12] of [1]diadamantane (**16**)[169,170] and [2]diadamantane (**17**)[171] exceed the sum of the strain energies of two adamantanes.



16



17

VI. Small-Ring Bicyclic and Spiro Compounds

A. Cis-Bicyclic Systems[172]

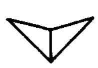
Cyclopropane and cyclobutane have a single angular constraint per carbon, and molecules such as bicyclo[1.1.0]butane (**18**), bicyclo[1.1.1]pentane (**19**), and spiropentane (**20**) contain one or more carbons having two independently constrained

TABLE IV. Strain Energies[a] of Some Cis-Bicyclic Small-Ring Compounds

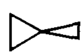
Compound	Strain energy, kcal/mol
Bicyclo[1.1.0]butane[176,177]	66.5[11]
Bicyclo[2.1.0]pentane[187]	57.3[11]
Bicyclo[3.1.0]hexane	33.9[11]
Bicyclo[4.1.0]heptane	30.3[12]
cis-Bicyclo[2.2.0]hexane[223]	50.7[12]
cis-Bicyclo[3.2.0]heptane	30.5[12]
cis-Bicyclo[3.3.0]octane	12.5[12]
Bicyclo[1.1.1]pentane[194]	60–64[197] (est) 92.5[13] (calcd)
Bicyclo[2.1.1]hexane[214a,224,225]	41.2[12]
Bicyclo[3.1.1]heptane	35.9[12]
Bicyclo[2.2.2]octane	13.0[12]
Bicyclo[3.2.1]octane	12.1[12]
Bicyclo[3.3.3]undecane[226,227]	25.3[12]

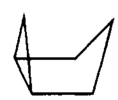
[a] Experimental standard heats of formation may be obtained from specific footnotes in ref 10—12 of this article, as well as from footnotes cited in S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neil, A. S. Rodgers, R. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).

angles.[173] Strain in these compounds is explicable in the same terms as for cyclopropane and cyclobutane.[173]


18

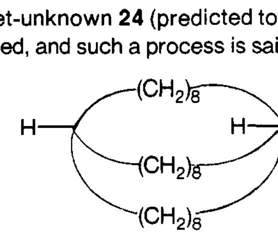

19


20

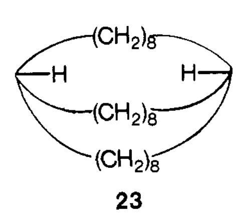

21

The first authentic derivative of bicyclo[1.1.0]butane[174] was reported in 1959,[175] and the parent compound appeared in the literature in 1963.[176,177] If it is assumed that the strain energy (Table IV) of a bridgehead carbon in **18** is about twice that of a bridging carbon, then each of the former is destablized by about 22 kcal/mol. This value may be compared with the 9.4 kcal/mol of strain per carbon in cyclopropane. Another view would be that the central bond in bicyclo[1.1.0]butane has 22 kcal/mol of destabilization energy compared with 9.4 kcal/mol for each bond in cyclopropane. (See section XV for a discussion of strain per carbon and strain per bond.) Comparison of the strain energies of cyclopropane and **18** discloses that "conceptual" fusion of the two cyclopropane moieties produces an extra destabilization increment of over 10 kcal/mol relative to the two separate rings. To what may this extra degree of strain be attributed? Molecular orbital descriptions[100,122,178] of bicyclo[1.1.0]butane, which calculate significant differences between the 1,2 and 1,3 bonds, contrast with the findings of a microwave study that these bonds are virtually the same length (although shorter than those in cyclopropane by about 0.02 Å).[179,180] An indirect determination of the hybridization of the central bond in bicyclo[1.1.0]butane indicated about 90% p character,[181] consistent with predictions of high p character by semiempirical and ab initio methods.[122] This finding was obtained through use of $J(^{13}C\text{–}H)$ of the bridgehead carbons, $J(^{13}C\text{–}^{13}C)$ between the bridgehead and bridging carbons, and assumption of unit s character at each carbon. There is no theoretical basis for this last assumption (see section III.G), so often taken for granted by chemists, and direct determination of $J(^{13}C\text{–}^{13}C)$ between bridgehead carbons of 1-cyanobicyclo[1.1.0]butane indicates about a 6% departure from unit s character.[130] The coupling constant correlates with about 83% p character for the central bond, about the same hybridization as in cyclopropane.[130] The bridgehead carbon–hydrogen bond is shorter than the bridge carbon–hydrogen bond, consistent with its greater s character, indicated by a higher value of $J(^{13}C\text{–}H)$, as well as the more acidic nature of the bridgehead protons.[180] Much of the chemistry of bicyclo[1.1.0]butane proceeds through the central bond in a manner reminiscent of reactions of π bonds.[172a,174,182–186] The chemical, physical, and especially thermodynamic properties of this compound make it a "unique chemical unit" in the sense that model compounds do not allow adequate prediction of its behavior. In contrast, the strain energy of bicyclo[2.1.0]pentane[187] is a simple sum of the strain energies of the component rings. Electron diffraction[188] and microwave[189] studies of this compound are somewhat contradictory; the former finds a rather short central (1,4) bond (1.44 Å) and a very long 2,3 bond (1.62 Å), while the latter study finds more normal bond lengths.[189a] Bicyclo[1.1.0]butane[184,186] and bicyclo[2.1.0]pentane[190–192] are both attacked by unsaturated compounds upon their electron-poor undersides. Bicyclo[3.1.0]hexane (**21**) and its heterocyclic analogues are most stable in the boat conformation, since the chair conformation maintains destabilizing vicinal hydrogen eclipsing interactions.[193] Calculated strain energies of a number of cis-bicyclic compounds are listed in Table IV.

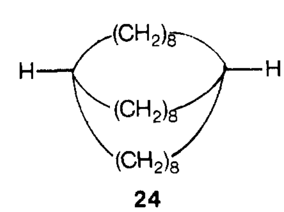
According to gas-phase electron diffraction studies, the bridgehead carbons in bicyclo[1.1.1]pentane (**19**)[194] are separated by only 1.885 Å.[195,196] This feature is also qualitatively reproduced by molecular orbital calculations.[197] The molecular structure of **19** has been discussed in terms of near sp^2-hybridized bridgeheads and p overlap between these formally nonbonded atoms.[195,197] The large value of $^4J_{HH}$ (18 Hz,[182] between bridgehead protons) has been cited as evidence supporting this view.[195] An estimated value of 60–64 kcal/mol for the strain energy in bicyclo[1.1.1]pentane, obtained through bond-additivity methods,[197] may be employed to calculate approximately 11 kcal/mol of strain per carbon–carbon bond in this compound. A higher value for the total strain energy,[13] ca. 93 kcal/mol, calculated by force field methods, implies about 15.5 kcal/mol of strain per bond. In either case, the bonds are more strained than those of cyclopropane and considerably less strained than the central bond of bicyclo[1.1.0]butane. In larger bicyclo[*l.m.n*]alkanes there is a general trend to decreased strain (Table IV and references cited) with increased bridge size: bicyclo[2.1.1]hexane (41.2 kcal/mol); bicyclo[2.2.1]heptane (17.0 kcal/mol); bicyclo[2.2.2]octane (13.0 kcal/mol); bicyclo[3.3.1]nonane (9.6 kcal/mol). However, there are discontinuities in this trend because of the unique balance of strain contributions in each hydrocarbon. There is also a reversal in trend as sufficiently large bridges force the bridgeheads to assume near planarity. An appreciable factor in the rather large strain energy of bicyclo[3.3.3]undecane (25.3 kcal/mol) is the forced planarity of the bridgehead carbons. Its analogue, 1-azabicyclo[3.3.3]undecane, has a virtually planar bridgehead nitrogen atom, a factor reflected in its singular properties as a base.[198,199] Large bicyclic bridged compounds permit the bridgehead carbons to be "inverted" relative to those in the smaller compounds. Isomeric bicyclo[8.8.8]hexacosanes **22** and **23** have this feature.[200] Conformational interconversion of **23** and the as-yet-unknown **24** (predicted to be less stable than **23**) is not observed, and such a process is said to be feasible only



22



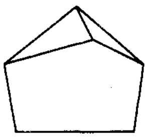
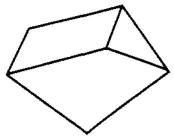
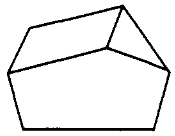
23



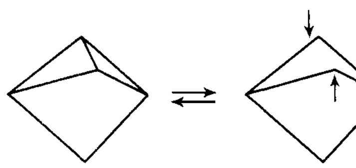
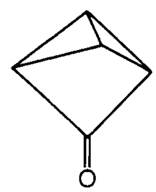
24

in larger homologues (bridges of ten or more carbons).[200] Macrobicyclic bridgehead diamines undergo the analogous (in–in)–(out–out) isomerization via nitrogen inversions.[202]

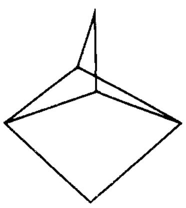
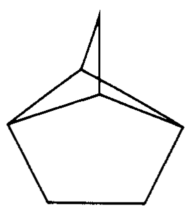
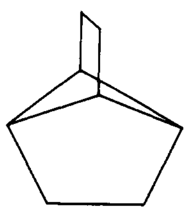
While hydrocarbons **25**,[203] **26**,[204] and **27**[205,206] have been


25

26

27

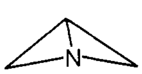
obtained, only substituted derivatives of **28**[207,208] and the related ketone **29**[209–211] are known. A novel aspect of **28** is the sug-

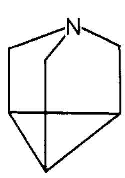

28 **28a**

29

gested presence of a "bond stretch isomer", **28a**, separated by a tangible energy barrier (due to the predicted symmetry-forbidden interconversion).[212] Derivatives of compound **29** have been investigated as potential precursors of substituted tetrahedranes (see section VII). No compounds related to **30** are known; only derivatives of **31** have been characterized,[213] and hydrocarbon **32** is a stable compound.[214] The long-range


30

31

32

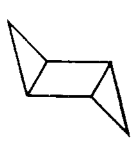
bridgehead proton coupling constants in the **31** series are virtually identical with those in the bicyclo[1.1.1]pentane compounds.[213] Strained bridgehead nitrogen compounds **33**[215] and **34**[216] are known although the latter has not been obtained in a pure state. Azabicyclic [1.1.0]butanes[217] and azabicyclic



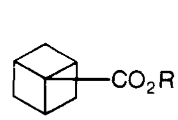
33


34

[2.1.0]pentanes[218] are unreactive to dienophiles which readily attack the analogous hydrocarbons. Fused hydrocarbons **35**,[219] **36**,[220] and **37**[221] as well as numerous derivatives have been described. Compound **38** is the first compound isolated which has a single carbon atom at the hub of three fused cyclobutane rings.[222]


35

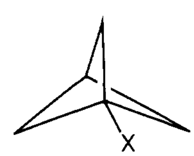
36

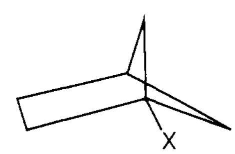
37


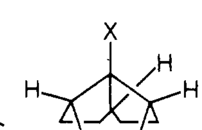
38

B. Strained Bridgehead Carbonium Ions

Small bicyclic molecules have well-defined spatial relationships within them which allow their employment as "chemical tweezers" [228] in studies of various chemical and physical properties that are geometry dependent. Reactions which generate bridgehead carbonium ions[228,229] have been extensively investigated and some of these intermediates have actually been observed in solution (see Table V). Incorporation at the bridghead of a small bicyclic skeleton usually prevents a tricoordinate carbon from attaining the planar structure preferred by acyclic species. (Planarity at the bridgehead would induce even more severe distortion in the remainder of the molecular framework.) Deviation from coplanarity is calculated to be the single greatest source of strain in these carbonium ions.[229] However, the bicyclo[3.3.3]undecyl system prefers planarity at the bridgehead, and the derived carbonium ion is less strained than the hydrocarbon.[199] An excellent correlation has been found between the logarithm of the solvolysis rate constant of a given bridgehead derivative, and the *difference* in calculated strain energies between the bridgehead carbonium ion and its corresponding hydrocarbon.[230,231] The calculated enthalpy difference is used here to approximate the enthalpy of activation assuming constant entropy and solvent effects.[230,231] Notably, bicyclo[1.1.1]pentyl and bicyclo[2.1.1]hexyl derivatives (**39** and **40**)



39


40


41

solvolyze much more rapidly than one would anticipate on the basis of these calculations alone.[229] This may be attributed to rearrangement accompanying solvolysis, or resonance stabilization by the cyclobutyl system or by the backlobe of the other bridgehead carbon's C–H orbital. The 10-perhydroquinacyl system (**41**) also deviates very markedly from the above correlation. Its solvolysis is about 10^{11} slower than expected, and this is attributed to replacement of three carbon–carbon hyperconjugative interactions by less stabilizing carbon–hydrogen hyperconjugative interactions.[230,231] Table V lists the calculated strain energies of some bridgehead carbonium ions. Although the 1-bicyclo[2.2.2]octyl cation has not yet been observed in solution because of its rapid rearrangement,[232] the strikingly stable 1,4-bicyclo[2.2.2]octyl dication (**42**) has been charac-

TABLE V. Calculated Strain Energies of Some Bridgehead Carbonium Ions[a]

Cation	Strain, kcal/mol[b]	Strain difference,[c] kcal/mol
1-Bicyclo[4.4.0]decyl[233]	6.7	4.8
1-Bicyclo[3.3.2]decyl	16.4	−2.8
1-Bicyclo[3.3.3]undecyl (1-manxyl)	18.7	−6.8
1-Adamantyl[234]	19.2	12.3
3-Homoadamantyl[235]	21.1	6.5
1-Noradamantyl	38.9	18.8
1-Bicyclo[3.3.1]nonyl	17.9	8.3
1-Bicyclo[3.2.2]nonyl[236]	22.0	6.6
1-Bicyclo[2.2.2]octyl	29.3	16.3
1-Tricyclo[4.4.0.0^{4,9}]decyl (1-twistyl-)	43.7	17.6
1-Bicyclo[3.2.1]octyl	30.8	18.7
1-Bicyclo[2.2.1]heptyl (1-norbornyl-)	40.5	23.5
10-Perhydroquinacyl	25.0	9.3
4-Tricyclo[2.2.1.0^{2,6}]heptyl (4-nortricyclyl)	75.5	28.5

[a] A reference is included where a carbonium ion has been observed in solution. [b] Strain energies are obtained from the calculated differences in strain between the carbonium ion and corresponding hydrocarbon as listed above and the strain energies of the hydrocarbons (cf. ref 12). [c] (ion) — (hydrocarbon).

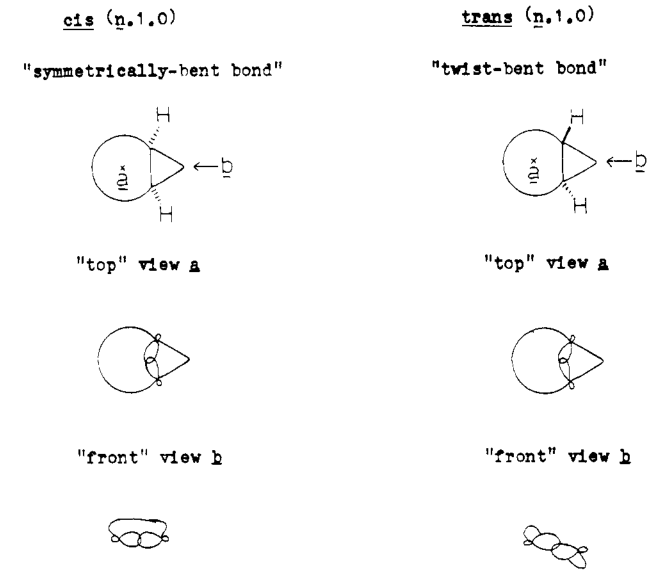
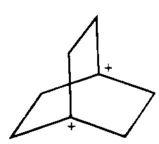


Figure 6. Overlap of the strained central bond in *cis*- and *trans*-bicyclo[*n*.1.0]alkanes.[237,238]

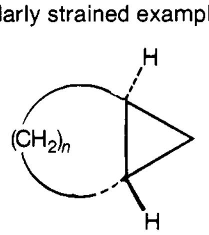
terized by NMR.[43] The stability of this species arises from its resemblance to the aromatic cyclobutadiene dication, as well as to (calculated) delocalization of positive charge on the 12 hydrogen atoms, thus minimizing electrostatic destabilization.[43]



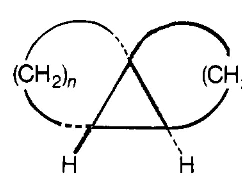
42

C. Trans-Fused Bicyclic Systems

The cis-fused cyclopropane (or cyclobutane) ring is symmetrically distorted in a geometrical plane. However, in suitably small bicyclic systems, trans-fused cyclopropane (or cyclobutane) is distorted in two planes. The resultant overlap of the central bond is smaller than in cis-fused molecules, and increased reactivity is anticipated.[237] The overlaps in cis- and trans-fused bicyclic systems are depicted in Figure 6. Chemical effects originating from the presence of highly strained trans-fused bonds are assumed to be significant for compounds in the **43** or **44** series where *m* and *n* are four or less.[237] Some representatives of **43** ($n = 4$) have been obtained,[238] while no similarly strained examples of **44** have been reported.

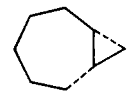


43
($n \leq 4$)

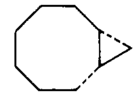


44
($n \leq 4; m \leq 4$)

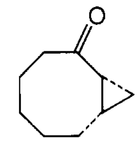
Derivatives in the *trans*-bicyclo[5.1.0]octane series (**45**) are known.[237,239-244] The liquid-phase enthalpy difference favoring a *cis*-bicyclo[5.1.0]octane over the trans isomer is about 9 kcal/mol.[244] If this value is assumed to be about the same in the gas phase, then the strain energy of **45** is about 40 kcal/mol. The strain within the central bond of **45** is evidenced, for example, by its abnormally high sensitivity to acid.[238] The difference in free energy between **46**[245,246] and its cis isomer is about 2.9 kcal favoring the latter.[244] It is thus apparent that a cyclopropane ring tolerates trans fusion better than does an olefinic linkage[241a] (see



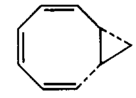
45



46

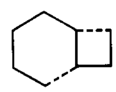


47

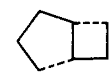


48

section X.B). Compounds **47**[247] and **48**[248] as well as many trans-fused bicyclic [*n*.2.0] compounds[249] (e.g., **49** and **50**) have also been characterized.



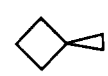
49



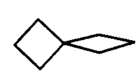
50

D. Small-Ring Spiro Compounds

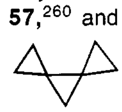
The strain energy of spiropentane (**20**)[250] is about 65 kcal/mol,[11] which exceeds the sum of the strain energies of two cyclopropane rings by about 10 kcal/mol. Thus, it is a "unique structural unit" in the same sense that bicyclo[1.1.0]butane is. A Coulson–Moffit-type view of bonding in this compound might assume that the central carbon is sp^3-hybridized. The deviation of the interorbital angle (109.5°) from the internuclear angle (62° [251]) is greater than that in cyclopropane, where the interorbital angle is calculated to be 104.5° (section III). However, spiropentane does not possess tetrahedral symmetry, and four sp^3-hybridized orbitals are not a requirement. A Walsh-type orbital picture of spiropentane is comprised of an sp-hybridized central carbon and four sp^2-hybridized peripheral carbons.[76] Strain in this compound contributes to its relatively facile thermal epimerization as well as thermal rearrangement to methylenecyclobutane.[252-254] Some other small spiro systems include **51**,[255] **52**,[256] **53**,[257] **54** and **55**,[258] **56**,[259] **57**,[260] and **58**.[261]



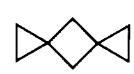
51



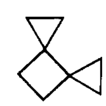
52



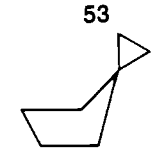
53



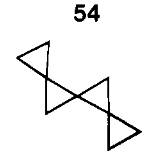
54



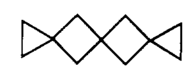
55



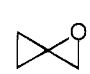
56



57

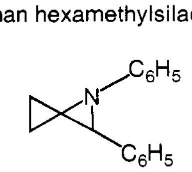


58

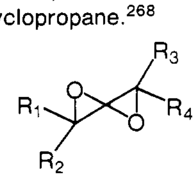


59

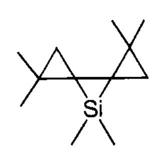
Heterocyclic analogues of spiropentane have about the same strain energy as the hydrocarbon but are also readily attacked by electrophiles and nucleophiles. Oxaspiropentane **59**[262] and some substituted derivatives are stable,[263-265] as is the aza compound **60**,[266] but **61** ($R_1 = R_2 = R_3 = R_4 = CH_3$) is a short-lived intermediate.[267a] Substitution of a *tert*-butyl group imparts kinetic stability to the dioxaspiro nucleus and a derivative of **61** (R_1 = H; R_2 = *t*-Bu; $R_3 = R_4 = CH_3$) has been isolated and characterized.[267b] Spirocyclopropane rings in **62** appear to afford some conjugative stabilization (perhaps through donation to empty silicon 3d orbitals) and this compound is more stable than hexamethylsilacyclopropane.[268]



60

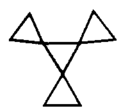


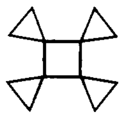
61

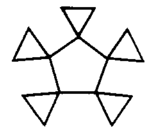


62

"Rotanes" (e.g., **63**,[269,270] **64**,[271,272] and **65**[273,274]) have the potential for cyclic delocalization of bent bond orbital electrons. In line with expectations (based solely on geometrical considerations), [3]rotane (**63**) exhibits negligible delocalization,[270] while [5]rotane (**65**) displays an ultraviolet spectrum consistent

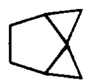

63

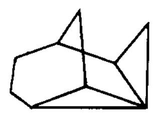

64


65

with significant delocalization of this type.[274]

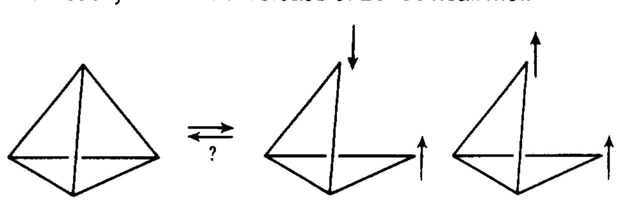
The spiropentane system has been further destabilized through introduction of a "twist" by incorporation in cyclic systems as exemplified by **66**[275] and **67**.[276] This distortion will be treated further in section XI.


66


67

VII. Tetrahedrane

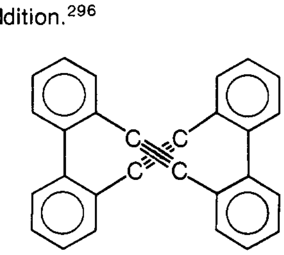
If tetrahedrane [bicyclo[1.1.0.0^{2,4}]butane, **68**] is indeed a discrete molecular entity, it is the possessor of enormous inherent thermodynamic instability due to strain. The most recent estimates of the strain in this molecule are between 129 and 137 kcal/mol.[277,278] On a per bond (C–C) basis, a calculated destabilization of ca. 22 kcal/mol might suggest reactivity similar to that which characterizes the central bond of bicyclo-[1.1.0]butane. However, the strain per carbon (ca. 33 kcal/mol) is far greater than in any known compound (see section XV for further discussion). Tetrahedrane is predicted to be much less stable than its unstable valence isomer[279] 1,3-cyclobutadiene[280,281] (70–84 kcal/mol calculated enthalpy difference[277,278,282]). Although concerted thermal rearrangement between these valence isomers is "symmetry forbidden",[279] ground-state conversion of tetrahedrane to cyclobutadiene is quite facile.[281] Similarly, concerted fragmentation of tetrahedrane to acetylene is thermally forbidden[279] but is calculated to occur readily[283–286] with release of 20–30 kcal/mol.[277,278,282]


68 68a 68b

However, the greatest source of pessimism concerning the isolation of this molecule is that the strain energy released in forming a biradical (**68b**) is very near the dissociation energy of a parafinic bond. The biradical is estimated to be only about 12 kcal/mol higher in enthalpy content.[277b] Obviously, this intermediate, once formed, will be highly reactive. Another cause for pessimism is that all substituents should stabilize the biradical,[277a] and attempts at destabilization through incorporation of the tricoordinate carbon atoms at geometrically constrained bridgeheads should not be successful since radical inversion barriers are low.[228] Before proceeding to a discussion of the evidence implicating a "tetrahedrally symmetric intermediate", a brief caveat on tetrahedral molecules is presented below.

Just as tetrahedrane is unstable relative to two molecules of acetylene, the hypothetical molecule N_4 (tetrahedral) is calculated to be well over 100 kcal/mol less stable than two nitrogen molecules[287,288] (this is due to what may be termed "anomalous stability" of the nitrogen molecule as well as to the instability of tetrahedral N_4). However, white phosphorus consists of tetrahedral P_4 molecules which are considerably more stable than diatomic phosphorus. Comparison of single bond strengths [D(N–N) $\simeq$ 38 kcal/mol; D(P–P) $\simeq$ 51 kcal/mol[289]] and triple bond strengths [D(N≡N) $\simeq$ 226 kcal/mol; D(P≡P) $\simeq$ 116 kcal/mol[290]] clarifies the above observations. Furthermore, the strain in tetrahedral P_4 is only about 20 kcal/mol,[289] due in part to decreased angular distortion (bond angle in PH_3 is about 94° [289] and the C–P–C angle in $P(CH_3)_3$ is about 99° [291]). Tetrahedral $(SiH)_4$ is to date unknown. The relatively strong silicon–silicon single bonds and very weak multiple bonds[292] may allow the tetrahedral compound to be more stable than $(SiH)_2$. (Characterization of these compounds is complicated by the extreme lability of the silicon–hydrogen bond in the presence of air or water.) The tetrahedral compound $(BCl)_4$ is difficult to synthesize in quantity but is isolable.[293]

Early claims for the existence of tetrahedrane derivatives have appeared in the literature[279,280] [we note early claims of many simple, highly strained systems also exist (Ring Index) most of which have also been later shown to be incorrect]. During the past decade a published claim[294a] of a diphenyltetrahedrane was later withdrawn.[294b,295] To date, the existence of **68** has not been established experimentally. Evidence implicating the existence of a tetrahedrally symmetric intermediate[283–286] is consistent with the existence of **68** in a potential minimum or its existence as an activated complex for interconversion of diradicals **68a** or **68b**. Of course, singlet–triplet interconversion is spin forbidden and should presumably occur less frequently than isotopic labeling studies appear to indicate. The most encouraging theoretical prediction, concerning the potential isolability of **68**, is made in a recent ab initio study[278] in which it is predicted that the barrier to formation of the biradical is greater than 18 kcal/mol (singlet more stable than triplet at a point on the energy surface at which the C1–C2 distance is about 1.81 Å). This would indicate that tetrahedrane should be observable via vibrational spectroscopy even if it is not isolable. Evidence for the actual trapping in a matrix at −196 °C of either tetramethyltetrahedrane or a biradical has recently been presented.[281] Combination of these last experimental observations with the theoretical calculations cited immediately above implies that tetramethyltetrahedrane has a finite existence in a matrix at −196 °C. We note in passing another potential approach to tetrahedrane through compound **69** in which sterically crowded triple bonds are held in a rigid and favorable orientation for photochemically allowed cycloaddition.[296]


69

We may ask if there is a discrete molecular entity, tetrahedrane, and if so, is it observable? Similar questions were posed concerning cyclobutadiene in the very recent past. Not only has cyclobutadiene been monitored spectroscopically (although under markedly unearthly conditions),[297–302] but tri-*tert*-cyclobutadiene has been monitored in solution at room temperature by NMR.[303] Not only have electronically perturbed "push-pull" cyclobutadienes been isolated,[304] but also two essentially unperturbed cyclobutadienes have likewise been purified and characterized.[305,306] Without claims of prophecy, it may well be that in a few years from now observations of tetrahedrane intermediates will appear frequently in the literature.

TABLE VI. Calculated Strain Energies[a–c] of Some Cycloalkenes, Methylenecycloalkanes, and Bicycloalkenes

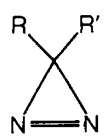
Compound	Strain, kcal/mol	Compound	Strain, kcal/mol
Acetylene(cycloethene)	9.1;[d] 58[e]	Bicyclo[2.1.1]hex-2-ene[313–315]	Est 50[f]
Cyclopropene	54.5[a,c]	Bicyclo[2.2.1]hept-2-ene	27.2;[a] 23.6[b]
Cyclobutene	30.6;[a] 34.0[c]	Bicyclo[2.2.1]hepta-2,5-diene	34.7;[a] 31.6[b]
Cyclopentene	6.8;[a] 6.9[b]	Bicyclo[2.2.2]oct-2-ene	16.0[b]
Cyclohexene	2.5;[a] 2.6[b]	Bicyclo[2.2.2]octa-2,5,7-triene (barrelene)[316]	25.6[b]
cis-Cycloheptene	6.7;[a] 7.35[b]		
cis-Cyclooctene	7.4;[a] 8.8[b]	1,3-Cyclopentadiene	2.9;[a] −0.9[c]
cis-Cyclononene	11.5[a]		
cis-Cyclodecene	11.6[b]	(Bismethylene)cyclopropane[317]	39.6[c,g]
Methylenecyclopropane	41.7;[a] 40.8[c]	(Trismethylene)cyclopropane[318,319]	28.8[c,g]
Methylenecyclobutane	28.8[a]	Methylenecyclopropene[320]	41.5[c,g]
Methylenecyclopentane	6.3;[a] 5.2[c]		

[a] See ref 11. [b] See ref 312. [c] Heats of formation calculated in N. C. Baird and M. J. S. Dewar, *J. Chem. Phys.*, **50**, 1262 (1969), and strainless heats of formation (cf. ref 11). For MINDO/3 calculations, see R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1294 (1975). [d] Relative to the "strain" in ethylene: ($2\Delta H_f$(ethylene) − ΔH_f(ethane)). [e] Comparison of ΔH_f(acetylene) with the sum of two strainless (CH) increments. [f] Obtained by adding ca. 10 kcal/mol to the strain energy of bicyclo[2.1.1]hexane (cf. ref 12). [g] The calculated *destabilization* energies appear to be too low and perhaps include an overestimate of resonance stabilization.

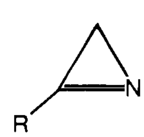
VIII. Normal Alkenes with σ Strain

A. Cycloalkenes, Bicycloalkenes, and Related Compounds

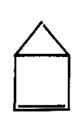
The extra strain energy present in molecules such as cyclopropene, cyclobutene, methylenecyclopropane, and norbornene relative to the saturated compounds may be attributed to increased strain in the σ framework. The strain energy in cyclopropene[307] is about 54.5 kcal/mol (Table VI), and it is logical to assume that part of this might be due to a weak π bond. The extreme reactivity of this bond (e.g., cyclopropene is a highly reactive dienophile[307]) supports this view. However, the double bond appears to be an abnormally strong one if judged by the criteria of bond length (1.30 Å[307,308]) and vibrational frequency [however, see discussion in section III (and indeed warning) concerning the vibrational frequency and bond strength of cyclopropane]. The σ framework, then, is the source of the strain energy, and if the π bond is abnormally strong, strain in the σ framework exceeds 54.5 kcal/mol. Increased angular strain at C-3 relative to a methylene group in cyclopropane ($C_1C_2C_3$ angle in cyclopropene is about 51° [307,308]), and increased angular strain at the trigonal C-1 and C-2 carbons, relative to the tetracoordinate carbons in cyclopropane, is responsible for part of the destabilization. The molecule's geometrical constraints impose increased deviations of the internuclear axes from the regions of maximum orbital overlap, relative to the deviations in cyclopropane. Addition across the double bond in cyclopropene is a mechanism for releasing at least 26 kcal/mol strain in the σ framework. Calculated strain energies for a number of cycloalkenes, methylenecycloalkanes, and bicycloalkenes are to be found in Table VI. Discussion of benzocyclopropene and benzocyclobutene is deferred until section XIII. One might note that numerous 3*H*-diazirine derivatives, **70**, are known[309] and



70



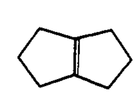
71



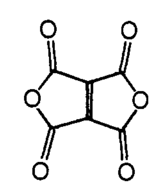
72

that the parent (R = R′ = H) has been found experimentally to be less stable than diazomethane by 1–15 kcal/mol.[310] (Cyclopropene is less stable than propyne or allene.) One aspect of the stability of many diazirines is the "thermally forbidden" nature of concerted nitrogen evolution. However, some of these explode upon impact. Photochemically, they are useful carbene precursors. 1-Azirine derivatives (**71**) have been isolated since the early 1960's.[311] Discussion of the unstable 2-azirine system is deferred until section VIII.B.

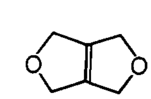
Annelation of a small cycloalkene ring may introduce additional strain. Bicyclo[2.1.0]pent-2-ene ("homocyclobutadiene", **72**[321]) has a half-life of about 2 h at ambient temperature and manifests its strain energy in thermal rearrangements (see discussion in section VIII.C). Another aspect of the instability of **72** is the calculated destabilizing orbital interaction between the "separated" cyclopropane and ethylene fragments which conceptually comprise it.[322] Thus, experimentally determined destabilization energies for this molecule would include this factor as well as the sum of the strain energies. This again illustrates the difficulties in apportioning destabilization energy. (The as-yet-unknown 2,3-dimethylenebicyclo[2.1.0]pentane is predicted to have a stabilizing interaction between the cyclopropane and 1,3-butadiene moieties).[322] The central bond in **72** is long (1.56 Å), but normal for a cyclobutene.[323] The σ system of a π bond may be appreciably distorted by its incorporation as the bridge of a small fused bicyclic system. $\Delta^{1,5}$-Bicyclo[3.3.0]octene (**73**) has been known for some time and is quite stable[324] (**74**[325] and **75**[326] have been characterized more recently), while $\Delta^{1,5}$-bicyclo[3.2.0]heptene (**76**),[327] the related (more strained and reactive) molecule **77**,[328] and $\Delta^{1,4}$-bicyclo[2.2.0]hexene (**78**)[329] have also been isolated. This last



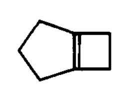
73



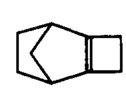
74



75



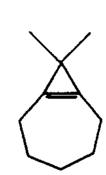
76



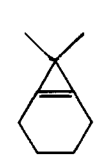
77

78

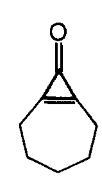
compound disappears over a period of hours in solution at room temperature.[329b] Similarly, while **79**[330,331] and **80**[332,333] are stable, isolable compounds, **81** has only been observed in solution at −60 °C.[330,331] Attempts at isolating **82** have failed,[332,333] but methyl substitution affords kinetic stability, and



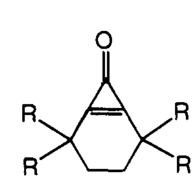
79



80

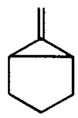


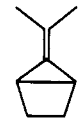
81



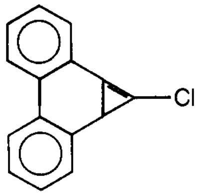
82, R = H
83, R = CH_3

83 is stable for 5 h at 100 °C.[334] (Cyclopropenone is discussed in section VIII.B.) Additional constraints imposed upon methylenecyclopropane systems lead to instability, notably by making the corresponding trimethylenemethanes (section VIII.C) more accessible. Thus, while 6-methylenebicyclo[3.1.0]hexane (**84**) is quite stable,[335] attempts at isolating **85** have failed.[336]

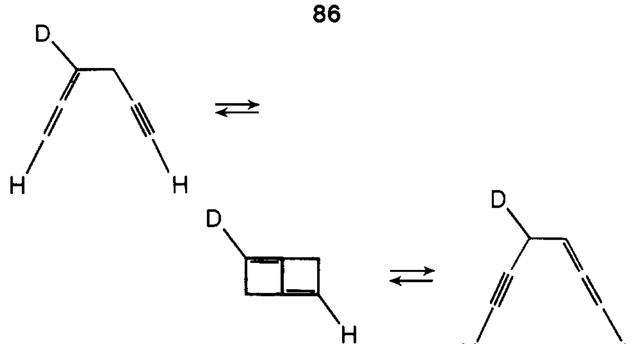

84


85

It is perhaps appropriate to mention at this time the compelling evidence for the existence of **86.**[337] This is a substituted dibenzologue of bicyclo[4.1.0]hepta-2,4,6-triene (this last species has been advanced as an intermediate in the phenylcarbene–cycloheptatrienylidene rearrangement, but it has not been trapped or even observed spectroscopically[338]). The existence of the bicyclohexadiene **87** has been deduced from deuterium-scrambling studies.[339] Similar studies implicate the discrete

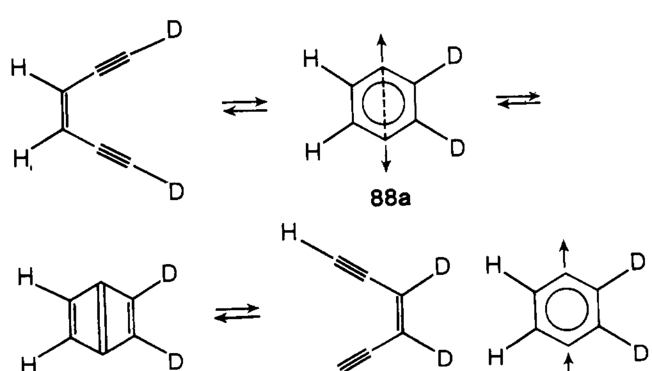


86



87

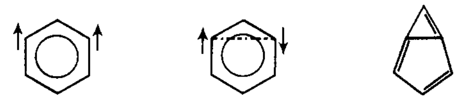
existence of 1,4-dehydrobenzene (*p*-benzyne) (**88**) (*o*-benzyne is discussed in sections XII and XIII). Flash photolysis of 1,4-benzenediazonium carboxylate yields a C_6H_4 species, presumed to be **88**, which is stable enough to be monitored for as long as 2 min in the gas phase.[341] *m*-Benzyne (**89**) has been generated



88a

88b **88c**

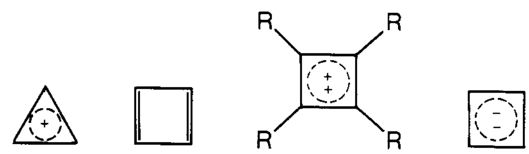
from 1,3-benzenediazonium carboxylate by flash photolysis[342] as well as by thermal means.[343] Published ab initio calculations of the three benzyne isomers assume normal benzene geometry.[344] Recent MINDO/3 calculations,[345] which include geometry optimization, do not allow a clear choice between singlet (**88a**) or triplet (**88c**) as the ground state of *p*-benzyne. They do


89a **89b** **89c**

predict appreciable 1,4-bonding in **88a** and the potential presence of an unstable bond-stretch isomer **88b.** These calculations also predict the structure of *m*-benzyne to be **89c** (central 1,5 bond length of 1.97 Å), and that this species and *o*-benzyne are of comparable stability. Apparently, bicyclo[3.1.0]hexatriene (**89c**) has actually been generated and trapped.[345a] The central bond is not the most reactive one in agreement with an ab initio prediction of 1.5 Å for its length.[345a] However, the simplifying assumption of C_{2v} symmetry made for the calculation might be too restrictive. The similarity of **89c** to azulene should be noted.

B. Strain Opposing Aromatic Stabilization or Reinforcing Antiaromatic Destabilization

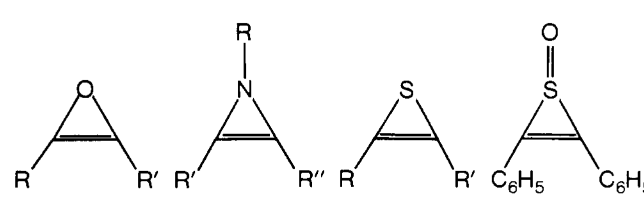
A discussion of aromaticity and antiaromaticity is completely beyond the scope of this review.[346] However, we wish to consider very briefly some simple aromatic and antiaromatic compounds in which there is appreciable strain. The cyclopropenium cation (**90**) is the best and simplest example of a system for which sizable aromatic resonance stabilization dominates strain-induced destabilization and renders the subject stable.[347]



90 **91** **92** **93**
(R = CH_3; C_6H_5)

The increase in strain upon transformation of a cyclopropane derivative to the corresponding ion is estimated at about 20 kcal/mol, but this is more than compensated for by about 40 kcal/mol of resonance stabilization.[347] The ion is stable enough to be observed as well as isolated.[348] In contrast, cyclopropenium anion[347,349,350] combines strain energy of similar magnitude with appreciable antiaromatic destabilization. Cyclobutadiene (**91**) is estimated to have about 20 kcal/mol of antiaromatic destabilization.[347] A rather conservative estimate of the strain in this compound would be about 35 kcal/mol (twice the strain of cyclobutene minus the strain of cyclobutane; this obviously does not consider the multiplicity of the ground state or second-order Jahn–Teller distortion in a singlet ground state). The net destabilization energy of at least 55 kcal/mol has made this compound highly elusive, and it is only very recently that it has actually been observed in rare gas matrices at exceedingly low temperatures.[297-302] Substituted cyclobutadiene dications (**92**) have been observed by NMR.[351,352] Evidence implicating the intermediacy of cyclobutadiene dianion (**93**) has also appeared recently.[353] Both ions are destabilized owing to electrostatic strain.

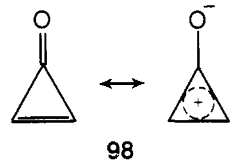
Oxirenes (**94**) have been postulated as transient intermediates in peroxy acid oxidation of alkynes[354,355] as well as in photochemical Wolff rearrangements,[356-360] but none of these have been observed even spectroscopically. Similarly, 1*H*-azirines (**95**) have also been proposed as intermediates but never ob-



94 **95** **96** **97**

served.[361,362] Strain and antiaromatic destabilization contribute to the lability of these species. Thiirene (**96,** R = H) has been generated photochemically, monitored, and has a half-life of about 2 s in the gas phase (dimethylthiirene has a half-life of about 7 s).[363] Compound **97,** however, is quite stable (d-orbital participation would lend some aromatic character).[365]

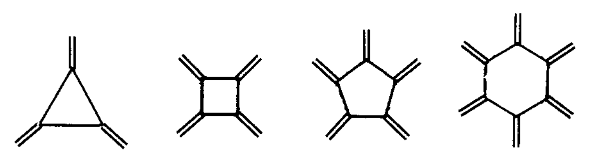
In contrast to methylenecyclopropene,[320] cyclopropenone (**98**) has been characterized and is isolable.[366-368] In fact, the di-*tert*-butyl derivative is quite stable.[369] Cyclopropenones do not form hydrates in aqueous solution as cyclopropanones do.[368] Such observations of reduced reactivity, supported by theoretical work,[370] suggest that cyclopropenone is aromatic. However,



98

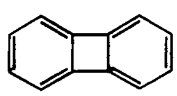
it appears that cyclopropenone is essentially no more aromatic in its ground-state properties than cyclopropene is.[371,372] Aromaticity appears to be a feature of cyclopropenone's reactivity rather than its ground-state properties. Experimental data on the heat of formation of this compound are unavailable at present for practical reasons. Dihydroxycyclopropenone (deltic acid) has been obtained and is a strong acid as anticipated.[372a]

"Radialenes" (**99,**[373-375] **100,**[376] **101,**[377] and **102**[378]) have the potential for cyclic delocalization of π electrons. They appear, however, to be essentially normal olefins.[379,380] An



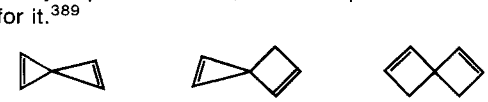
99 100 101 102

evaluation of the strain energy in [4]radialene (**100**) might be useful in estimating this parameter for cyclobutadiene. While no thermochemical data are available for **100,** the experimentally determined destabilization energy of biphenylene (**103**) is about 60 kcal/mol and is largely attributable to the four-membered ring[381] (however, distortion in the aromatic ring is also a factor; see section XIII.A).

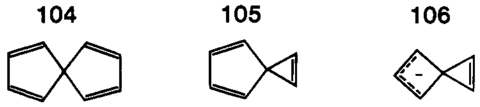


103

Small-ring, spiro-connected cycloalkenes have been studied in line with predictions of spiroconjugation in them or in their derivatives.[382,383] Although spiropentadiene (**104**) is unknown (its strain has been calculated at 145 kcal/mol[384]), derivatives of **105** have been isolated,[385] and hydrocarbon **106** has been characterized.[386] Spectral evidence has been cited for spiroconjugation in **106,**[386] **107,**[387] and **108.**[388] Although the ion **109** is potentially "spiroaromatic", no such special stability is reported for it.[389]



104 105 106



107 108 109

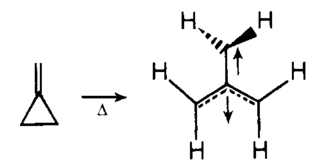
Ultraviolet,[390] NMR,[391] and photoelectron studies[392] of spiro[2.4]hepta-1,3-diene (**110**) indicate considerable cyclopropane conjugation with the diene system which might lend this compound some aromatic stability. However, gas-phase electron

110 111

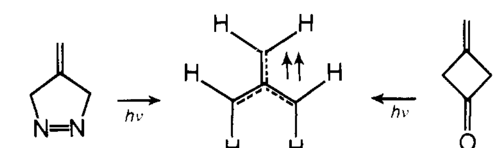
diffraction studies do not support this view.[393] Some conjugation of the cyclobutane ring in **111** is also indicated by its ultraviolet absorption spectrum.[394] Thermochemical data on these compounds are, unfortunately, unavailable.

C. Relief of Strain with the Formation of Unstable Intermediates

Strain in many cyclic molecules combined with resonance stabilization of the corresponding acyclic species allows the occurrence of numerous facile ring-opening reactions. (Concerted ring-opening reactions to stable molecules, e.g., cyclobutene to 1,3-butadiene, have been treated extensively.[395]) For example, rearrangements of various methylenecyclopropanes appear to proceed by way of singlet trimethylenemethane diradicals (perpendicular geometry **112**).[396-400] Photolysis of 4-methylene-Δ^1-pyrazoline (**113**)[401] or 3-methylenecyclobutanone (**114**)[402] yields the more stable planar (D_{3h}) triplet **115.**[400,403-405] The triplet diradical is stable for several months

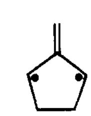


112

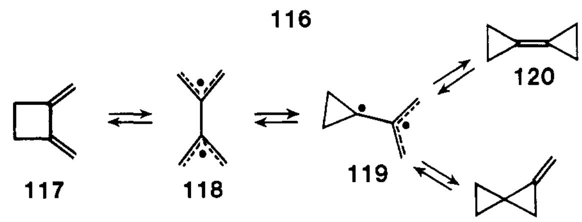


113 115 114

at −196 °C and has been monitored by ESR spectroscopy.[404] The highly strained fused bicyclic molecule **85** forms a strained trimethylenemethane diradical, **116,** which rapidly dimerizes before it can be isolated.[336] Scrambling of deuterium labels in 1,2-dimethylenecyclobutane (**117**) proceeds via tetramethyleneethane (**118**).[406,407] This diradical may also be obtained

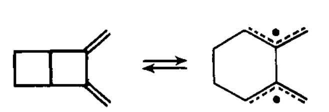


116



117 118 119 120 121

through thermally induced isomerization of **120** or **121.**[408] Additional strain (relative to that in **117**) in **122** lowers the energy barrier to **123.**[409]



122 123

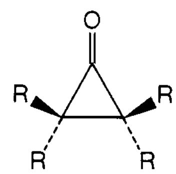
Substituted cyclopropanones (**124**)[410-412] rearrange and undergo cycloaddition reactions through intermediate oxyallyl

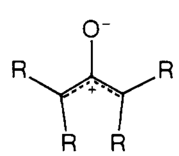
TABLE VII. Historical, Theoretical, and Experimental Data Concerning Benzene Valence Isomers

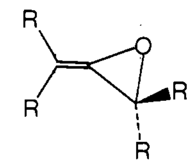
Isomer	Publication dates		Relative enthalpies, kcal/mol			Thermal stability of parent compound
	Substd	Parent	Exptl[436]	Exptl[437]	Theor[438]	
Benzene		1825	0	0	0	
(132)	1962[444]	1963[445]	+59.5[a]	+28.0[b]	+49.5	$t_{1/2}$RT 2 days[445,446]
(133)	1964[447]	1967[448]		+34.4[b]	+58.9	$t_{1/2}$RT ~10 days[448]
(134)	1965[c] 1966[449,450]	1973[451]	+91.2[a]	+59.0[b]	+80.9	Stable (RT)[451] $t_{1/2}^{90°}$ = 11 hr[451]
(135)	1959[451]				d	

[a] Hexamethyl series. [b] Hexakis(trifluoromethyl) series. [c] A tri-*tert*-butylprismane was obtained in 82% purity (see ref 460). [d] Estimated by group incremental schemes to be about 15 kcal/mol less stable than prismane.

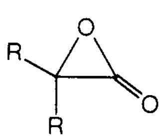
isomers (**125**) (rearrangement of cyclopropanone to allene oxide (**126**) without the intermediacy of oxyallyl has been suggested[413]). Although an early calculation predicted that oxyallyl was

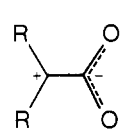

124


125

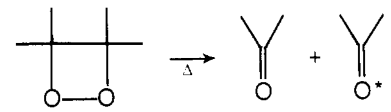

126

more stable than cyclopropanone,[414] subsequent work, including a microwave study of the parent,[415] has disproven this view. Cyclopropanone itself has thus far eluded reactions characteristic of oxyallyl.[410-412] Semiempirical[416] and ab initio[417] molecular orbital calculations predict enthalpy differences of 66 and 83 kcal/mol between cyclopropanone and oxyallyl. Incorporation of configuration interaction should significantly lower this energy difference since oxyallyl is calculated to have a slightly bonding unoccupied molecular orbital.[417] A calculated enthalpy difference of 54 kcal/mol has been obtained through application of bond-additivity methods.[418] The barrier to ring opening of di-*tert*-cyclopropanone is about 27 kcal/mol.[419] Allene oxides, **126**, isomers of the cyclopropanones, have been isolated only when afforded kinetic stability through substitution by bulky groups.[419,420] In sharp contrast to cyclopropanones are the α-lactones **127**, which open very readily, presumably to highly reactive dipolar species (**128**).[421-423] Only the bis(trifluoromethyl) derivative has been isolated.[424] Recently, evidence has been presented which implicates the intermediacy of α-sultine (sulfur analogue of α-lactone).[424a]

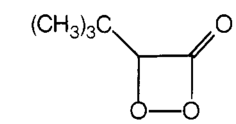

127

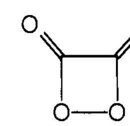

128

A novel aspect of some strained molecules is their ability to generate excited-state species when they rearrange or decompose upon heating. For example, the thermally induced rearrangement of bicyclo[2.1.0]pent-2-ene (**72**) is thought to yield 1,3-cyclopentadiene in a vibrationally excited state[425-427] (ca. 63 kcal/mol above the ground state[425]). Rearrangement of vibrationally excited cyclopentadiene appears to be competitive with its collisional deactivation.[425-427] Thermal generation of molecules in electronically excited states is the basis for phenomena termed "photochemistry in reverse" [428] or "photochemistry without light".[429] The numerous theoretical, practical, and esthetic aspects of these processes include the potential understanding of bioluminescence.[428,429] For example, tetramethyl-1,2-dioxetane (**129**) generates triplet acetone thermally[428] as does the trimethyl compound.[429] The first derivative of a 1,2-dioxetan-3-one, **120**, has been characterized and luminesces upon heating.[430] This molecule is similar to the reactive


129

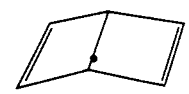
portion of the presumed intermediate responsible for firefly luminescence.[430] Bond-additivity calculations suggest the discrete intermediacy of **131** in the reaction of hydrogen peroxide with various oxalates, and its decomposition to form a molecule of triplet carbon dioxide.[431] Thermal production of excited-state benzene derivatives from the corresponding valence isomers will be discussed in section IX.

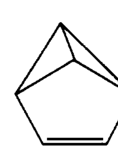

130

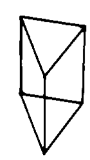

131

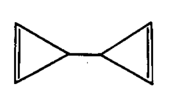
IX. Valence Isomers of Benzene and Related Systems

Valence isomers[279] (**132–135** in Table VII) of benzene[432-434] are of historical[435] as well as modern theoretical and conceptual interest. The recent isolation of these compounds and their


132


133

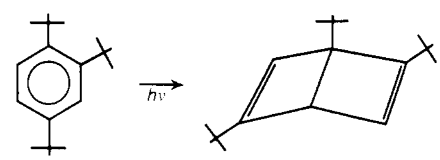

134


135

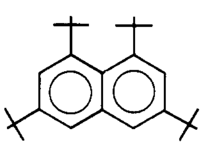
derivatives is a triumph of modern synthetic artistry. These compounds have provided some of the most spectacular examples of reactivities which are contrary to intuition yet in accord with the theory of the conservation of orbital symmetry.[395] As the result of their significant strain energies, many valence isomers are higher in energy than some of the excited states of the corresponding benzenoid compounds. Thus, "photochemistry without light" [428] has also been studied in some of these compounds.

In Table VII experimental[436,437] and theoretically calculated[438] relative enthalpies and observed thermal stabilities in the benzene valence isomer series are listed along with historical data. Two ab initio calculations have appeared,[439,440] but the agreement between experimental and calculated enthalpy differences between isomers is rather poor although the ordering of relative stabilities is consistent with other work. "Dewar benzene" [bicyclo[2.2.0]hexa-2,5-diene, **132**], "benzvalene" [tricyclo-[3.1.0.0^{2,6}]hexene, **133**], and "prismane" [tetracyclo-[2.2.0.0^{2,6}.0^{3,5}]hexane, **134**] as well as benzene have been viewed topologically as multigraphs resulting from pairwise connections of hexagon vertices[440] or equivalently having a "maxi-ring" of six (see section XV). The isomer 3,3′-bicyclopropenyl (**135**) is topologically distinct by this definition. It is interesting to note in Table VII that the first valence isomer isolated was a derivative of **135**, the latter compound being the only unsubstituted valence isomer to elude synthesis.[441] Furthermore, a very reasonable estimate[442] of +122 kcal/mol for the standard heat of formation of **135** predicts that it is the least stable benzene valence isomer even though it is *less* strained than prismane. The strain in **135** may be taken as 107–108 kcal/mol (the strain of two cyclopropene rings) and that of **134** may be estimated at 127–129 kcal/mol from the standard heat of formation of hexamethylprismane (+70.4 kcal/mol based upon the data in Table VII and the standard heat of formation of hexamethylbenzene) and group incremental schemes. The strain in prismane is very nearly equal to the sum of the strain energies of three cyclobutane rings and two cyclopropane rings, just as the strain in cubane is about equal to the strain of six cyclobutane rings.[443] Thus, neither prismane nor cubane appears to be "unique units" in the sense that bicyclobutane and spiropentane are.

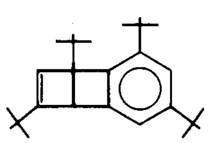
The first unsubstituted benzene valence isomer reported was bicyclo[2.2.0]hexa-2,5-diene (commonly referred to as "Dewar benzene"), **132**.[445] The positions of the carbon atoms of **132** are very similar to those in benzene, and one might expect facile conversion to the most stable isomer. The half-life of 2 days at room temperature is attributed to a "thermally disallowed" interconversion having a high activation carrier. Hexamethyl(Dewar benzene) is the most readily available benzene valence isomer hydrocarbon due to the facile catalyzed trimerization of 2-butyne.[453] The central single bond in this compound measures 1.63 Å.[454] Decreased steric repulsion between groups in the 1 and 2 positions of Dewar benzene compared to the ortho positions in benzene suggest a means of stabilizing the former. This approach was utilized in the first synthesis[444] of a Dewar-type derivative (**137**) as well as other compounds.[453,455,456] Similarly, the peri interaction in **138** facilitates the synthesis of **139**.[457] A novel method of stabilizing a Dewar-type structure is the bridging of the 1 and 4 positions with a suitable short chain. This approach was successful in obtaining **140**,[458] whose corresponding benzene isomer would be a considerably less stable [4]paracyclophane derivative (see section XIII.C). The unsubstituted analogue of **140** has been reported[459a,b] as has its shorter bridged homologue **141**.[459c] The equilibrium between the as-yet-unknown compounds **142** and [5]paracyclophane should be of considerable interest since these two may have comparable stabilities (section XIII.C). An attempt[446] at synthesis of **143** from [2.2]paracyclophane was unsuccessful.



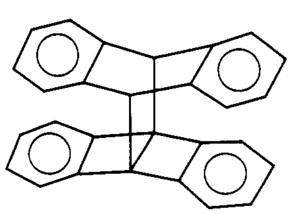
136 **137**



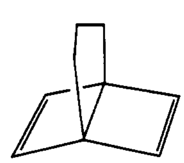
138



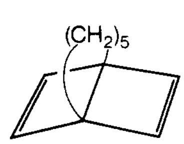
139



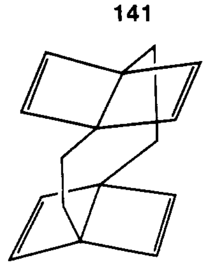
140



141

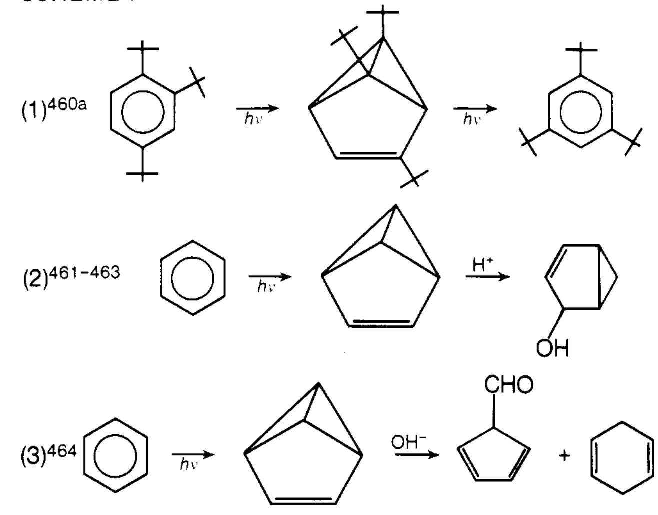


142



143

SCHEME I



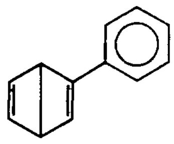
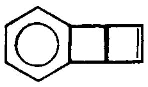
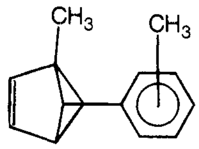
Benzvalenes have been shown to be intermediates in a number of interesting chemical reactions including those described below. However, a word of caution has appeared in the literature warning against the postulation of benzene valence isomer intermediates in cases where other mechanisms have not been eliminated.[460] It would appear that the necessary degree of substitution required to substantiate a mechanism might invalidate conclusions on the parent systems (see Scheme I). In each of these cases, proof of the mechanism involved subjecting the benzvalene in question to prevailing reaction conditions. The initial photochemical preparations of benzvalene[448,465,466] were limited to 1% yield. A recent multistep synthetic route provides 24% yield, although the authors note the necessity of small-scale preparation of benzvalene due to its explosive nature.[463]

Prismane has been likened to "an angry tiger unable to break out of a paper cage".[395] That is, in spite of an excess of greater than 90 kcal/mol of energy relative to benzene it is stable at room temperature and has a half-life of 11 h at 90 °C.[451] This latter figure corresponds to an additional input of over 25 kcal/mol in order to affect thermal decomposition. This high activation barrier is explained in terms of a "thermally disallowed" pathway.[395]

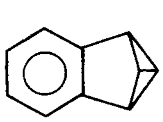
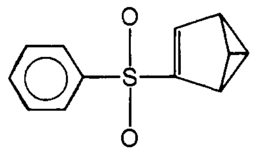
The most stable and readily accessible groups of benzene valence isomers are those in the pertrifluoromethyl[467,468] and perpentafluoroethyl series.[468] A published explanation cites dipolar destabilization of the benzene isomer as the primary basis for the accessibility of these isomers.[437] "Dewar($CC_2F_5)_6$" is, in fact, actually more stable than the distorted benzene isomer at temperatures over 280 °C, although the latter is more stable at lower temperatures.[469]

Novel "mixed" valence isomer compounds include **144**,[470] **145**,[471] **146**,[472] **147**,[463] and **148**.[473] Numerous valence isomers of heterocyclic nitrogen compounds have been reported[474–477] and oxoniabenzvalenes[478,479] and an oxonia(Dewar benzene)[479] have been proposed.

The destabilization of Dewar benzene relative to benzene has been utilized to generate, by thermal means, an excited elec-

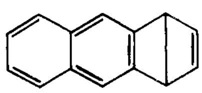




144 **145** **146**

147 **148**

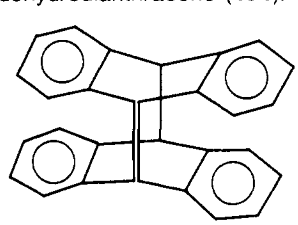
tronic state of benzene.[480a] Heating of Dewar benzene provides this molecule with energy comparable to that of the lowest triplet state of benzene (85 kcal/mol higher than the ground state), but not enough energy to obtain the first excited singlet state (115 kcal/mol higher than the ground state). Quenching of benzene triplet states, generated in this manner, by anthracene derivatives has been observed.[480a] However, an attempt at obtaining by thermal means, energetically feasible excited states of anthracene from **149** failed.[481] A discussion of the electronic states of benzene and their relationship to the valence isomers, as well as some novel aspects of benzvalene photochemistry is in the literature.[480b]



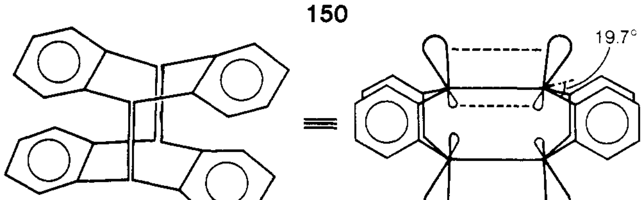
149

X. *Torsionally Distorted π Bonds*

When four groups attached to an olefinic linkage deviate significantly from coplanarity with the trigonal centers, the π bond is weakened due to poor overlap to a first approximation.[482,483] Such distortions may be induced by constraining the double bond in certain cyclic, bicyclic, or polycyclic systems or in the presence of crowded bulky substituents. Two highly interesting examples of compounds having strained olefinic linkages are 9,9′-didehydrodianthracene (**150**)[484] and 9,9′,10,10′-tetradehydrodianthracene (**151**).[485] The four substituents attached to double bonds in these compounds are "tied back" below the plane of the olefinic linkage (deviation of 19.7°).[485] There is no torsion in the double bond as in *trans*-cyclooctene or the other compounds discussed in this section, but it is obvious that pure p orbitals would have less than optimal overlap. Actually, the imposed distortion mixes idealized sp^2 and p orbitals, and the π orbital has considerable s character.[485] One should also note that the distortion in **150** and **151** is similar in nature to that in *o*-benzyne.[485] The remainder of this section will deal with double bonds having appreciable torsional character.



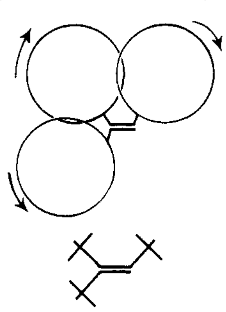
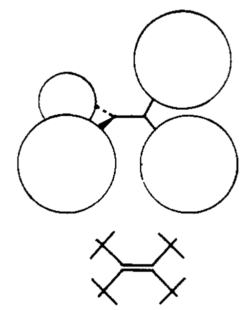
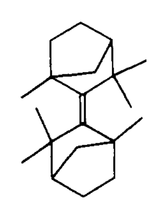
150



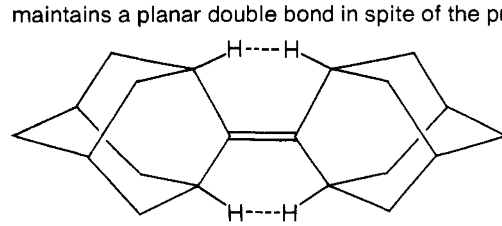
151

A. Sterically Crowded Double Bonds

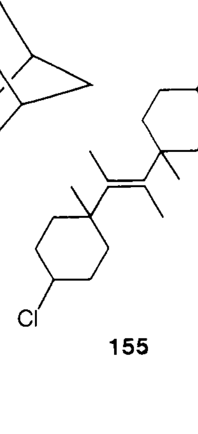
The most stable conformation of propene has a methyl hydrogen eclipsing the double bond, and two such eclipsing interactions are present in *trans*-2-butene.[486] However, in *cis*-2-butene maintenance of two such eclipsing interactions would place nonbonded hydrogens only 1.80 Å apart in an ideal geometry. This potentially destabilizing interaction is in large measure relieved by slight opening of the C═C—C angles to about 127°,[148,486,487] and the strain in *cis*-2-butene, relative to *trans*, is only 1.24 kcal/mol. The situation is more extreme in the series of *tert*-butyl-substituted ethylenes. For example, 1,1-di-*tert*-butylethylene and *cis*-1,2-di-*tert*-butylethylene may relieve a substantial portion of their repulsive nonbonded interactions by widening bond angles. Calculations suggest a (C═C—C) angle of about 135° in the latter compound, but indicate slight distortion (ca. 5°) about the double bond.[312,487] Calculated strain energies for this compound (10.36,[312] 11.6 kcal/mol[487]) are in good agreement with the experimental value (10.7 kcal/mol[488]). The calculated strain energy of 1,1-di-*tert*-butylethylene is 12.05 kcal/mol.[487] Tri-*tert*-butylethylene (**152**)[489] also may, in principle, relieve nonbonded repulsions without disturbing π overlap. However, the molecule is calculated to have an olefinic torsional angle of 16° accompanying (C═C—C) angle opening,[487] and this is consistent with the low olefinic vibrational frequency[489] and long ultraviolet absorption wavelength[490] observed for this compound. Its strain energy is calculated at about 32 kcal/mol.[487] Interestingly, the weakened double bond in **152** adds bromine slowly because of steric hindrance.[491] Tetra-*tert*-butylethylene (**153**) has not yet been reported.[491a] Steric repulsion in this compound might be relieved by a totally unrealistic stretch of the double bond or by substantial torsion. Calculations suggest a 75° twist[487] which would give this compound substantial diradical character. Ironically, once obtained, **153** may be surprisingly stable in analogy to the sterically hindered tri-*tert*-butylmethyl radical.[492] Compound **153a** (or its cis isomer) has, however, recently been characterized.[491b] Ultraviolet spectral data for a number of neopentyl-substituted ethylenes are in the literature.[493] Biadamantylidene (**154**)[494] maintains a planar double bond in spite of the presence of sig-

152 **153** **153a**



154



155

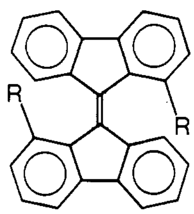
TABLE VIII. Experimental and Calculated Thermodynamic and Kinetic Parameters of Small and Medium *trans*-Cycloalkenes

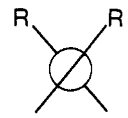
Compound	$\Delta G°$, kcal/mol (trans − cis)	$\Delta H°$, kcal/mol (trans − cis)	Strain,[11] kcal/mol	$\Delta G^{\ddagger}_{rac}$, kcal/mol
trans-Cycloheptene		Calcd + 20.3[312]	~+27[b]	
trans-Cyclooctene		+9.2[c]	+16.7	36[d]
trans-Cyclononene	+4.04[a]	+2.9[a,c]	+14.4	20[d]
trans-Cyclodecene	+1.86[a]	+3.6;[a] +3.3[c]		10[d]
trans-Cycloundecene	−0.67	−0.12[a]		
trans-Cyclododecene	−0.49	+0.41[a]		

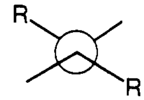
[a] A. C. Cope, P. T. Moore, and W. R. Moore, *J. Am. Chem. Soc.*, **82**, 1744 (1960). [b] Add strain in *cis*-cycloheptene (6.7 kcal/mol, cf. ref 11) to calculated (trans − cis) enthalpy difference of +20.3 kcal/mol (cf. ref 312). [c] R. B. Turner and W. R. Meador, *J. Am. Chem. Soc.*, **79**, 4133 (1957). [d] A. C. Cope and B. A. Pawson, *ibid.*, **87**, 3649 (1965).

nificantly repulsive nonbonded hydrogen interactions (1.95 Å separation).[494a] Tetracyclopropylethylene[495a,b] and tetraisopropylethylene[495c,d] have been isolated. The latter exhibits a high barrier to isopropyl group rotation due to the operation of the "gear" or "cogwheel" effect.[495c,d] A double bond torsional angle of 16° has been found for 2,3-bis(*cis*-4-chloro-1-methylcyclohexyl)-*trans*-2-butene (**155**)[496] in fair agreement with a calculated twist of 22° in di-*tert*-butyl-*trans*-2-butene.[487]

An idealized coplanar bifluorenylidene, **156** (R = H), would maintain nonbonded carbon–carbon and hydrogen–hydrogen distances of 2.5 and 0.7 Å, respectively. The associated repul-

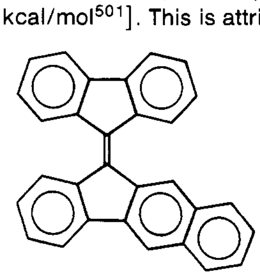




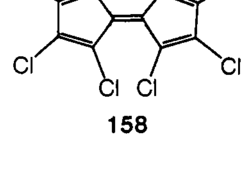


156 (*trans*) **156a** (*trans*) **156b** (*trans*)

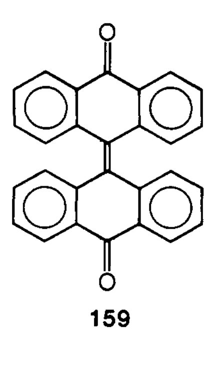
sive interactions could be relieved by torsion around the double bond or folding in opposite directions at the olefinic termini. [Newman projection of the twisted conformation (**156a**) and the folded conformation (**156b**), respectively]. Early X-ray results favor **156b**,[497] but more recent studies on a derivative of **156** [R = $CO_2CH(CH_3)_2$], for which structure **156a** (torsional angle 40°) was deduced, indicate that the twisted conformation is best for bifluorenylidene.[498a] This expectation appears to be confirmed and a torsional angle of 43° is reported.[498b] Barriers to cis–trans isomerism in these compounds are quite low [**156** (R = $CO_2CH(CH_3)_2$), 20–21 kcal/mol;[499] **156** (R = CH_3), 19 kcal/mol;[500] **157**, 23.5 kcal/mol[501]]. This is attributed to steric de-



157



158

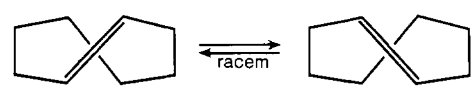


159

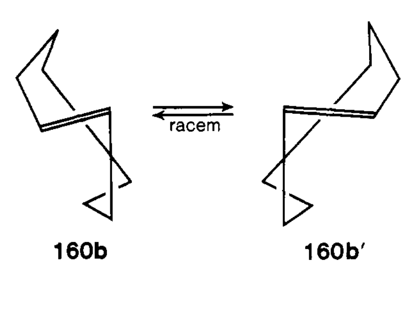
stabilization of the ground state and resonance stabilization of the diradical transition state. Octachloropentafulvene (**158**)[502] is a stable (in marked contrast to the hydrocarbon), blue-violet substance having a 41° torsional angle about the olefinic linkage.[503] In an ideal coplanar arrangement, nonbonded chlorine–chlorine distances of 2.2–2.3 Å (1.2–1.3 Å less than the sum of the van der Waals radii) would be maintained. Torsion increases the nonbonded distance to 3.2 Å.[503] Bianthrone (**159**) and its derivatives are fascinating compounds because they exhibit thermochromism (heat-dependent color changes). The A isomer (A, B, and C refer to distinct isomers of decreasing stability[504]) maintains a folded conformation similar to **156b**.[505] The B isomer is photostable but thermally labile and is responsible for the thermochromic properties of **159**.[506] It exists in a twisted conformation, having a torsional angle calculated at 57°, and is less stable than the A isomer by 5 kcal/mol.[506] (The C isomer has not yet been observed for **159**[506]).

B. *trans*-Cycloalkenes

Small- and medium-sized *trans*-cycloalkenes also suffer twisting of their double bonds and concomitant rehybridization. Poor π overlap, strained σ systems, and nonbonded repulsions make some of these compounds highly reactive and often very difficult to isolate. To date, no experimental evidence has been found implicating the existence of *trans*-cyclohexene.[507] *trans*-Cycloheptene has been generated and trapped, but not yet observed spectrophotometrically.[508] The smallest stable compound in this series is *trans*-cyclooctene (**160**), first isolated by Cope and his coworkers in 1953. The strain energy of *trans*-cyclooctene is 16.7 kcal/mol (Table VIII) and may be largely attributed to the twisted double bond. While X-ray determination of a platinum complex of a *trans*-cyclooctene derivative indicates a crossed conformation (**160a**) for the ring,[509] gas-phase electron diffraction studies of *trans*-cyclooctene indicate a distorted chair conformation (**160b**) in which there is a 23° "twist" angle.[510] However, recent X-ray results[510a] on *trans*-2-cyclooctenyl 3′,5′-dinitrobenzoate as well as more recent electron diffraction data[510b] on the parent compound favor **160a** with an 18° "twist". The twist nature of this compound



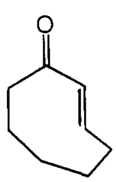
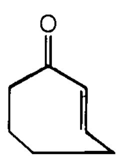
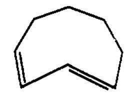
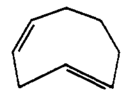
160a **160a′**



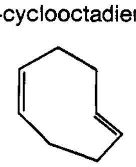
160b **160b′**

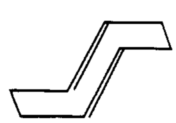
makes it dissymmetric, and it has been optically resolved.[511] Furthermore, the inherently dissymmetric chromophore of *trans*-cyclooctene is responsible for its very high specific rotation.[512] [Hexahelicene (see section XIII) exhibits a similar property.] *trans*-Cyclooctene retains full optical activity after heating at 61 °C for seven days.[513] This high barrier to racemization results from steric destabilization of the transition state caused by hydrogens forced into the interior of the ring en route to a 180° rotation around the double bond. Table VIII lists experimental free energy differences and experimental and calculated enthalpy differences between some *cis*- and *trans*-cycloalkenes, as well as strain energies of *trans*-cycloalkenes and experimental free energies of racemization for these compounds. Increased ring size allows more facile passage of vinylic hydrogens through the center of a ring. Thus, at room temperature *trans*-cyclononene racemizes as it is formed, and observation of optically active *trans*-cyclononene is feasible by polarimeter only at temperatures of 0 °C and lower.[513] The strain imposed by incorporation of a trans olefinic linkage in a cyclic structure decreases with increasing ring size. As is evident from Table VIII, *trans*-cycloundecene and *trans*-cyclododecene are more stable than the cis isomers.

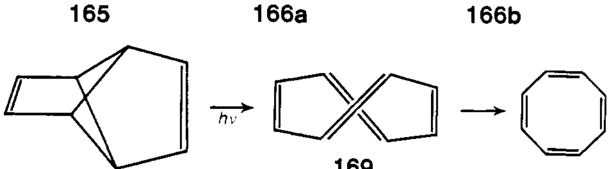
One might imagine that in a small-ring *trans*-cycloalkene, the triplet state may be more stable than the corresponding triplet in the cis isomer, because of decreased repulsions in the former, between electrons of like spin.[514] This principle has been applied in the photogeneration of *trans*-2-cyclooctenone (**161**) from the cis isomer.[514] *trans*-2-Cycloheptenone (**162**) has likewise been


161

162

163

164

generated but, in contrast, not isolated.[515,516] *cis,trans*-1,3-Cyclooctadiene (**163**),[517] *cis,trans*-1,4-cyclooctadiene (**164**),[518] *cis,trans*-1,5-cyclooctadiene (**165**),[519,520] and *trans,trans*-1,5-cyclooctadiene (**166**)[521] have been obtained. The NMR data

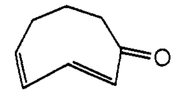
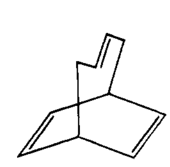
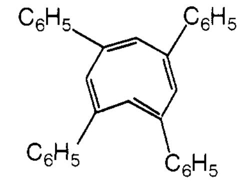

165

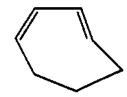
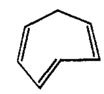
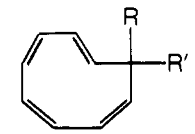
166a

166b

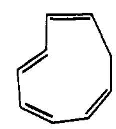
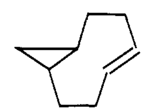


167 **169** **168**

on **166** do not allow assignment of structure **a** or **b** to *trans,-trans*-1,5-cyclooctadiene.[521] This compound has been cited as a possible intermediate in the photochemical rearrangement of *cis,cis*-1,5-cyclooctadiene to **32**,[521,522] much as the photochemical conversion of **167** to all *cis*-cyclooctatetraene (**168**) is thought to proceed through **169**.[523] Attempts at observing **169** via NMR at −60 °C were unsuccessful.[523] Dimers of *trans,cis*-2,4-cyclooctadienone (**170**) were obtained by irradiation of the cis,cis isomer.[524] The compound **171** has also been obtained.[525] The presence of *cis,cis,cis,trans*-1,3,5,7-cyclooctatetraene has been suggested[526] and the tetraphenyl derivative, **172**, has been isolated and has a half-life of 18 h at 25 °C.[527] The intermediacies of **173**,[528,529] **174**,[530] and **175**[531] have been suggested, and *cis,cis,trans,cis*-cyclononatetraene (**176**) has been trapped.[532] Two highly strained isomeric *trans,trans*-


170

171


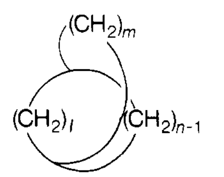
172

173

174


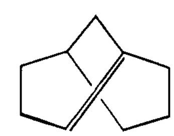
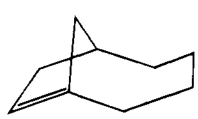
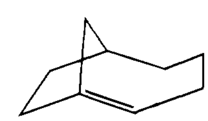
175

176

176a

bicyclo[6.1.0]non-4-enes have been obtained.[533] The "parallel" isomer (**176a**) exhibits an unprecedented facile thermal conversion of an isolated trans to cis olefinic linkage.[533]

C. Bridgehead Olefinic Linkages

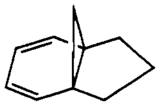
The distorted bridgehead double bonds of small bicyclic systems ($l,m,n \neq 0$ in **177**; compounds having $m = 0$ will be considered in section XI) are similar to those in small *trans*-cycloalkenes.[482,535] Bicyclo[3.3.1]non-1-ene (**178**),[534,535] $\Delta^{1,8}$-bicyclo[4.2.1]nonene (**179**),[536] and $\Delta^{1,2}$-bicyclo[4.2.1]-nonene (**180**)[536] each contain a *trans*-cyclooctene ring and are,



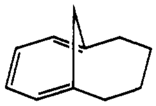
177

178

179

180

in an analogous way, the smallest isolable members of the **177** series. The strain energies in *trans*-cyclooctene and **178** are rather similar in magnitude (9.2 and 12 kcal/mol for the double bond in **178**). However, one should note that the conformation of *trans*-cyclooctene is not yet firmly established (section X.B) and comparison with **178** is not obvious.

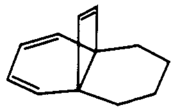
The strain in molecules such as **178–180** was recognized by Bredt during his investigations of camphor and pinane derivatives between 1900 and 1924. His original formulation[538] of the rule presently bearing his name might be interpreted as an absolute "prohibition" of bridgehead olefinic linkages,[482] or "prohibition" of these double bonds in small and medium-sized ring systems.[535] Systematic investigations of the limits of Bredt's rule were undertaken during the late 1940's,[539] and a review was published in 1950.[540] In this review a stability parameter ($S = l + m + n$) was defined for which the smallest observed value at the time was 9. Later, recognition that the determining factor was the size of the smallest ring containing a trans linkage[535] replaced the S criterion for stability. In a recent review[507] it has been noted that this second criterion does not allow prediction, for example, of the relative stabilities of $\Delta^{1,2}$-bicyclo-[4.3.1]decene and $\Delta^{1,9}$-bicyclo[4.3.1]decene, each of which has a *trans*-cyclononene ring and an S value of 9. The chemical manifestations of Bredt's rule have been summarized.[228,507] An example is the exclusive presence of the norcaradiene **181**[541] (cycloheptatriene valence isomers are normally more stable,[542] and the norcaradiene homologue of **181** is considerably less stable than its isomer **182**[541]). Similarly, **183,** rather than its



181

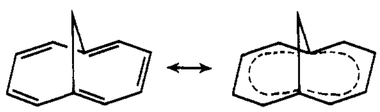


182

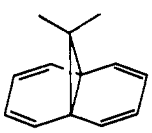


183

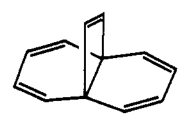
valence isomer, is observed exclusively.[543] One may note that the aromatic compound 1,6-methano[10]annulene (**184**)[544] obviously maintains distorted bridgehead overlap. The standard



184



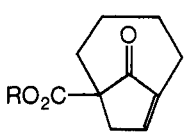
185



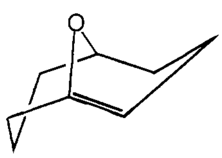
186

heat of formation of this compound has been measured recently, and difficulties in properly apportioning strain and aromatic stabilization have been discussed.[545] Relatively slight perturbation of this system, as in **185,** is enough to favor the norcaradiene structure shown,[546] and this is also the case for **186.**[547]

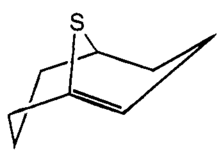
In addition to **178–180**, compounds **187,**[548] **188,**[549] **189,**[550] **190,**[551] and **191**[552] have been isolated. All of these molecules



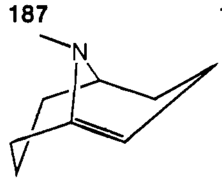
187



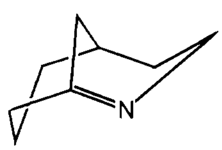
188



189



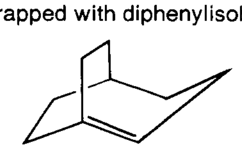
190



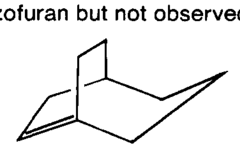
191

are thought to exist in the *zusammen* conformation shown in which the double bond is trans in the larger of the two rings in which it is endocyclic.[553] The formally conjugated molecules **187–190** all exhibit spectral properties very different from those of their acyclic counterparts.[548–551]

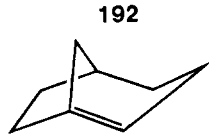
$\Delta^{1,2}$-Bicyclo[3.2.2]nonene (**192**) and $\Delta^{1,7}$-bicyclo-[3.2.2]nonene (**193**), each of which contain *trans*-cycloheptene rings, have been observed by NMR at −80 °C and their dimers isolated at higher temperatures.[554] $\Delta^{1,2}$-Bicyclo[3.2.1]octene (**194**) and $\Delta^{1,7}$-bicyclo[3.2.1]octene (**195**) have been generated and trapped with diphenylisobenzofuran but not observed.[555]



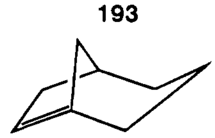
192



193

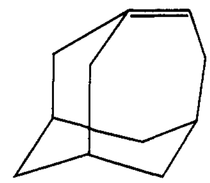


194

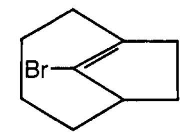


195

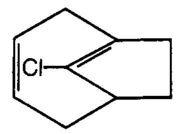
Δ^{12}-Homoadamantene (**196**) has been generated and its dimers characterized.[556] The intermediacies of **197,**[557] **198,**[558] and **199**[559] have also been implicated.



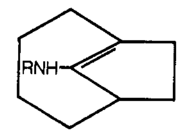
196



197

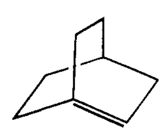


198

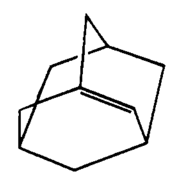


199

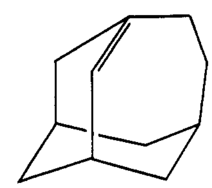
As stated previously, no experimental evidence for even the transient existence of *trans*-cyclohexene has been presented.[507] Bicyclo[2.2.2]oct-1-ene (**200**)[560,561] has been generated and trapped as has adamantene (**201**)[562–564] and $\Delta^{1,7}$-homoadamantene (**202**).[565] These compounds all contain *trans*-cyclohexene rings. The brief existence of 1-norbornene (**203**) has been established by its trapping with furan.[566] Interestingly, substitution



200

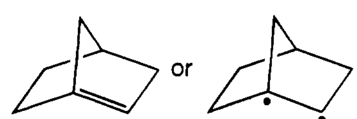


201

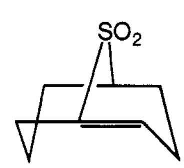


202

of a fluorine atom at the 4 position (opposite bridgehead carbon) of **203** has a somewhat stabilizing effect[567] (section XVI.B). The only compound, isolated to date, having a trans six-membered ring is **204.**[568]

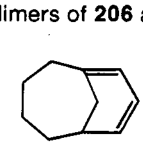


203

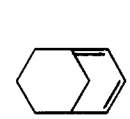


204

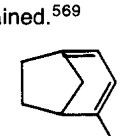
Inclusion of an extra double bond in small bicyclic systems introduces additional constraints. Thus, while **205** is isolable, only dimers of **206** and **207** have been obtained.[569]



205

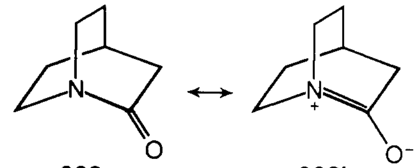


206

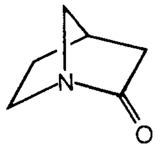
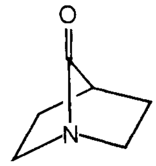


207

Bridgehead amides such as 2-quinuclidone (1-azabicyclo[2.2.2]octan-2-one, **208**) are of interest as potential indicators of stability of the analogous olefins. 2-Quinuclidone is isolable and displays an infrared spectrum atypical for an amide and explicable in terms of reduced contribution from resonance contributor **208b.**[570] A failed attempt at synthesis of 1-azabicyclo[3.3.1]nonan-2-one is reported,[571] although in light of the stability of both **178** and **208** it should also be isolable. The bridgehead amides **209** and **210,** neither of which has been reported, should have virtually zero resonance stabilization of the dipolar type. These compounds may help to shed some light on the question of the role of resonance in the thermodynamic and chemical stabilities and physical properties of amides.



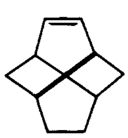
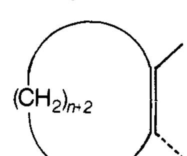
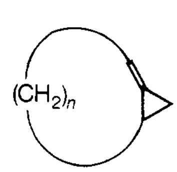
208a 208b

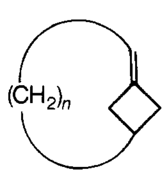
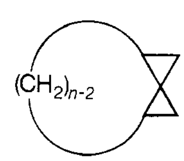
209 210

XI. "Bredt Compounds" and Cyclic Allenes

Köbrich has coined the term "Bredt compound", defined as ". . . bicyclic (and polycyclic) systems (alicycles and heterocycles) that, in addition to a strained σ-bond skeleton, have a twisted π-bond at a bridgehead, and *purely* because of this ring strain, in contrast with compounds having the same structure but without this π-bond, are unstable at room temperature".[482] According to this definition, **178** is not a "Bredt compound" since it is isolable at room temperature, while **192** is a "Bredt compound". Twistene (**211**)[572] has a torsionally distorted nonbridgehead double bond, is isolable at room temperature, and therefore is not a "Bredt compound". 9,9′-Didehydrodianthracene (**150**) and 9,9′,10,10′-tetradehydrodianthracene (**151**) are not "Bredt compounds" since they are isolable and also because their olefinic linkages are not twisted. Köbrich also postulates the similarity in torsion, strain, and stability in the series of molecules **212–215.**[482] Thus, knowledge of the physical and chemical properties of one may allow reasonable expectations of the properties of the others.[482] An idealized (C=C=C) angle of 180° and torsional angle of 90° dictates the requirement for relatively large rings in the cyclic allene (**212**) series. Geometrical

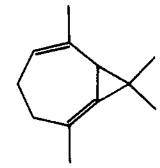
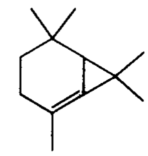
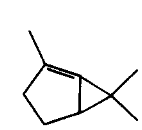
  

211 212 213

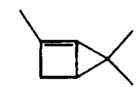
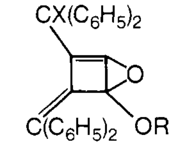
 

214 215

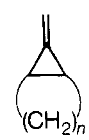
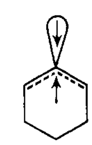
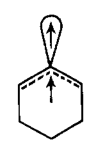
constraints opposing ring incorporation are less severe for **213** and **214,** and even less so for **215.**[482] This relationship is successful in predicting the observed stability of $\Delta^{1,2}$-bicyclo[5.1.0]octene (**213,** n = 4),[335] since 1,2-cyclononadiene (**212,** n = 4)[573,574] and tricyclo[4.1.0.0^{1,3}]heptane (**215,** n = 4)[575] are stable. It would appear that $\Delta^{1,2}$-bicyclo[5.1.1]nonene (**214,** n = 4) should also be isolable.[482] The bicyclic diene **216** has also been characterized.[576] Compound **217** has a half-life of about 70 h at room temperature[577] and is also considered to be a "Bredt compound".[482] Only dimers of **218** have been isolated, and at temperatures of −40 °C and higher this compound forms a strained, highly reactive trimethylenemethane intermediate similar to **116.**[482] The fact that **219** could not be generated under conditions which are feasible for **218**[482] casts considerable doubt on a claimed isolation of **220.**[578] On the basis of these findings, moderate and short lifetimes at room temperature may be predicted for $\Delta^{1,2}$-bicyclo[4.1.1]octene (**214,** n = 3) and $\Delta^{1,2}$-bicyclo[3.1.1]heptene (**214,** n = 2), respectively.[482] Related work includes the findings that while $\Delta^{1,2}$-bicyclo[6.1.0]nonene (**213,** n = 5) is more stable than 8-methylenebicyclo[5.1.0]octane (**221,** n = 5), 7-methylenebicyclo[4.1.0]heptane (**221,** n = 4) is more stable than $\Delta^{1,2}$-bicyclo[5.1.0]octene (**213,** n = 4) largely due to the rigidity (and lower entropy) of the latter.[335] Since **217** has some stability at room temperature, perhaps a similarly substituted (for purposes of enhanced kinetic stability) 1,2-cyclooctadiene might behave in a like manner. Unsubstituted 1,2-cyclooctadiene has thus far only been observed spectroscopically at low temperature.[579] 1,2-Cycloheptadiene and 1,2-cyclohexadiene are both transient intermediates that have been trapped.[580–584] The allenic groups in these small cycloallenes are assumed to be distorted both by bending of the (C=C=C) angle and twisting of the C_1–C_2 linkage.[585] 1,2-Cyclohexadiene has also been discussed in terms of a planar allenic linkage having either singlet (**222a**) or triplet (**222b**) character.[584,585] Intermediacy of the homoaromatic

216 217 218

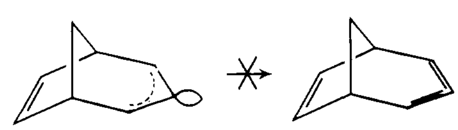
 

219 220

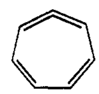
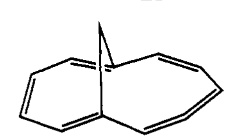
  

221 222a 222b

carbene **223,** related in a formal sense to the bicyclic (and enormously distorted) allene **224,** has also been postulated.[586,587] The structure 1,2,4,6-cycloheptatetraene (**225**) is calculated to be more stable than singlet cycloheptatrienylidene,[338] and the related bicyclic allene **226** has been trapped.[588] *meso*-

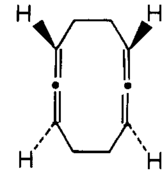
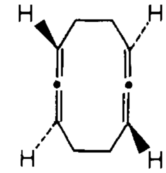
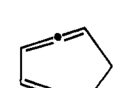


223 224

225 226

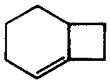
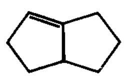
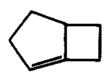
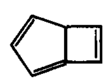
1,2,6,7-Cyclodecatetraene (**227**) is known, but the *dl* isomer **228** has yet to be characterized.[574,589] The possible intermediacy of **229** has been considered.[590]

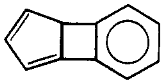
  

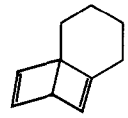
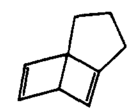
227 228 229

Bridgehead olefinic linkages in suitably small bicyclo-[$m.n.$0]alkenes possess considerable torsional character. While

$\Delta^{1,2}$-bicyclo[4.2.0]octene (**230**),[591] bicyclo[3.3.0]oct-1-ene (**231**),[592] and $\Delta^{1,2}$-bicyclo[3.2.0]heptene (**232**)[593] are isolable at room temperature, bicyclo[3.2.0]hepta-1,3,6-triene (**233**) is not[594,595] (half-life at 25 °C of 3 h in dilute solution) nor is its benzologue **234**.[596] Indications are that bicyclo[2.2.0]hex-1-ene (**235**) is probably not isolable.[482] The novel Dewar benzene **236** has a half-life of 58 min in solution at room temperature,[459a,b] while **236a** was generated but could not be detected.[459c,597]

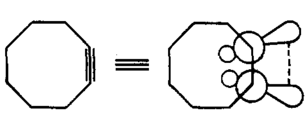
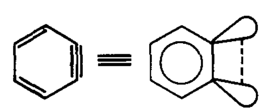

230

231

232

233

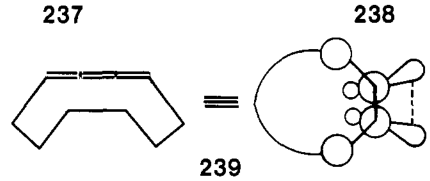

234

235

236

236a

XII. Cycloalkynes, Benzyne, and Cyclocumulenes

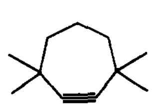
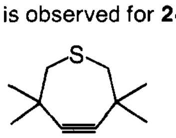
The deformations present in cyclooctyne (**237**), benzyne (**238**), and 1,2,3-cyclodecatriene (**239**) (and other cyclic cumulenes


237

238


239

having an odd number of cumulative double bonds) are somewhat similar in nature. In each instance a relatively weak and reactive π bond is formed by orbitals perpendicular to an essentially normal π system. The bending in each case is associated with mixing of s character into the reactive π bond. A comprehensive review of the chemistry of these compounds has appeared.[598] A discussion of the strain energy of *o*-benzyne is deferred until section XIII.A.

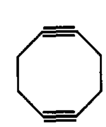
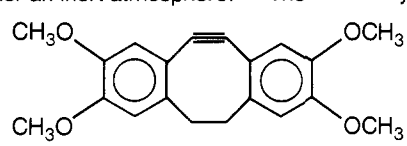
The smallest unsubstituted cyclic alkyne isolated to date is cyclooctyne.[599] The strain in this molecule's triple bond, relative to that in 4-octyne, is about 10 kcal/mol (i.e., the difference in monohydrogenation enthalpies).[600] The corresponding strain energy in cyclononyne is about 2.9 kcal/mol, and cyclodecyne and higher homologues have essentially normal triple bonds.[600] Cycloheptyne has been generated and trapped.[601] Steric hindrance afforded by the methyl groups in 2,2,6,6-tetramethylcycloheptyne (**240**) enhances the kinetic stability of this isolable compound.[602] Even greater stability is observed for **241** due in

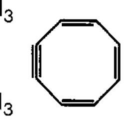

240


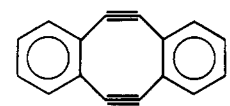
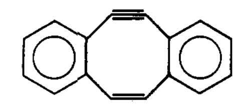
241

part to the long carbon–sulfur bonds which mitigate the imposed angular distortion of the acetylenic linkage.[603] Nevertheless, this compound is more reactive to cycloaddition reactions than is cyclooctyne.[603] The intermediacies of cyclohexyne and cyclopentyne have been inferred through trapping of these transients[601] as well as by radioactive-labeling studies.[604] Attempts at deducing even the transient existence of cyclobutyne have been unsuccessful.[601,604] Photoelectron spectroscopic studies indicate that in small cyclic alkynes, the strained π bond is much higher in energy than the essentially normal π bond perpendicular to it.[605]

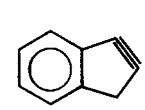
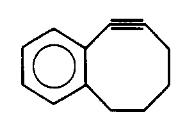
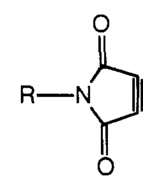
1,5-Cyclooctadiyne (**242**) is a crystalline material that is stable at 0 °C under an inert atmosphere.[606] The heat of hydrogenation


242


243

244

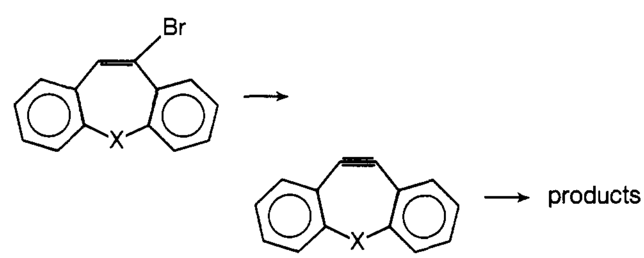

245

246

of 1,6-cyclodecadiyne indicates the presence of essentially normal triple bonds in this compound (although the complexities in assigning strain in this molecule have been discussed).[600] Compound **243** has been characterized,[607] while 1,3,5-cyclooctatrien-7-yne (**244**) has eluded isolation or even spectroscopic observation.[608] Both **245** (a dibenz-annelated derivative of **242**) and **246** (a dibenz-annelated derivative of **244**) have been isolated.[609] Both compounds are destabilized by strain as well as by antiaromaticity associated with the presence of planar $4n$ π systems.[609] The intermediates **247**,[610] **248**,[610] and **249**[611]


247

248


249

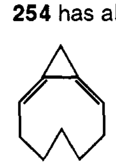
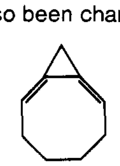
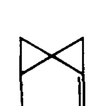
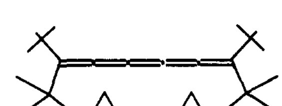
have been trapped. The relative rates of elimination to form **250** again reflect the relatively low strain in compounds having long carbon–sulfur bonds.[612]



250

relative rate = 1 (X = CR_2)
relative rate = 10^5 (X = SO_2)

The smallest cyclic cumulene isolated is **239**.[613] Recalling the analogy discussed in section XI, isolation of **239** suggests potential stability for **251**, **252**, and **253**, the last of which has been observed spectroscopically.[614,615] The higher cumulene **254** has also been characterized.[616]

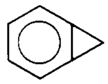

251

252

253

254

XIII. Distorted Aromatic Rings

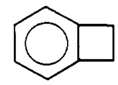
Various structural features induce distortion in aromatic rings and these will be considered in this section. The apparent measured destabilization of distorted aromatic molecules is not only a composite of bond stretching, angular distortion, torsional effects, and nonbonded interactions, but also decreased resonance stabilization. This last feature may result from deviations from coplanarity, which would decrease π overlap, as well as from partial bond fixation (alternation).

A. 1,2-Bridged Aromatic Rings

Benzyne (**238**), benzocyclopropene (**255**), and benzocyclobutene (**256**) constitute a series of 1,2-bridged derivatives of decreasing strain and increasing stability. Benzyne is normally



255



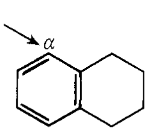
256

a transient intermediate[598] that has, however, recently been observed using infrared spectroscopy of a matrix at 8 K.[617] The most recent experimental value for the heat of formation of this species is 100 kcal/mol.[618] One may calculate a "lower limit" for the heat of formation of benzyne by "conceptual combination" of benzene and a normal triple bond:

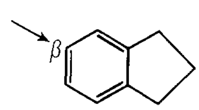
$$\Delta H_f(\text{benzyne}) = \Delta H_f(\text{benzene}) + \Delta H_f(\text{2-butyne}) - \Delta H_f(\textit{cis}\text{-2-butene})$$

The calculated value (+56 kcal/mol) would indicate the presence of about 44 kcal/mol of destabilization energy. (If an ortho diradical were chosen as an "upper limit" model, benzyne would appear to be resonance stabilized.) The destabilization energy in benzyne may be divided between poor overlap of the reactive bond, distortions in the aromatic nucleus, and decreased aromatic character resulting from partial bond fixation. The infrared evidence appears to favor an increased contribution of the structure having a short 1,2 bond (i.e., appreciable triple bond character) relative to the other Kekule resonance contributor, and the relatively low frequency for out-of-plane distortion of benzyne is also consistent with reduced aromatic character.[617] Before returning to other 1,2-bridged aromatics, a very brief discussion of bond fixation is presented below.

The concept of bond fixation has been under active investigation since 1930 when Mills and Nixon explained predominant α substitution in **257** and β substitution in **258** in terms of the bond-fixated structures shown.[619] Although the experimental



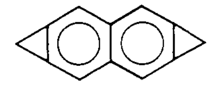
257



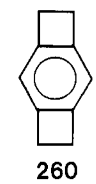
258

data upon which these investigators based their conclusions have been substantially corrected, there remains ample evidence for some bond fixation in certain molecules (e.g., benzyne as noted above). The Mills–Nixon effect is often used today as a term denoting nonequivalence of bonds in a substituted benzene ring arising from the distortion of bond angles in ortho-ring-anellated aromatic derivatives. The reduced reactivity of the α hydrogen in **258** has been explained both in terms of strain[620,621] and hybridization.[622]

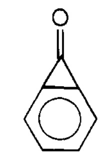
The first substituted benzocyclopropene[623] was reported in 1964[624] and the parent compound, generated by a clever Diels–Alder–retro-Diels–Alder sequence, appeared in the literature during the following year.[625] The strain in benzocyclopropene[626] (ca. 68 kcal/mol[627]) is evidenced by its facile ring opening under conditions of electrophilic substitution.[623] The excess of 15 kcal/mol destabilization energy relative to cyclopropene may, at least in part, be attributed to distortions in the aromatic ring and the accompanying reduced resonance stabilization. X-Ray data on a substituted benzocyclopropene[628] as well as naphtho[*b*]cyclopropene[627] are not readily interpretable in terms of bond-fixated structures since both of these contain three consecutive short bonds. Semiempirical calculations predict bond localization in **255–258.**[629a] The decreased aromatic character associated with bond fixation is not evidenced by the observed diamagnetic ring current of **255** which would indicate a normal aromatic system.[629b] However, facile addition of iodine across the central π bond of benzocyclopropene may be taken as evidence of reduced aromaticity.[625] The apparent discrepancies arise from differences in ground-state and transition-state properties. The compound 1,4-dihydrodicyclopropa[*b,g*]naphthalene (**259**) has been isolated and characterized as a true naphthalene.[630] Its strain energy (considerably greater than 100 kcal/mol) is manifested in a tendency to decompose explosively, behavior which leads the investigators to be pessimistic about future isolation of 1,3-dihydrodicyclopropa[*a,d*]benzene.[630]



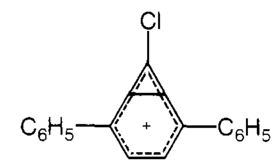
259



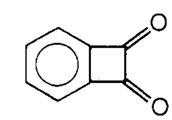
260



261



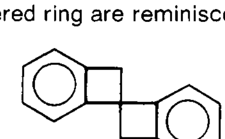
262



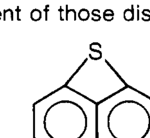
263

Benzocyclobutene[631] also has a tendency to ring open under electrophilic substitution conditions, but it is considerably less reactive than benzocyclopropene. The x-ray structure[632] of *cis*-1,2-dichlorobenzocyclobutene indicates that there is no significant bond fixation. Similarly, **260**[633] does not appear to be appreciably bond fixated.[634] X-Ray[635] and gas-phase electron diffraction[636] studies on biphenylene (**103**) indicate marked bond localization strongly favoring the resonance contributor shown. This is a distortion which decreases the antiaromatic character of the central ring. The experimental heat of formation of biphenylene may be compared with that of a model ($2\Delta H_f$(biphenyl) − $2\Delta H_f$(benzene)) in order to obtain a value of about 68 kcal/mol destabilization energy attributable (although not readily apportionable) to a four-membered ring strained by the presence of four trigonal carbons, some antiaromaticity of this ring, distortion of the benzene rings, and some decreased aromatic character in these rings resulting from bond fixation.

Some additional 1,2-bridged species having unique features include benzocyclopropenone (**261**), apparently detected by infrared spectroscopy at 8 K in an argon matrix,[617] and the carbonium ion **262** observed in solution and isolated as the chloride.[637] These two are more strained than benzocyclopropene but also benefit from resonance stabilization incorporating the additional trigonal carbon. Benzocyclobutadiene is a short-lived intermediate[280] (only a 1,2-diphenyl derivative of benzocyclobutadiene has been isolated[638]), while **263** is isolable.[280] The strain in **264** allows the corresponding spiro-conjugated diradical to be relatively accessible.[639] Although compound **265** is not 1,2-bridged, the distortions introduced by the four-membered ring are reminiscent of those discussed in this section.

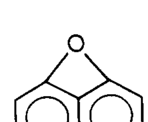


264

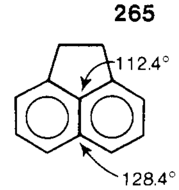


265

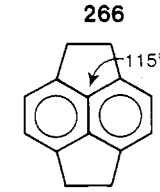
266



267



268

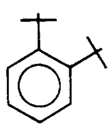


269

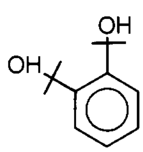
The peri-bridged naphthalene **265**,[640a] the related sulfoxide,[640a] related sulfone,[640b] and 1,8-methanonaphthalene (**266**)[640c] have all been isolated and characterized. Evidence has appeared in the literature supporting the transient existence of **267**.[641] Acenaphthene (**268**) experiences angle pinching due to the presence of the five-membered ring, accompanied by corresponding opening of the opposite angle as shown.[642] The heat of formation of **268** indicates a strain energy of about 9 kcal/mol [relative to 1,5-dimethylnaphthalene (or a *hypothetical* unstrained 1,8-dimethylnaphthalene) and 1,2-diphenylethane],[643] which is only about 2 kcal/mol greater than that actually found for 1,8-dimethylnaphthalene.[644] The symmetric nature of pyracene (**269**) precludes the cooperative angular distortion observed in acenaphthene, and the corresponding bond angle is 115°.[645]

B. Aromatic Systems Destabilized by Steric Strain

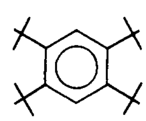
Steric repulsions are often the origin of distortion in aromatic rings. Although *o*-di-*tert*-butylbenzene derivatives had been claimed for many years, the first such authentic compound, 1,2,4-tri-*tert*-butylbenzene (**136**), was reported in 1961.[646] Shortly thereafter, compounds **270**,[647,648] **271**,[649] **272**,[650,651] and **273**[652] appeared in the literature. The strain energies of **136**



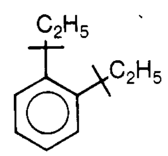
270



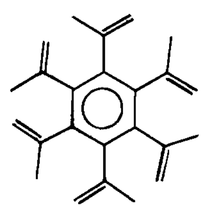
271



272



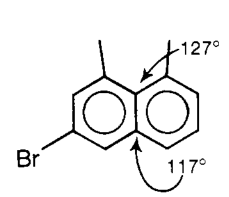
273



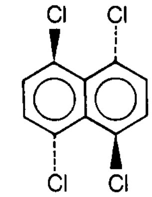
274

and **270** (relative to the meta or para isomers) are both about 22 kcal/mol.[653] With the exception of relatively facile acid-catalyzed "de-*tert*-butylation", the reactivity and spectra of these two compounds indicate that they are essentially normal aromatics. In spite of the presence of about 30 kcal/mol of strain energy, **272** is known to be planar.[654] The inter *tert*-butyl angles are widened to about 130° and abnormally long benzene–*tert*-butyl bonds further decrease steric repulsions.[654] Steric interactions inhibit resonance in **274** and cause the olefinic bonds to be unreactive.[655]

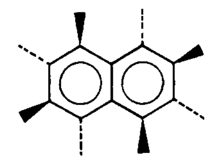
Peri (1,8) interactions in naphthalene derivatives are greater in magnitude than ortho interactions.[642] For example, x-ray studies[656] of 3-bromo-1,8-dimethylnaphthalene (**275**) indicate considerable distortion of the bond angles in the ring containing bromine and some buckling in the other ring. In this compound the nonbonded methyl groups are about 0.5 Å closer than the sum of the van der Waals radii. The strain energy (actually the value found for 1,8-dimethylnaphthalene[644]) is about 7 kcal/mol (the steric destabilization of *o*-methyl groups is approximately 1 kcal/mol). The propeller-like nature of **276**[657,658] and **277**[659,660] has been disclosed and results from bending which places the repelling groups above and below the molecular plane. A number of 1,8-di-*tert*-butylnaphthalenes (e.g., **138**) have been synthesized.[661] The interacting bulky groups are also constrained above and below the plane of the ring system.[661,662] Likewise, as the result of ring skewing, two isomers of **278** are observable via NMR at low temperatures.[663] Steric destabilization in **279** (12.6 kcal/mol[664]) is more severe than the peri-dimethyl interaction, but still smaller than that in **280** (15 kcal/



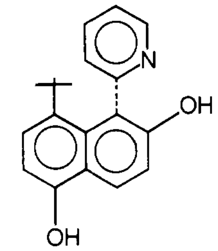
275



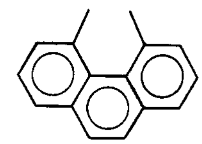
276



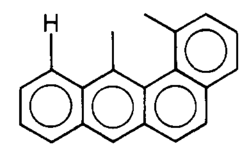
277



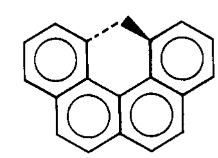
278



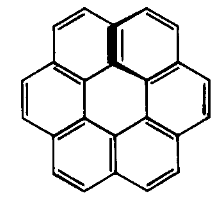
279



280



281

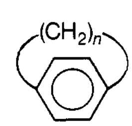


282

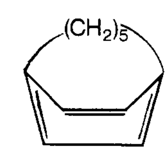
mol, attributed in part to "buttressing" by the peri hydrogen shown[664]) or in **281** where steric repulsions produce dissymmetry by skewing and which has been optically resolved.[665] The racemization enthalpy of activation for hexahelicene (**282**) is about 35–36 kcal/mol.[666,667] The racemization is apparently a conformational process, and its relative ease compared to the extremely high-energy predictions of molecular models serves to demonstrate how readily a large molecule distributes strain among its many component atoms or bonds.[667] The racemization barrier for pentahelicene is not as high ($\Delta H^{\ddagger}$ = 23 kcal/mol[668]) since the overlap between the terminal aromatic rings is smaller than that in hexahelicene. The six bonds on the inner periphery of hexahelicene average 1.437 Å and those on the outer periphery average 1.334 Å.[667b]

C. Paracyclophanes, Metacyclophanes, and Related Compounds

Paracyclophanes[669–671] **283**,[672] **284**,[672] **285**,[672,673] **286**,[674,675] **287**,[676,677] and **288**[678] have been isolated and are all quite stable. In fact, [6]paracyclophane (**288**), in spite of a



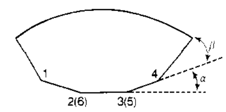
283, n = 12 **286**, n = 8
284, n = 10 **287**, n = 7
285, n = 9 **288**, n = 6



289

calculated deviation of 22° from coplanarity of the benzene ring,[679] and a calculated strain energy of 29 kcal/mol,[679,680] is aromatic by the ring current criterion.[678] It would appear that the as-yet-unknown [5]paracyclophane[681] may (a) define the limit of aromaticity in the [n]paracyclophane series, (b) define the limit of isolability in this series, and (c) denote the crossover

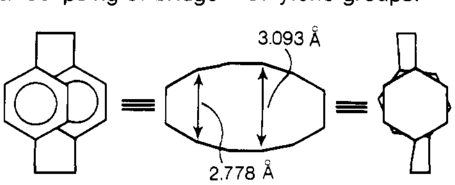
TABLE IX. Strain Energies and Distortions of the Aromatic Rings of Some Paracyclophanes (or Substituted Derivatives)



Compound	Strain energy, kcal/mol	Bending (α), deg
[8]Paracyclophane (**286**)	Calcd 16.8[679]	9;[689] calcd 12.5[679]
[7]Paracyclophane (**287**)	Calcd 20.9[679]	15–17;[680] calcd 18.2
[6]Paracyclophane (**288**)	Calcd 28.7[679]	Calcd 22.4[679]
[5]Paracyclophane (**289**)	Calcd 39[679]	Calcd 26.5[679]
[2.2]Paracyclophane (**290**)	31;[688] 33[689]	12.6[687]
[3.3]Paracyclophane	12[693]	6.4[695]
[2.2]Metaparacyclophane (**292**)	24[693]	14[700] (para ring)
[1.8]Paracyclophane	2[693]	
[2.2]Paracyclophane-1,9-diene (**293**)	Estd 39[695]	13.5[701]
[2.2]Metaparacyclophane-1,9-diene		18.4[702] (para ring)

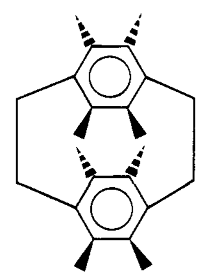
boundary between stability of benzene and Dewar benzene valence isomers. The strain energy of [5]paracyclophane has been calculated at about 39 kcal/mol,[679] which would make it over 25 kcal/mol more stable than the corresponding benzylic diradical,[682] and over 25 kcal/mol more stable than the Dewar isomer (see Table VII). It may be most appropriate to depict [5]paracyclophane as the bond-fixated structure **289.** The Dewar isomers of [4]- and [3]paracyclophane have been isolated,[459] but no corresponding paracyclophanes have been detected. In medium and small [*n*]paracyclophanes benzene rotation is hindered, and an asymmetric derivative of [10]paracyclophane has been resolved.[683]

The highly strained compound [2.2]paracyclophane (**290**) was first obtained in trace amounts in 1949 from reaction products of the unstable intermediate *p*-xylylene.[684] X-Ray data[685–687] indicate that the aromatic ring has a boat-like shape which deviates from coplanarity by 12–13° (see Table IX). The benzene rings are held much more closely than the 3.4–3.5 Å predicted from the sum of the van der Waals radii. Skewing of the rings partially relieves the resulting coulombic repulsion. The strain energy of 31–33 kcal/mol[688,689] is due to nonplanarity of the aromatic nucleus, deformation of the benzene-bridge bond angle (*β* in Table IX), coulombic repulsion between the aromatic rings, and partial eclipsing of bridge methylene groups.[690] Although

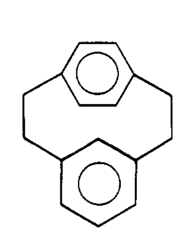


290

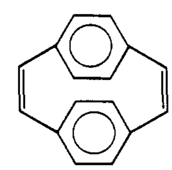
290 is a stable compound, increased steric strain produced by the methyl groups in **291** make this species unstable.[691] The acid-catalyzed conversion of [2.2]paracyclophane to [2.2]metaparacyclophane (**292**)[692] proceeds because the strain in the latter is only 23 kcal/mol.[693] This is a result of decreased eclipsing of the aromatic rings in **292** and substantially reduced distortion in the meta-substituted ring (however, the para-substituted ring is even more deformed than those in **290**). One should note that **292** was, in effect, the first [7]paracyclophane system to be characterized. The "classically conjugated but orbitally unconjugated" compound [2.2]paracyclophane-1,9-diene (**293**)[694] features aromatic rings that are more distorted than those in **290,** but it also maintains a greater nonbonded distance between aromatic rings.[695] [1.7]Paracyclophane (**294**)[696] is the smallest known member of a series of compounds having a one carbon bridge. Table IX lists experimental or calculated strain energies for a number of paracyclophanes as well



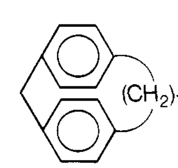
291



292

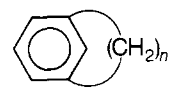


293

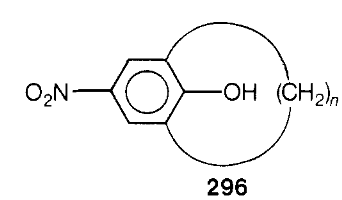


294

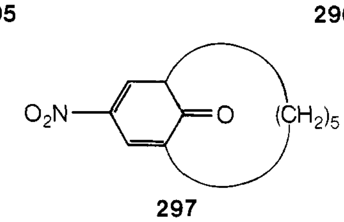
as distortions of the aromatic rings. Theoretical evaluations of 1,4-bending distortions of benzene have appeared.[697,698] Paracyclophanes have been extensively studied for their interesting stereochemistry, transannular-directing chemical effects, inter-ring interactions, and the resulting effects upon basicity and charge-transfer complexes and spectra,[669–671] as well as for their specific use as "chemical tweezers". An example would be the published studies of the effect of syn and anti orientation in an intramolecular redox reaction.[703]



295

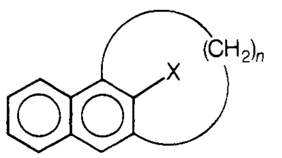


296

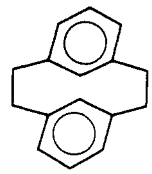


297

The border between stability and instability in [*n*]metacyclophanes (**295**) appears to be reached when *n* is 5. Thus, while the series of compounds **296** including $n = 6$ have been obtained,[704] only the tautomer **297** has been characterized.[705] Similarly, **298**[706] and **299**[707] have been isolated while **300** has been generated as a transient intermediate.[707] The relatively low strain in [2.2]metacyclophane (**301**) (12 kcal/mol[693]) re-

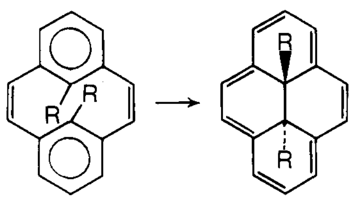


298, n = 8; X = Br, Cl
299, n = 6
300, n = 5

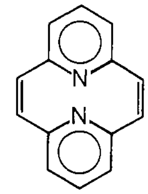


301

flects slight distortion of aromatic nuclei and staggering of the aromatic rings (only the anti form is known).[670] Although 8,16-dialkyl[2.2]metacyclophane-1,9-dienes (**302**) spontaneously isomerize to the corresponding *trans*-15,16-dihydropyrenes (**303**), the parent compound (**302**, R = H) is stable and isolable.[708] The diazo analogue **304** is also isolable.[709]

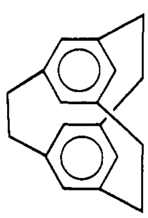


302 **303**

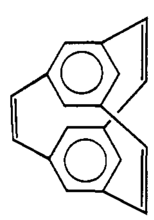


304

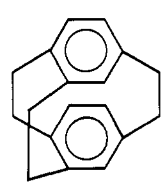
Cyclophane compounds having more than two bridges often exhibit interesting properties. For example, the aromatic rings in [2.2.2](1,3,5)cyclophane (**305**) are closer than in [2.2]paracyclophane and also more distorted.[710] [2.2.2](1,3,5)Cyclophane-1,9,17-triene (**306**) exhibits a novel inversion in the order of the chemical shifts of the vinylic and aromatic protons as a combined result of strain and the forced proximity of the two rings.[710] The benzene rings in **306** are constrained into chair-like conformations.[710b] Photoelectron spectra of **305** and **306** are consistent with decreased nonbonded benzene distances relative to [2.2]paracyclophane.[711] The distortion produced by a third ethano bridge in [2.2.2](1,2,4)cyclophane (**307**) is manifested by some polyolefinic reactivity not observed in its homologue [3.2.2](1,2,4)cyclophane or in [2.2]paracyclophane.[712] The compound [2.2.2.2](1,2,4,5)cyclophane (**308**) has also been reported.[712a] Other examples of novel multibridged compounds include **309** and **310**,[713] **311** which has a five-carbon meta bridge,[714] **312**,[715] **313**,[716] and **314** in which severe crowding



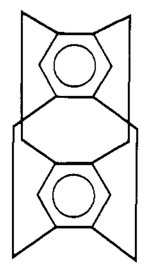
305



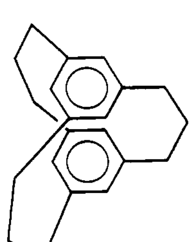
306



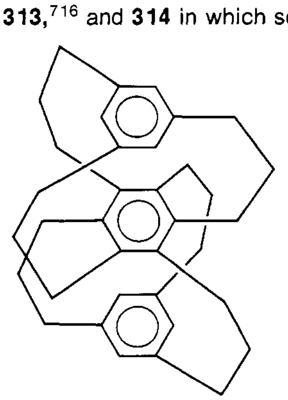
307



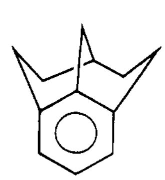
308



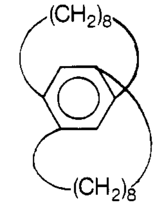
309



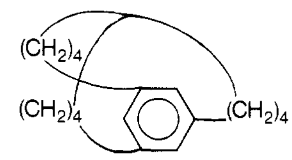
310



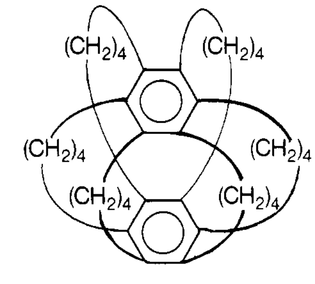
311



312

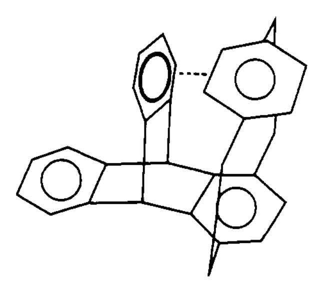


313



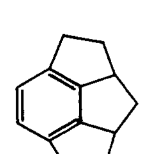
314

of the bridging methylene groups allows only concerted motion, thus producing a high barrier to bond rotation in these bridges.[717] A number of stacked paracyclophanes[713,718–723] have been outlined and their stereochemistry[723] and cumulative basic properties[713] studied. A series of stacked metacyclophanes has also been described.[724] Finally, it should be noted that a rather severe nonbonded interaction between two almost perpendicular aromatic rings in **315** forces skewing of the aromatic rings which comprise the [2.2]paracyclophane moiety.[725]

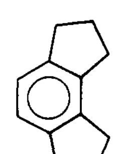


315

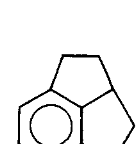
Severe distortion of the aromatic ring in **316** is sufficient to endow this compound with the spectral properties of a cyclohexatriene.[726] Its chemical properties, which include facile hydrogenation, reaction with atmospheric oxygen, and rapid reaction with perbenzoic acid, are suggestive of an olefin.[726] Model compounds **317**[726] and **318**[727] are normal aromatic systems, but **319** may also have considerable polyolefinic character.[728] The localized structures **316** and **319** are meant to emphasize cyclohexatriene-like character and do not imply absolute bond fixation nor a bias toward the particular Kekule form shown.



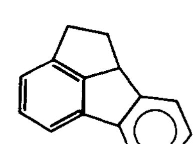
316



317



318



319

Other novel distorted aromatics include the cup-like corannulene (**319a**)[728a,b] and the (presumably) saddle-shaped 1,16-didehydrohexahelicene (**319b**).[728c] The compound 4,8-dihydrodibenzo[*cd,gh*]pentalene (**319c**)[728d] is (surprisingly) planar, is estimated to have about 66 kcal/mol of strain, and has a number of unique structural features.[728e,f] The compound may also be regarded as a [5]metacyclophane as can **266.** Benzocarborane[728g] appears to have a benzene ring sharing a 1.65-Å

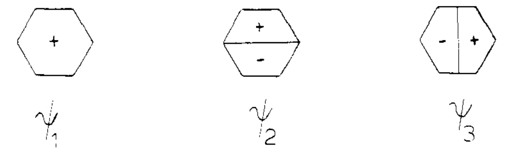
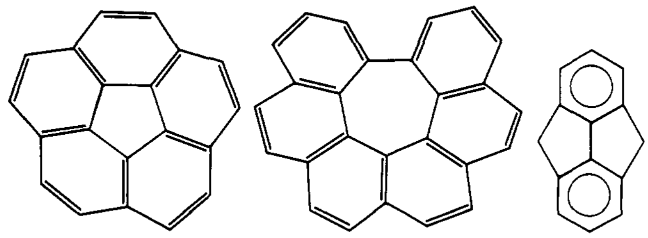


Figure 7. Occupied π molecular orbitals of benzene.

carbon-carbon bond with a carborane skeleton. However, it is questionable whether one can actually classify the attached ring as benzenoid.[728h]



319a **319b** **319c**

D. Secondary Orbital Interaction in [*m.n*]Paracyclophanes and Related Species

As indicated earlier in this section, many [*m.n*]paracyclophanes and related species are highly strained. Considerable destabilization arises from the contact of two benzene rings at distances less than the sum of the van der Waals radii (ca. 3.4 Å). We may explain the repulsion of the two rings also through the use of simple molecular orbital logic. If the occupied π orbitals of benzene are examined, we find a low-lying orbital and a degenerate pair of higher lying ones (i.e., of equal energy) (see Figure 7). Para substitution, ring bending, and interaction with the methylene bridges, all found in paracyclophanes, split the degeneracy of ψ_2 and ψ_3.[729] However, for our simple discussion, we will neglect this splitting. We note that the unoccupied orbitals of benzene consist of another pair of "degenerate" orbitals, also split, and a still higher lying nondegenerate orbital.

Let us consider a symmetric, i.e., $m = n$, paracyclophane. Because of the interaction of the two rings, the bonding and antibonding combination of all of the benzene orbitals are formed (see Figure 8). As we had started with six doubly occupied orbitals, we wind up with six doubly occupied orbitals. As such, all of the six orbitals in Figure 8 are thus occupied. Since antibonding is usually more antibonding than bonding is bonding, we expect a net destabilization. Analogous, but admittedly more complicated, effects arise in the asymmetrically bridged compounds such as [*m.n*]paracyclophanes, metaparacyclophanes, and those containing two different ring systems.

To alleviate some of this destabilization, the two rings may be slid as to be not parallel or superimposed. Indeed, a geometry may be drawn that has the two + regions in ψ_2–ψ_2 overlapping, and thus the molecule would be stabilized. Whereas this corresponds to the geometry for [3.3]paracyclophane, arguments[695] have been given why this structural choice is not governed by π orbital effects. Alternatively, some stabilization may be achieved by removal of an electron from either the ψ_2–ψ_2 or ψ_3–ψ_3 orbital. This may be accomplished either by ionization to the radical cation or complexation with a strong π acid. Not surprisingly, the ionization potentials for paracyclophanes are low[711] and strong complexes with tetracyanoethylene are easily formed.[730]

What about removal of two electrons? We do not expect to form dications of our species; few molecular dications are known. However, electron pair removal may also be accomplished by protonation. That is, we go from benzene to a homocyclopentadienyl cation,[731] from a 6π to a 4π species (see compounds **320–322**). Experimentally, this is manifest in the high

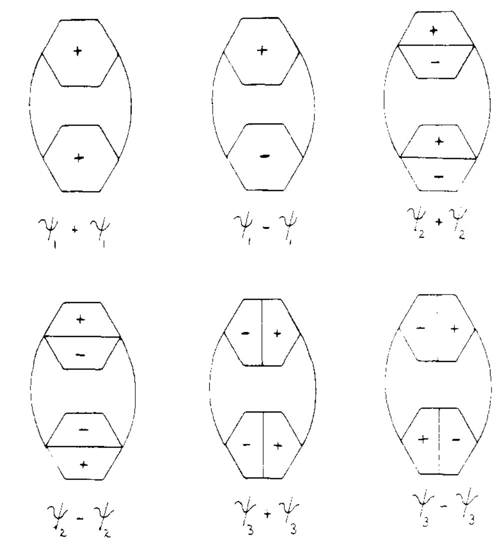
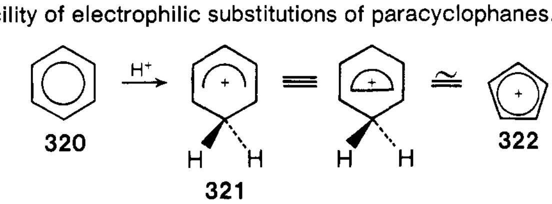


Figure 8. Occupied π molecular orbitals of symmetric [*m.n*]paracyclophanes (*m.n*).

stability of protonated [2.2]paracyclophane[732] and the extreme facility of electrophilic substitutions of paracyclophanes.[733]



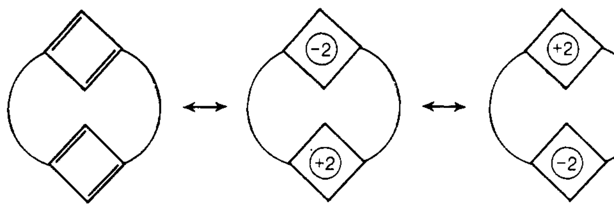
320 **321** **322**

All of the results we have described are also compatible with the Goldstein-Hoffmann topological description of (three-dimensional) aromaticity.[346c] That is, we consider the highest occupied molecular orbital of one ring, HOMO, and the lowest unoccupied molecular orbital of the other ring, LUMO. When the HOMO and LUMO are of the same symmetry, stabilization is expected, while if they are of different symmetry, destabilization may be expected. The HOMO of a benzene ring is ψ_2 and ψ_3 (recall the degeneracy). The LUMO of a homocyclopentadienyl cation is ψ_3, by analogy to both the open-chain pentadienyl and cyclic cyclopentadienyl cations. As such, stabilization is expected. The odd-electron species such as the above-mentioned paracyclophane radical cations are harder to describe. We suspect that a radical will mimic the compound with one more electron but be neither as stabilized nor as destabilized as the corresponding electron rich species.[734] As such, the radical cation will be stabilized relative to the neutral paracyclophane. This argument may be used to explain the facile formation of paracyclophane radical anions,[735,736] a most surprising result when discussed solely in terms of π-electron repulsion effects. We note the thermal instability of these radical anions has been ascribed to the formation of the dianion,[736] an even more surprising species, that subsequently decomposes by simple CH_2–CH_2 bond cleavage.[737]

We may reconcile a seeming paradox in paracyclophane chemistry via the HOMO-LUMO aromaticity analysis. Analogous to the high stability of protonated [2.2]paracyclophane,[732] solvolytic formation of the PC-CH_2^+ and PC-$(CH_2)_2^+$ ions is very facile.[738] The charge on the CH_2^+ groups is delocalized into the ring by benzylic resonance (or ethylenephenonium ion formation), and then these cations are further stabilized by transannular C-C bond formation. However, formation of the PC-O^- species by deprotonation of the phenol is seemingly inhibited "primarily reflect[ing] the loss of resonance stabilization of the anion due to the bent nature of the adjacent benzene ring".[739] While no data on the C-H acidity of PC-CH_3 are known to us and the acidity of PC-NH_3^+ confused by solvent effects,[739,740] it is nonetheless surprising that ring deformation does not affect

$PC-CH_2^+ \leftrightarrow PC^+ = CH_2$ resonance while $PC-O^- \leftrightarrow PC^- = 0$ resonance is greatly impeded. We merely note that delocalization in the cation converts the 6π benzene into a derivative of the 5π homocyclopentadienyl cation. However, delocalization of the anion converts the 6π benzene into a derivative of the 6π homocyclopentadienyl anion. No HOMO–LUMO stabilization ensues.

We derive one additional benefit from our HOMO-LUMO analysis in that we predict some new paracyclophanes of high stability. The first is that formed from benzene and cycloheptatrienide, $6-7^-$, which is expected to gain stability relative to the $6-7^+$ compound.[741] The second are the rather initially disturbing 4-4 and 8-8 species, and we additionally note that the $4^{2+}-4^{2-}$ and $8^{2+}-8^{2-}$ resonance structures contain aromatic rings; see compounds **323a–c.** Lest the reader dismiss this compound until it is synthesized, please recall cyclobutadiene largely dimerizes to form the syn, i.e., face-to-face, product.[742]

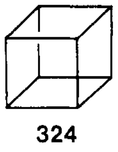
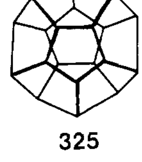
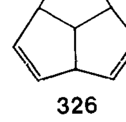
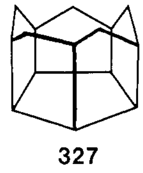


323a **323b** **323c**

XIV. Polycyclic Hydrocarbons: Cumulative Strain and Esthetics

Polycyclic hydrocarbons may be viewed as being comprised of some of the "building blocks" (e.g., small bicyclic molecular frameworks) described in earlier sections of this review. Alternatively, they may be examined in any number of unique ways which bear no resemblance to the "building block" approach (e.g., adamantane may be viewed as being topologically related to cyclooctane as further (but briefly) discussed in section XV). Although the "building block" method is perhaps the approach that is most conventional and thus frequently employed, there seems to be at present no "correct" way of viewing polycyclic molecules and relating their properties to those of models. When the strain in a polycycle is greater than the sum of its "parts", the extra increment is usually attributable to either or both geometrical constraints imposed by "building blocks" upon the frameworks of other "building blocks", or by the presence of steric repulsions between the "building blocks". Section XV will consider methods of viewing polycyclic molecules and postulation of appropriate conceptual models. The present section will, of necessity, only consider a very small sampling of strained polycyclic hydrocarbons (we remind the reader of the multivolume compendium "Ring Index"). Small-ring propellanes and paddlanes will be considered in section XVII.

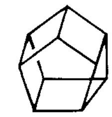
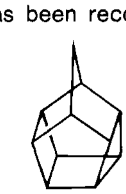
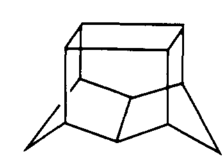
Many polycyclic molecules (characterized or theoretically feasible) are appealing objects for study because of their actual or anticipated chemical and physical properties as well as their esthetic nature.[743] Foremost in these features are tetrahedrane (section VII), cubane (pentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, **324**), and dodecahedrane (**325**) which are topologically equiv-


324

325

326

327

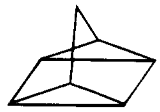
alent to the platonic solids tetrahedron, hexahedron (cube or square prism), and (pentagonal) dodecahedron. The remaining platonic solids, the octahedron and icosahedron, are not likely to have hydrocarbon equivalents (see section XVII). Examples of these two polyhedra are known when mostly other atoms are present at the vertices.[744] The first authenticated derivative of cubane (this and other $(CH)_n$ are reviewed in ref 279) was reported in 1964,[745] and the parent hydrocarbon appeared shortly thereafter.[746–748] The strain energy of cubane (157 kcal/mol) may be considered to represent the sum of the strain energies of six cyclobutane faces.[443] This figure translates as 20 kcal/mol per carbon or about 13 kcal/mol per carbon–carbon bond making these bonds more strained than those of cyclopropane but less so than the central bond of bicyclobutane (section VI).

Dodecahedrane (**325**) has thus far eluded synthesis. It is theoretically obtainable through ("photochemically allowed") concerted dimerization of triquinacene (**326**).[749] One may approximate a standard heat of formation for triquinacene (assuming no homoaromatic stabilization) of about +55 kcal/mol [ΔH_f(perhydroquinacene)[12] + 3ΔH_f(cyclopentene) − 3ΔH_f(cyclopentane)] and compare this with calculated heats of formation for **325.** Unfortunately, there is a large discrepancy between the calculated values: −0.22 kcal/mol (Schleyer et al.);[12] +45.28 kcal/mol (Allinger et al.)[13] (the discrepancy is discussed in ref 12). It would appear that the formation of dodecahedrane from two molecules of triquinacene should be exothermic by 55–110 kcal/mol. The problem would appear to be the slow rate of this reaction relative to rates of competing reactions. Concerted cycloaddition reactions normally exhibit sizable negative entropies of activation due to losses in translational and rotational degrees of freedom as well as highly specific alignments in the activated complex. The extreme requirement for precise orientation is partially reflected in the enormous increase in symmetry upon transformation of triquinacene (C_{3v}, symmetry number = 3) to dodecahedrane (I_h, symmetry number = 60).[17] Perhaps the answer to the orientation problem may be solved through dimerization of triquinacene under enzyme-like conditions (e.g., in a micelle or in the cavity of a suitable cyclodextrin under aqueous conditions) where the two rings might be constrained in a face-to-face orientation while occupying a small hydrophobic volume. A more conventional synthesis of dodecahedrane through a derivative of peristylane (**327**) is in progress.[750] The calculated increase in strain upon transformation of **327** to **325** is between 4 and 27 kcal/mol.[12]

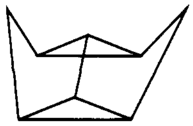
Another group of esthetic strained polycyclic species are those comprising the prismane family.[743] The proposed nomenclature[743] for this group of compounds would refer to the compound tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexane (**134**) (usually and in section IX termed "prismane") as triprismane. Cubane is, then, tetraprismane. An unsuccessful attempt at obtaining pentaprismane (**328**) has been recorded.[751] Homopentaprismane


328

329

330

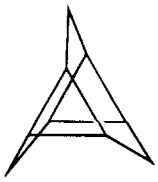
(**329**)[752] and bishomopentaprismane (**330**) (also termed "birdcage hydrocarbon")[753] have been isolated. Similar homologues of prismane (triprismane) include quadricyclane (**331**)[754,755] (experimental strain energy of 95 kcal/mol[756]), bishomoprismane **332,**[757] and triasterane (**333**) which has three cyclohexane boat faces.[758] Derivatives of homoprismane **334**[759] and bishomoprismane **335**[760] (dihydrocubane) have also been characterized. Homocubane (**336**)[761] and bishomocubanes including **337**[762] as well as tetrasterane (**338**)[763] are known, and pentacyclo[6.3.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane (**339**) is a trishomocubane which may be viewed as a fusion product of six equivalent cyclopentane rings[764] (adamantane may be thought of as hexahomotetrahedrane[153]). Trishomocubane **339** (D_3 symmetry) is the only $C_{11}H_{14}$ pentacycle without a three- or four-membered



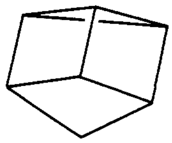
331



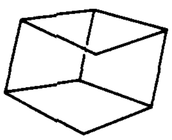
332



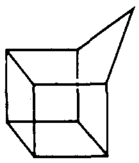
333



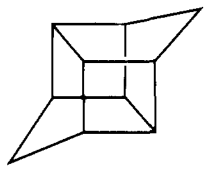
334



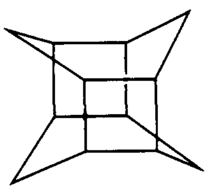
335



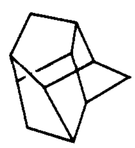
336



337

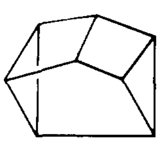


338

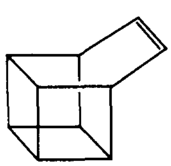


339

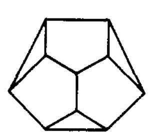
ring, and its relative stability allows its formation via rearrangements of isomers.[764a] In addition to cubane, numerous other strained $(CH)_n$ exist (we do not discuss bullvalene and other fascinating fluxional molecules; see ref 279 for discussion). Among these are cuneane (**340**),[765] basketene (**341**),[766,767] diademane (**342**),[768] as well as **343**,[769] **344**,[770] **342a**[770a] and **344a**.[770b]



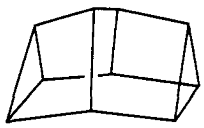
340



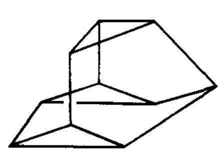
341



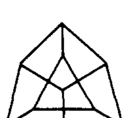
342



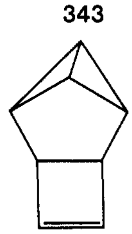
342a



343

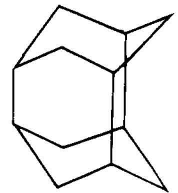


344

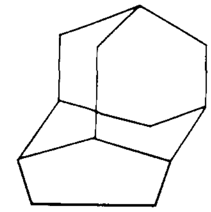


344a

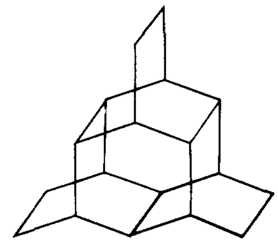
Iceane (**345**) has only recently been won from the $C_{12}H_{18}$ manifold through judicious choice of starting material.[771] This rigid symmetric molecule features two cyclohexane chair faces and three boat faces and rearranges via acid catalysis to ethanoadamantane (**346**), the most stable $C_{12}H_{18}$ isomer, with the release of 6–7 kcal/mol.[771,772] Iceane is the first member of an hexagonal diamond family.[773] The novel hydrocarbon **347** has bicyclo[2.2.2]octane as its building unit and maintains eclipsed



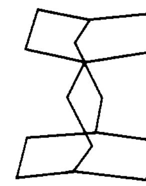
345



346

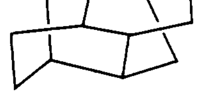


347

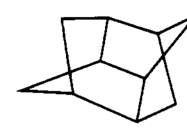


348

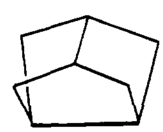
interactions between all pairs of nonbonded hydrogens.[710b] The strain energy of perhydro[2.2]paracyclophane (**348**),[774] a highly crowded molecule, is 26 kcal/mol.[693] "Superstoichiometric" poly(carbon monofluoride) is composed of sheets of chair cyclohexane rings and is remarkably stable.[775] Some other novel species include [8]ditwistane (**349**) and bisnortwistane (**350**),[776] bisnoradamantane (**351**) which is a lower homologue of adamantane having four cyclopentane faces,[777,778] and the novel cage hydrocarbon **352**.[779] 2,4-Didehydroadamantane (**353**),[780]



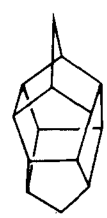
349



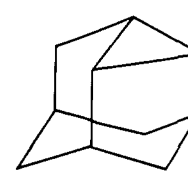
350



351

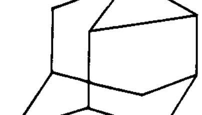


352

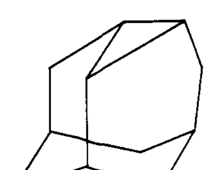


353

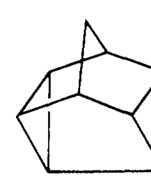
2,4,6,9-tetradehydroadamantane (**354**),[781] and 2,4-dehydrohomoadamantane (**355**)[782] have been isolated as has **356**.[783,784] Dibenzoequinene (**357a**), a derivative of equinene which is obtainable in principle from a twofold intramolecular cycloaddition of [2.2]paracyclophane, contains two highly puckered cyclobutane rings.[785,786]



354

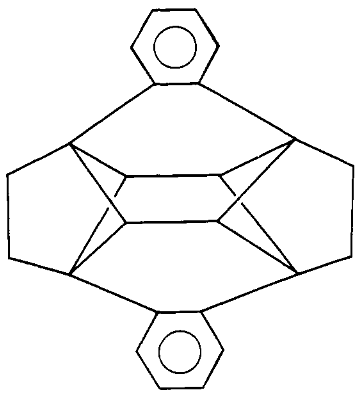


355

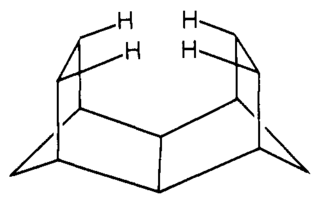


356

As stated previously, polycyclic species may add an extra increment of strain to the sum of the strain energies of the "building blocks" by maintaining repulsive steric interactions between parts. As one illustration, we consider the molecule *endo,endo*-tetracyclo[$6.2.1.1^{3,6}.0^{2,7}$]dodecane (**357b**).[787] In an idealized geometry the nonbonded hydrogens shown are separated by only 0.2 Å.[787] The resulting distortions which relieve this interaction are associated with a calculated strain energy of about 112 kcal/mol,[12] and this may be compared to a total of 34 kcal/mol calculated strain energies for two isolated



357a



357b

norbornanes[12] (the "building blocks"), yielding a sterically induced increment of about 78 kcal/mol. When the nonbonding hydrogens are removed and the corresponding pairs of carbon atoms connected by single bonds, "bird-cage hydrocarbon" (**330**), having a calculated strain energy of 57.5 kcal/mol,[12] is the result. The strain energy of **330** is not very different from that calculated through summation of the strain energies of two norbornanes, one cyclobutane, and two cyclopentanes.

XV. Strain Energy Reference States for Later Reference

In this article, the reader has seen many strained, and indeed strange, organic compounds. We have tried to present accompanying strain energies, that single number which denotes the instability of the molecule of interest relative to a well-defined reference state. We now wish to present some other possible indices of molecular strain energy. Their usefulness will not be evaluated here; rather the reader should consider them in the context of those species of personal research interest. This section is highly speculative and perhaps has no immediate applications. The reader may omit it with no discontinuity in the review.

First, we recall the group increment scheme which fragments the molecule into the CH_3–, –CH_2–, –CH<, and >C< groups. So far, we have largely neglected substituted derivatives. As such, we can disregard the CH_3 group except when discussing alkanes and other acyclic species. However, we are not limited to the three remaining groups. Other groups we could introduce include –CH=CH–, –CH=C< and >C=C<.[3] We thus tacitly admit cycloethane is not really as meaningful or as useful as ethylene (note that in principle –CH=CH– is synthesizable from two –CH<). Likewise, the isomeric phenylene groups may also be considered since aromaticity remains too subtle for our treatment.[788] Hence, taking a general, pragmatic approach suggests any hydrocarbon of interest may be written

$$(C)_\alpha\,(CH)_\beta\,(CH_2)_\gamma\,(CH_3)_\delta\,(\text{–CH=CH–})_\epsilon\ldots(p\text{-}C_6H_4\text{–})_\eta\ldots$$

Several immediate benefits arise from this analysis. First of all, intermolecule comparisons are greatly simplified by limiting discussion only to sets of compounds with the same values of $\alpha, \beta, \gamma, \ldots$. For example, while adamantane and twistane remain interrelatable as both are $(CH)_4(CH_2)_6$ species, we are exempt from having to consider 1,2-cyclodecadiene, 3,3,7-trimethylcycloheptyne (3,3,7,7-tetramethylcycloheptyne is known[602]), and all monoterpene hydrocarbons with the formula $C_{10}H_{16}$.

Secondly, we may generalize the notion of strain energy. We have usually referred to strain energy (SE) per se, i.e., per molecule, although the strain energies per (carbon) atom (SEc) and per bond (SEb) were also employed in this article. These latter two notions appeared useful but also distinct and even contradictory. We note for unsubstituted, saturated polycyclic hydrocarbons such as adamantane and twistane, SEc equals $SE/(\alpha + \beta + \gamma)$ while SEb equals $SE/(2\alpha + \frac{3}{2}\beta + \gamma)$. Both quantities may be expressed as $SE/(a\alpha + b\beta + c\gamma)$ where (a,b,c) are (1,1,1) and $(2,\frac{3}{2},1)$, respectively. We are not limited to the choice of these two triplets. Indeed, the earlier assertion that the strain energy of a bridghead carbon is twice that of a bridging atom (section VI.A, on bicyclobutane) is equivalent to $(a,b,c) = (1,1,\frac{1}{2})$. We suspect specific classes of compounds will suggest special values of *a, b,* and *c* although admittedly the triplets (1,1,1) and $(2,\frac{3}{2},1)$ have a certain conceptual "uniqueness". If we additionally view (a,b,c) as a vector, we know there are (only) three linearly independent vectors. That is, we can have (only) three linearly independent strain indexes. One simple option is thus to choose the above (1,1,1) and $(2,\frac{3}{2},1)$ and one of the user's own choice. We emphasize that while SEb and SEc may seem contradictory, they are not mutually exclusive.

Related to the previous approach and first employed with bicyclobutane is the term "superstrain". It attempts to help answer the question of how many kcal/mol of energy of a given polycyclic hydrocarbon is due "merely" to the component rings. For example, we had earlier shown that while the strain energy of cubane was essentially the sum of the six square faces or cyclobutane rings, the strain energy of bicyclobutane was in noticeable excess of that of the two-component cyclopropane rings. This strain excess was labeled "superstrain". However, left unasked and unanswered was how do we incorporate the four-membered ring in bicyclobutane or the six- and eight-membered rings in cubane? Several essentially unedited options exist. The first is to consider all of the component rings. This severely overcounts both the (carbon) atoms and bonds although the results for cubane seem satisfactory. Alternatively, we can attempt normalization of either atoms or bonds. That is, the calculated strain energy in bicyclobutane (4 atoms) would be the sum of two cyclopropanes (3 atoms each) and one cyclobutane (4 atoms) multiplied by the correction factor $4/(2\cdot3 + 4)$. The bond normalization has the multiplicative factor $5/(2\cdot3 + 4)$ since bicyclobutane, cyclopropane, and cyclobutane have 5, 3, and 4 bonds, respectively.

A second option, already computationally implemented for a different chemical problem, suggests two criteria for the set of rings[146]: (1) it "must contain all the bonds which are members of any ring" and thus contain all of the atoms; (2) "the sizes of the individual rings are as small as possible". Again, there is both atom and bond overcounting and a similar choice with regard to normalization must be made. We strongly suspect that the sizes of the individual rings can be chosen by other criteria such "as large as possible" or "as close to six-membered, i.e., strain free, as possible" with but little change in the existent literature algorithm.[146]

Presenting another approach, we choose some framework atoms and bonds and then "suture" this species to the desired compound. By means of bond additivity considerations, strain energies may be deduced. For example, cubane (**324**) may be obtained from cyclooctane by:

$$(CH)_8 = (CH_2)_8 + 4[CH_3\text{–}CH_3 - (CH_3\text{–}H + H\text{–}CH_3)].$$

However, the carbons in cyclooctane that are "stitched" to form cubane are bound to two other carbons while those of methane that form ethane are not bound to any other. This is easily corrected for by the modified "synthesis":

TABLE X

l/mn	ΔH_f°[suture]	l/mn	ΔH_f°[suture]
0/22	−7.05	1/33	−7.02
0/23	−8.37	2/22	+3.52
0/33	−10.99	2/23	+3.47
1/22	−1.45	2/33	+3.36
1/23	−3.70		

$$(CH)_8 = (CH_2)_8 + 4[(CH_3)_2CH\text{-}CH(CH_3)_2 - ((CH_3)_2CH\text{-}H + H\text{-}CH(CH_3)_2)].$$

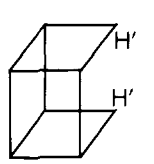
The strain energy of cubane is thus

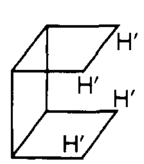
$$\begin{aligned}\Delta H_f^\circ(CH)_8(\text{exptl}) - \Delta H_f^\circ(CH)_8(\text{calcd}) &= \Delta H_f^\circ(CH)_8(\text{exptl}) - \Delta H_f^\circ(CH_2)_8 \\ &\quad + 4\{\Delta H_f^\circ[(CH_3)_2CH\text{-}CH(CH_3)_2] \\ &\quad - [\Delta H_f^\circ((CH_3)_2CH\text{-}H) + \Delta H_f^\circ(H\text{-}CH(CH_3)_2]\} \\ &= \Delta H_f^\circ(CH)_8(\text{exptl}) - \Delta H_f^\circ(CH_2)_8 \\ &\quad + \text{sum of } \Delta H_f^\circ[\text{sutures}]\end{aligned}$$

The general suture is a polymethylene chain of length or number of carbons l, connecting two carbons, bound to m and n other carbons, respectively. As such, in the cubane case, the recommended sutures are thus all labeled as 0/22, i.e., $l = 0$, $m = 2$, $n = 2$. Likewise, homocubane (**336**) could be synthesized from either cyclooctane, three 0/22 and one 1/22 sutures or cyclononane and four 0/22 sutures. Table X presents some common sutures and the accompanying thermochemical increments of ΔH_f°[sutures]. All of the necessary thermochemical data needed for the sutures were obtained from Cox and Pilcher,[4] except for 2,2,5-trimethylhexane in the 2/23 and 2,2,5,5-tetramethylhexane in the 2/33 sutures. These were obtained from "Physical Constants of Hydrocarbons C_1 to C_{10}", ASTM Special Publication No. 109A, American Society for Testing and Materials, Philadelphia, Pa., 1963.

We admit somewhat belatedly that the component rings rarely have the same geometry in the compound of interest as in the "free" one-ring species. This is the primary origin of "superstrain", but factoring out individual ring effects is difficult. Several options exist, all of which seem worthy of further exploration: first of all, simply cataloging the strain energy increments or "superstrain" associated with a given ring in all conceivable environments. For example, four-membered rings are common to cyclobutane, cubane, and tetrahedrane (listed in increasing strain energy per atom or per bond). Secondly, the analogous catalog of energies associated with the various l/mn sutures would be of use, as would more complicated sutures such as $HC(CH_2\text{-})_3$ (which is found in adamantane, but not twistane).

Finally, in an approach that can be employed in either or even both directions, how does the energy of a v-cyclic species compare with a related w-cyclic one? For example contrast the following compounds: cubane (**324**), dihydrocubane (**325**), tricyclo[4.2.0.0^{2,5}]octane (**37**), bicyclo[4.2.0]octane, and cyclooctane. Computationally, energies for all of these species can be obtained in either the idealized or the minimum energy geometry. For the former, subtracting out "irrelevant" hydrogen-hydrogen interaction, e.g., compounds **335** and **37,** redrawn as shown below where the H′ are the "irrelevant" hydrogens, should prove instructive.





This final approach, in any of its three modifications, can be furthered systematized to allow still more intermolecule comparisons. We take a polycyclic compound and cut enough bonds (i.e., replace enough C–C bonds by C–H bonds) to make it acyclic. (It is simply shown that a v-cyclic compound requires v such cuts.) By decree, we ask that the acyclic compound have as long a chain as possible with minimal substitution.[789] This species constitutes the zeroth member of our hierarchy of reference states. Two carbons are then rejoined via a bond that has two constraints. First, this bond must appear in the v-cyclic compound, and, secondly, the new ring formed must be maximum in size.[790] This just synthesized mono or 1-cyclic compound is the first reference state of our hierarchy. A second ring so constrained is then formed, then a third, and so on yielding the second, third, and so on reference states. The molecule of interest is finally formed when v bonds have been made. For convenience, the chain (0-ring or 0-cyclic) 1-ring (or 1-cyclic or monocyclic), 2-ring (or 2-cyclic or bicyclic) . . . reference states are labeled maxi-0-ring (maxichain), maxi-1-ring (maxiring), maxi-2-ring . . . . Alternatively, we could have asked for the smallest chain or rings or those closest to six as before. We then have the mini and midi hierarchies. Our biases suggest the use of the maxi series. Excessively hindered acyclic hydrocarbons and small rings are most probably treated poorly by calculational methods (cf. the discussion on tri-*tert*-butylmethane) and additionally are much harder to experimentally synthesize for confirmation.

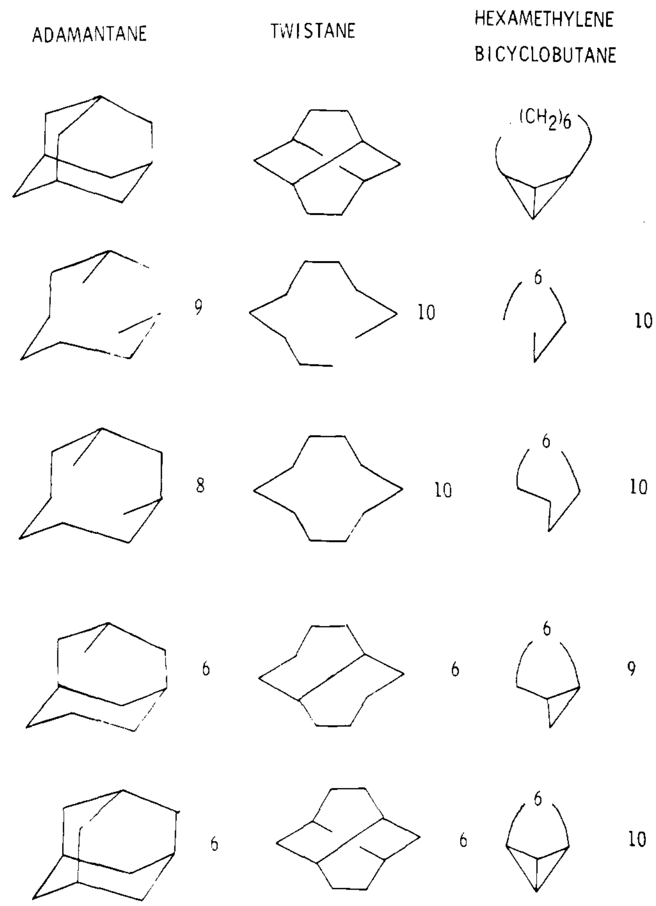


Figure 9. The maxi-ring hierarchy of bicyclobutane, adamantane, twistane, and a hexamethylene derivative of bicyclobutane. The number besides the various structures is the chain or ring size.

As exemplary of the maxi-ring hierarchy, we show the results for the isomeric $\beta = 4$, $\gamma = 6$, adamantane, twistane, and a hexamethylene derivative of bicyclobutane in Figure 9.

Regarding the usefulness of this final concept and those before it, we again admit this "will not be evaluated here; rather the reader should consider them in the context of those species of personal interest". We hope these methods provide links between compounds as bonds provide links within compounds.

XVI. Substituted Derivatives of Strained Molecules

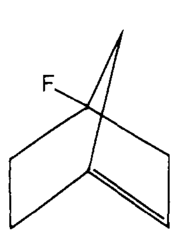
A. Noneffect?

Numerous strained molecules have been chronicled in this article. Almost all of these species contained only hydrogen and carbon, yet it is obvious that substituted derivatives amply exist, at least in principle. (We used the term "substituted derivatives" to include replacement of skeletal carbon by some polyvalent atom. We therefore implicitly include hetero analogs of the species of interest.) For example, while the $\Delta H_f°$ values are known for the set of isomeric bicyclooctanes **1**, **2**, and **3**, what can we say about the 1- (or bridgehead) halo derivatives? What about the 1-aza compounds? 1-Azabicyclo[2.2.2]octane is well known as quinuclidine, but its isomers enjoy no such corresponding popularity. One assumption seems to have been made with regard to the effect of interest: the $\Delta\Delta H_f°$ of a pair of isomers is essentially unchanged if a carbon group is replaced by another of the same covalence.[791] For example, CH_3 may be replaced by H or Br, $-CH_2-$ by –O–,[792] >CH– by >N– and >C< by >Si<. We may, in agreement with the literature, assume that in general substitution is without effect on relative thermochemical stabilities. Equivalently, isomerization of monosubstituted hydrocarbons[793] is considered equivalent to the less selective and often more difficult Lewis acid catalyzed with unsubstituted hydrocarbons.[794]

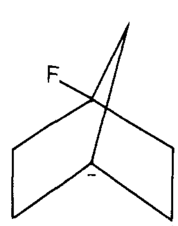
We might expect substituent effects to be maximized when the substituent (a) strongly conjugatively interacts with the rest of the molecule, (b) is large and so introduces considerable additional strain, and (c) is extremely electron withdrawing or donating. These effects are rarely quantitatively separable. For example, let us contrast the $\Delta\Delta H_f°$ of the isomeric 2-substituted allyl and 1-substituted cyclopropyl cations. Taking a composite of theoretical results, we find the stability of the cyclopropyl species increases in the order H, CH_3, F, OH, NH_2, and O^-.[795] For another example, recall the dimerization of the triphenylmethyl radical and its substituted and annelated analogs.[796] We merely note that planar CH_3 has been theoretically shown to have no tendency to dimerize.[797]

B. Fluorine Substitution

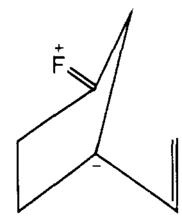
One superficially simple case is fluorine substitution. The fluorine atom is small and the C–F unit has comparable steric requirements to C–H.[798] It has also been argued that conjugative interaction of fluorine with a benzene ring, and therefore by inference with other π systems, is small.[799] Finally, as fluorine is the most electronegative element, we expect considerable electron withdrawal from the atom it is attached to.[800] We now present several examples of fluorine substitution and its effect on molecular strain energies. Our first example has already been cited: 1-norbornene, a highly strained bridgehead olefin, is seemingly stabilized by fluorination at the other bridgehead.[567] We expect that the C=C bond will have considerable biradical and dipolar character. As carbanions tend to be pyramidal while carbonium ions prefer planarity, we anticipate the following major resonance structures for both compounds, **358a**, **358b**, and **358c**. As the carbon in a C–F bond is markedly positive, coulombic attraction between the olefin C^- and the C^+–F^- dipole is expected. In other resonance structures, such as the propellane **358d**, stability is also predicted to be favored by X = F. We thus conclude correctly that bridgehead fluorination increases the stability of 1-norbornene. Varying the bridgehead subtituent to CH_3O, $(CH_3)_2N$, and aryl would prove useful in the determination of the relative importance of the various resonance structures.



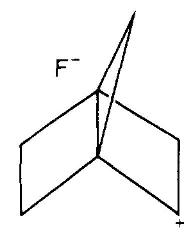
358a



358b



358c



358d

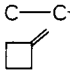
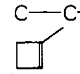
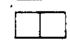
Let us now turn to polyfluorinated compounds. We acknowledged that a series of increasingly fluorinated derivatives would be useful but thermochemical data are generally lacking. By analogy to our treatment of strained hydrocarbons, we will commence with the simplest series, the perfluorocycloalkanes, $(CF_2)_n$. A reference $-CF_2-$ has been constructed ($\Delta H_f°(-CF_2-)$ = −98.1 kcal/mol) and the strain energy per CF_2 group derived.[801] Unlike the hydrocarbon case, only the values for n = 2, 3, and 4 have been measured and are 20.6, 22.9, and 8.0 kcal/mol, respectively.[801] While these values are uniformly higher than for the corresponding hydrocarbons, we are unable to explain why C_3F_6 has a higher strain energy per CF_2 than C_2F_4. It has been suggested that the π bond in C_2F_4 is relatively weak in comparison to that in C_2H_4 and that fluorine does not "like" being on formally sp^2 hybridized carbon.[802] However, we note that removal of a π electron from C_2F_4 requires approximately the same energy as from C_2H_4, while removal of a σ electron from C_2F_4 requires much more energy than from C_2H_4.[803] This would naively suggest that the π bond in C_2F_4 is of comparable strength to that in C_2F_4 while the σ bond of the former is stronger than of the latter. Accordingly, C_2F_4 should be less, not more, strained than C_2H_4. The reader may recall related arguments when comparing C_2H_2, C_2H_4, and C_2H_6 in section III.F. Common to both cases is the finding that ionization potential logic seems to provide only frustration at our ignorance.

While we cannot explain the trends in strain energies, we may still present some other differences between hydrocarbon and fluorocarbon thermochemistry (see Table XI) and recommend ref 804 through 806 as thorough reviews of general fluorine chemistry.

Turning to the heavier halogens, we find little information exists on the thermochemistry of derivatives of strained compounds.[807] It has been found that tetrachlorocyclobutadiene is relatively stable and resistant to dimerization.[808,809] While this has been explained in terms of "push-pull" resonance,[808] steric hindrance in either the transition state or product dimer itself may also provide an explanation. Steric hindrance reasons are almost always creditable, but we note that CCl_2 gives a higher yield of cyclopropane with C_2HCl_3[810a,b] than with *cis*-$C_2H_2Cl_2$[810a] or C_2Cl_4[810b,c] which in turn is higher than with C_2H_4.[810c,d] Intuitively, we believe $(CCl_2)_3$ or $(CCl_2)_2CHCl$ is more strained than $(CHCl)_2CCl_2$ or $(CH_2)_2CCl_2$. However, recalling our ignorance as to the origin of the relative strain in C_2H_4, C_3H_6, and C_3F_6, we abstain from predicting the relative strain energies in chlorocarbons.[810a] As with fluorine containing compounds, data on partially substituted compounds are sorely lacking.

Let us now consider other electron-withdrawing groups. We earlier noted that CF_3 and C_2F_5 groups destabilize the Kekulé or ordinary benzene valence isomer relative to the Dewar form (see section IX). As this letter form and other valence isomers allow more rotational freedom and have less crowding than the former, one would predict both the C_2F_5 and C_2H_5 derivatives

TABLE XI

Carbon skeletons		Relative Stability		
Compd A	Compd B	H case	F case	Ref
C=C=C	C—C≡C	A < B	A > B	*a*
2C=C		A < B	A < B	*b*
		A < B	A > B	*c*
C=C—C=C		A > B	A < B	*d*
C=C—C=C	C—C≡C—C	A < B	A > B	*e*
C=C—C—C=C	C—C—C≡C—C	A > B	A < B	*e*
C=C—C—C=C	C—C=C=C—C	A > B	A < B	*e*
C—C—C=C=C	C—C—C≡C—C	A > B	A > B	*f*
		A < B	A < B	*g*
C=C—C—C—C=C		A > B	A < B	*h*

[a] R. E. Banks, M. G. Barlow, W. D. Davies, and R. N. Haszeldine, *J. Chem. Soc. C*, 1104 (1969). [b] The reader should recall the earlier strain energy per CH_2 vs. per CF_2 discussion of ethylene, cyclopropane, and cyclobutane and their perfluorinated analogs. [c] B. E. Smart, *J. Am. Chem. Soc.*, **96**, 927 (1974). [d] J. L. Anderson, R. E. Putnam, and V. H. Sharkey, *ibid.*, **83**, 382 (1961). These authors additionally showed that $F_2C{=}CHCH{=}CF_2$ is less stable than the cyclobutene. In addition, $F_2C{=}C(CF_3)C(CF_3){=}CF_2$ is almost thermoneutral with respect to isomerization to the cyclobutene: J. P. Chesick, *ibid.*, **88**, 4800 (1966). [e] W. T. Miller, W. Frass, and P. R. Resnick, *ibid.*, **83**, 1767 (1961). [f] R. E. Banks, A. Braitwaite, R. N. Haszeldine, and D. R. Taylor, *J. Chem. Soc. C*, 454 (1969). [g] Dr. Bruce Smart, personal communication. The same trend is also found for H and F cases of methylenecyclopentane and 1-methylcyclopentene (footnote *f*). [h] A. H. Fainberg and W. T. Miller, *J. Am. Chem. Soc.*, **79**, 4170 (1957).

of Kekulé benzene to be relatively destabilized. Numerical thermochemistry data are largely lacking; the apparently marked stabilizing effect of CF_3 and C_2F_5 groups has been labeled the "perfluoroalkyl effect".[437] The electron-withdrawing power of CF_3 and C_2F_5 would be expected to be between F and H. As such, we would expect some destabilization of C=C bonds by these groups. If so, we may explain the facile conversion of Kekulé $C_6(CF_3)_6$ into the Dewar form (relative to $C_6(CH_3)_6$) in terms of converting three double bonds and their accompanying aromatic stabilization into two double bonds and two four-membered rings. The highly desirable thermochemistry on simple CF_3 containing compounds is largely absent.[812a] While we earlier noted that the interconversion of $F_2C{=}C(CF_3)C(CF_3){=}CF_2$[812b] and its corresponding cyclobutene is essentially thermoneutral, no data seem available on the related $F_2C{=}C(CH_3)C(CH_3){=}CF_2$ or $H_2C{=}C(CF_3)C(CF_3){=}CH_2$.

C. Carbonium Ions and Carbanions: Are Vacant Orbitals and Lone Pairs Idealized Substituents?

We now wish to consider idealized electron donating and withdrawing groups. If we have a strictly covalent ⩾C–X bond, then both the ⩾C and X species have one electron each. If X is strongly electron donating, then C has nearly two electrons. As such, the idealized electron donating group would correspond to the carbon having exactly two electrons. As such, the model compound for electron-donating substituents with a given carbon skeleton is thus the carbanion ⩾C:⁻. Analogously, reversing this logic suggests that the idealized electron-withdrawing model causes the carbon to have no electrons, and the model compound for electron-withdrawing substituents is the carbonium ion ⩾C⁺.[813] We realize that carbonium and carbanions contain three-coordinate carbon and hence the above should be considered with dire caution.

Without considering all of the earlier discussed compounds, let us briefly discuss a few select carbanions and carbonium ions. Hopefully without boring the reader, we requote "highly strained rings have a proclivity commensurate with the degree of internal stresses present for acidity . . . and large $J(^{13}C\text{–}H)$ coupling constants".[135] Despite the empirical success of this relation,[135,812,815] we now present some iconoclastic remarks. Implicit in the success is the tacit assumption that differential solvation effects are small. That is, we expect the differences in solvation energy of any hydrocarbon, R–H, and its carbanion, R^-, to equal that for any other hydrocarbon and carbanion, R′–H and R'^-. Equivalently, the differences in solvation energy for the hydrocarbon pair R–H and R′–H must be essentially equal to that of the carbanion pair R^- and R'^-. While we would have expected the hydrocarbon differential solvation energies to be small, as the individual solvation energies are, it is not expected that the differential solvation energies of the carbanions would also be small. While this is possible,[815] we cannot disprove the hypotheses that the carbanions are solvated solely by one amine molecule R^-: ···H–N< of constant hydrogen bond energy. Apparently the carbanion is only weakly solvated. The intrinsic, i.e., gas phase, basicity differences have not yet measured.

Isoelectronic comparisons with amines and ammonium ions may also be made. It is known from gas-phase studies that strained small ring amines such as azetidine are poorer bases than the unstrained analogs such as piperidine.[816] As such, the isoelectronic cyclobutyl anion is predicted to be a poorer base than the cyclohexyl anion. Equivalently, cyclobutane is correctly predicted to be more acidic than cyclohexane.[135,814,815] While this appears eminently simple and reasonable and even suggests another way of obtaining hydrocarbon acidity data, considerable caution is recommended. First of all we note the surprising finding that the gas-phase basicity of aniline is higher than that of ammonia.[815] This suggests, most definitely erroneously, that toluene is less acidic than methane. While ammonia and methane are atypical since they are unsubstituted, how do we reliably predict the "atypicality" of other species and/or other comparisons?[818] We also note that considerable discrepancies arise in the general comparison of gas-phase and aqueous basicity of amines.[816,819] Gas-phase and aqueous reaction conditions are most antithetical: how do we interpolate for the pure or mixed solvents that are usually used in organic chemical studies?[819]

We also recall that 1-azabicyclo[2.2.2]octane (quinuclidine) is a stronger Lewis base than the acyclic analog triethylamine even though they are of comparable Bronsted basicity.[820] The customary explanation argues there is less steric hindrance in the former for complexation. A proton (solvated or not) is further assumed to be sufficiently small that this effect is irrelevant for differentiating the basicity of the two amines. If we return to hydrocarbon analogs, we thus must compare bicyclo[2.2.2]-octane (R_cH), 1-methylbicyclo[2.2.2]octane (R_cCH_3), 1,1,1-triethylmethane (3-ethylpentane, R_aH), and 1,1,1-triethylethane (3-ethyl- 3-methylpentane, R_aCH_3).[821] From isoelectronic and isosteric arguments, we would conclude $\Delta H_f°(R_c\text{–}H) - \Delta H_f°(R_c\text{–}CH_3) > \Delta H_f°(R_a\text{–}H) - \Delta H_f°(R_a\text{–}CH_3)$. However, from the earlier postulated equivalence of substituents of equal covalence, an equal sign replacing the ">" is in order. We must seemingly sacrifice either the isoelectronic and isosteric equalities or else the substituent's effect (or lack of it). Alternatively, we forego quantitation and admit that, even qualitatively, intermolecule comparisons are often ill-defined and uncertain. Investigation of a series of hydrocarbons and amines of various ring sizes and numbers would prove instructive. For example, a systematic study of bicyclo[*m.n.p*]alkanes and their nitrogen and methylated analogs would help in our understanding. Indeed, interpolation via the monocyclic compound ethylcyclohexane and (e.g., *N*-ethylpiperidine in the above [2.2.2] case)[821] also seems essential in this study. We now note an additional complication based on Nyholm–Gillespie or valence shell electron pair repulsion[28] logic. Lone pairs are considered to be larger than bond pairs, and the lone pairs of anions are still larger. As such, we conclude the steric requirements of the lone pair in $>C:^-$ will be considerably larger than the corresponding bond pair in the neutral hydrocarbon $>C-H$. In most of the strained ring systems of interest, the groups bonded to the carbon bearing the acidic hydrogen are tied back. As such, the lone pair has "naturally" more room, the carbanion is thus more stable, and the hydrocarbon is more acidic. No correlation of lone-pair room and hybridization seems apparent. Indeed we note that cubane has been found to be approximately 10^3 times more acidic than cyclopropane[822] despite the same formal C–H hybridization. While we remain too ignorant as to how to quantitate the lone-pair room and so compare cubane and cyclopropane, it is intuitively obvious that either species (as well as ethylene) should be more acidic than propane or cyclobutane. Recent quantum chemical calculations have been performed on the effect of structural distortion on the acidity of methane, ethylene, and ethane.[823] Greater geometry variation, a systematic study, or CH_3–H,[823a] CH_3CH_2–H,[823b] $(CH_3)_2CH$–H, and $(CH_3)_3C$–H, and interrelation with theoretical conformational analysis methods[151] should be able to provide the above desired quantitation. As of now we must conclude that the correlations between hybridization, $J(^{13}C-H)$ and acidity remain highly useful but also highly theoretically suspect.

All of the above complications also arise when considering carbonium ions. These positive ions are produced in considerably more polar media than corresponding anions with the same carbocyclic skeleton. As such, solvation energies are expected to be much higher for the carbonium ions of interest. Furthermore, when comparing bridgehead carbonium ions with the acyclic *tert*-butyl cation,[228–231] two opposing trends arise. In bridgehead carbonium ion, only one face of the cation may be solvated while for the *tert*-butyl cation, both faces may be. However, to the extent that bridgehead carbonium ions are relatively pyramidal, we would anticipate solvation to be stronger because there is more room for the solvent and because the positive charge would classically be assumed to be more localized.[824] Quite surprisingly, good correlations are found with the calculated difference in strain energy of the hydrocarbon and cation (see section VI.B). Analogous correlations exist between the gas-phase appearance potential of the cation (as derived from the bromide) and the above calculated difference.[229]

It would thus appear that solvation is either unimportant or constant for closely related (e.g., bridgehead) carbonium ions of interest.[824,825] This parallels the conclusion for carbanions, but we have corresponding warnings. First of all, we cited the assumption of equivalence of CH_3, H, and Br[792] on the grounds that they are all univalent groups. However, the univalent *p*-nitrobenzoates and bromides often show meaningful differences in relative solvolysis rates.[826] Secondly, appearance potential data are often deceiving. While it is simply defined as $AP(R^+) = D(R-X) + IP(R^+)$, we must assume that R–X bond strengths are equal within a series of compounds for appearance potential and ionization potential data to be numerically parallel. Even within this assumption, the gas-phase ion R^+ might not have the structure derived from R–X merely by "deleting" X^-. For example, the allyl cation but not the cyclopropyl cation is "synthesized" from cyclopropane–H^-.[827] Does 1-bromobicyclo[2.2.1]heptane yield the bicycloheptyl cation or does the 4-methylenecyclohexyl cation form immediately instead? Solution results should not be assumed by rather individually tested.

It is also well established that hydrocarbon and carbonium ion stabilities are not always parallel for a set of isomers. For example, while $C(CH_3)_4$ is more stable than $CH_3CH_2CH(CH_3)_2$, it comes as no surprise that the primary $(CH_3)_3CCH_2^+$ is considerable less stable than the tertiary $CH_3CH_2C(CH_3)_2^+$. Even comparison among a set of all primary or tertiary carbonium ions can be deceiving; for example, let us return to compounds **1, 2,** and **3**, the isomeric set of bicyclooctanes. We had noted very early in our article that the [2.2.2] and [3.2.1] species **1** and **3** were of essentially equal strain energy while the cis [3.3.0] isomer **2** was considerably higher in energy (see section I). If we consider bridgehead carbonium ions, it would be highly doubtful that $\mathbf{1}^+$ and $\mathbf{3}^+$ are the most stable. Carbonium ion $\mathbf{2}^+$ should be the most stable as it has the most planar, and therefore classical, geometry at the cationic center. If we are allowed to use solvolysis data and parallel them to ion stability, this is confirmed: derivatives of **2** solvolyze over 10^4 faster than those of **1** or **3**.[229] But how much (if at all) is the **2**-Br or tosylate the most stable? Or is solvolysis so rapid because these species are the least stable of the three bromides or tosylates in our series?

Let us consider bridgehead dicarbonium ions. Among the very few molecular dications is the 1,4-bicyclo[2.2.2]octyl dication (**42**).[43] Despite the extreme "electrostatic strain", it is highly stable and has been labeled aromatic by the original authors.[828] Dications corresponding to either **2** or **3** remain unknown and are highly unlikely in both cases. Comparison of doubly bridgehead substituted derivatives of **1, 2,** and **3** is again impossible as the necessary thermochemistry remains undone. Indeed, we may summarize substituent effects in general by noting the general absence of the necessity thermochemical data.

D. Rearrangements, Unstable Intermediates, and Strained Compounds

Molecular rearrangements are usually characterized by converting one "reasonable" structure into another through the intermediacy of unisolated, unobserved, and often unprecedented species. These unstable intermediates may likewise be characterized by relatively low kinetic barriers to reaction and high internal energy. These attributes are shared by numerous strained molecules, although the valence isomers of benzene provide legendary contradictions. This suggests that the literature on rearrangements is a rich source of strained species. Let us chronicle some possibilities. The first is the reaction of α-halo ketones with base to yield a contracted carboxylic acid, the Favorskii rearrangement.[829] Long hypothesized to proceed through cyclopropanone intermediates,[829] the parent ketone has only recently been isolated.[418] The two carbons "holding" the -CO- group may be part of a cyclic or bicyclic ring system. Bicyclic or tricyclic cyclopropanones may thus be hypothesized, the latter including derivatives of the elusive [2.2.1]propellanes (see section XVII.B). While other reaction mechanisms have been written (e.g., the "semibenzilic" shown applicable for cyclobutanones),[830] no data are known to the authors for the above case of interest.

The second possibility involves cycloalkynes. While the smallest isolated unsubstituted cycloalkyne remains cyclooctyne (see section XII), we believe 1-azonia analogs of smaller rings should prove directly observable if not isolable. These seemingly esoteric cationic hetero derivatives are "merely" intermediates in the Beckmann rearrangement of cyclic oximes.[831] While admittedly no data exist as to the ease of bending –C≡C– and

$-C{\equiv}N^+-$, intuition armed with the alternative resonance structure $-^+C{=}N-$ for the latter suggest small ring 1-azoniacycloalkynes will enjoy greater stability than the neutral carbocycle[832] (see section X.C).

The third possibility relates to bridgehead olefins and again we capitalize on cationic hetero analogs. For example, *N*-chloroadamantylamines facilely rearrange with $AlCl_3$ to form *endo*-7-aminomethylbicyclo[3.3.1]nonan-3-ones through the probably intermediacy of 2-azonia-$\Delta^{1,2}$-homoadamantene derivatives.[833] While no direct thermochemical comparison has been made with the corresponding all-carbon system,[834] we recall the isoelectronic synthesis of $\Delta^{1,2}$-homoadamantane **196** from adamantylcarbene.[556]

Our final example correlating unstable intermediates and strained compounds returns us to carbonium ions. Let us "merely" consider the simple $C_3H_7^+$ ions.[835,836] While the isopropyl cation is well defined as $(CH_3)_2CH^+$, no such simplicity exists in the discussion of the "normal" propyl cation. Should it be viewed as (1) $CH_3CH_2{-}CH_2^+$, i.e., ethylmethyl cation; (2) $CH_3^+{\cdots}CH_2{=}CH_2$, i.e., methyl cation + ethylene; or (3) $(CH_2)_3{\cdots}H^+$, i.e., protonated cyclopropane? These structural options suggest different models and accompanying strain energies. The first structure is perhaps the simplest as it relates the cation with ethylmethane or propane. There is some additional complexity in that there are two fewer 1,2 hydrogen–hydrogen repulsions and three fewer 1,3 hydrogen–hydrogen repulsions in the cation than in the neutral hydrocarbon. The second structure is rather simple except that the "···" is quite vague. What kind of methyl carbon–ethylene carbon interactions (both attractive and repulsive) do we anticipate? Are the free "solute" CH_3^+ and "solvent" C_2H_4 suitable models? The third structure suffers from the same ambiguities as the second but still further problems arise. First of all, there are the corner, edge, and face protonated cyclopropane, of which $CH_3^+{\cdots}CH_2{=}CH_2$ is an example of the corner possibility. Secondly, electron transfer from cyclopropane to H^+ is exothermic. While $(CH_2)_3^+{\cdots}H$ is also an acceptable model for $C_3H_7^+$, the conceptual complexity of cyclopropane (section III) bodes poorly for simple understanding of its radical cation. We thus cannot simply ascertain whether C_3H_8, C_2H_4, or $(CH_2)_3$ is the best model for the "normal" propyl cation. To answer "consider resonance contributions from all of the above structures and all of the above model compounds" is no answer. Decoupling resonance and strain energies of organic compounds is where we commenced the review article.

XVII. A Potpourri of Pathologies

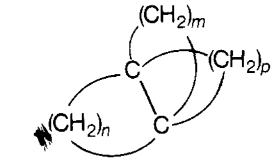
A. When Is Tetracoordinate Carbon Tetrahedral?

Few of the strained species we have discussed have the possibility of containing any strictly tetrahedral carbon atoms. We know enough to ask for four identical groups on such a carbon (see section V) and yet automatically exclude such species as spiropentane (**21**). Even with such awareness, we are ill-prepared to explain the results of highly accurate crystallographic investigations on tetraphenylmethane; there are small distortions from tetrahedral symmetry around the central carbon that are *not* attributable to *inter*molecular interactions.[837] Analogous studies of a series of substituted tetraphenylmethanes would prove instructive.[838]

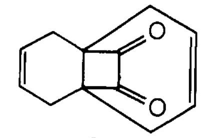
Moveover, methane itself is *not* strictly tetrahedral.[839] However, as the distortion is negligible in magnitude to that in other organic compounds, and is inexplicable in terms of conventional structural and bonding models,[839] we will now ignore this most surprising fact. Instead, let us ask the obvious question—why is methane tetrahedral? The simplest answer is that carbon is sp^3 hybridized, but our earlier discussions of hybridization (sections I and III.G) dismiss this answer as both naive and false.[840] We may also cite valence shell electron pair repulsion theory[28] which predicts tetrahedral geometry in methane. While WSEPR also correctly predicts that the methylene H–C–H angles in propane[52] and cyclopropane[50,51] are respectively less and more than the "natural" 109.5°, little else can be said about neutral hydrocarbons. Although no means of achieving quantitation seems apparent, we acknowledge this defect is shared by other qualitative geometry predictors. Recently, it was shown that nuclear repulsion between the hydrogens is the determining factor for the tetrahedral geometry of methane.[841] This clearly cannot be a general conclusion about molecular geometry since, if it were, the isoelectronic ammonia and water would have trigonal planar[842] and linear geometries. While the problems with such a hydrogen repulsion scheme are obvious, a simple solution evades us.[843]

B. Propellanes, Paddlanes, and Inverted Tetrahedra

Let us now leave methane and return to polycyclic species. In particular, consider a selected a select group of hydrocarbons, the [*m.n.p*]propellanes[844–846] **359**. These species may be

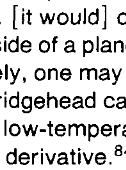


359



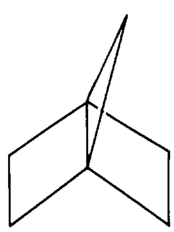
360

"defined as tricyclic systems conjoined "in" or "by" a carbon–carbon single bond".[847] For sufficiently large values of *m*, *n*, and *p* (m, $n \geq 4$, $p \geq 2$), these species behave essentially normally as chronicled in the initial articles[844–846] and by Ginsburg, a founder of and the major historian of these.[846,847] Idiosyncracies admittedly remain such as the pink color of the [4.4.2]propelladienedione[848] **360.** In contrast, the saturated dione like most α-diketones is yellow.[848] Regrettably, there appears no way of interrelating strain to the above-mentioned phenomenon nor with the use of "propellanes as substrates for stereochemical studies".[847c] Let us thus consider only the smaller propellanes. We will commence with the smallest propellane, $m = n = p = 1$, **361** (i.e., tricyclo[1.1.1.0^{1,3}]pentane).



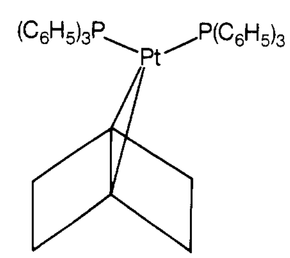
361

This species is experimentally unknown. Nevertheless, several features of general interest may be suggested. Firstly, all four bonds lie in the same hemisphere, i.e., "with the structural formula taken literally, . . . [it would] contain four carbon–carbon bonds to the molecule side of a plane containing the bridgehead carbon".[197] Alternatively, one may speak of " 'inverted' tetrahedral geometry at a bridgehead carbon",[849] a feature experimentally observed via low-temperature x-ray crystallography on a [3.2.1]propellane derivative.[849] Secondly, the possibility of bond stretch isomerism has been discussed for this and other small propellanes.[850,851] This possibility was discounted for the [1.1.1]propellane (and indeed all others except for the [2.2.2][850]). However, we may still consider the bond stretched form and describe it as an excited state. The geometry of this biradical or excited state mimics bicyclo[1.1.1]pentane,[851] and so conforms to the general rule that the geometry of a mono (or bi) radical usually is approximately the same as the species with one (or two) more electrons or hydrogen atoms appended to it.[852] Thirdly, on the basis of the above cited quantum chemical calculations and bond energy analyses,[851] it was concluded that the strain energy of [1.1.1]propellane (**361**)[853] lies between bicyclobutane (**18**) and tetrahedrane (**68**). That is, [1.1.1]propellane interpolates an experimentally well-documented species (section VI.A) and one that continues to evade synthesis (see section VII). Fourthly, we may likewise conclude from these calculations and bond energy analyses that [1.1.1]propellane lies ca. 30 kcal/mol higher in energy than its isomer 1,2-dimethylenecyclopropane.[854] We recognize the propellane as a bridged bicyclobutane and this isomerization as an "allowed" bicyclobutane–butadiene interconversion.[855] As such, this bodes poorly for the isolation of simple [*n*.1.1]propellanes in general except for those having *n* sufficiently large as to be without interest here.[856] Finally, the length of the C–C bond in [1.1.1]propellane that joins the bridgehead carbons is calculated at 1.6 Å. Although only 0.06 Å longer than a normal C–C bond,[38] it is apparently a "nonbonding, or possibly antibonding interaction".[197,851] While this has been explained in terms of charge density, orbital occupancies, and nonbonded repulsions, it suggests subtleties untreatable by normal methods as normally applied. We doubt that "empirical force field" or "molecular mechanics" [151] calculations are properly calibrated for species such as these [*n*.1.1]propellanes. As such, we are thus forced to conclude that they and, indeed, many other compounds to be discussed in this terminal section of our review may well evade simple understanding. Let us now consider [*n*.2.1]propellanes. The value $n = 1$ will be neglected as [1.2.1]- and [2.1.1]propellane are synonymous. The next member of this series, [2.2.1]propellane, (**362**) remains unknown although the evidence



362

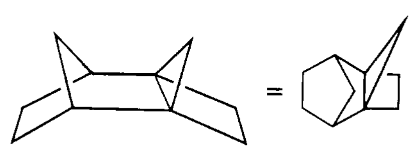
is highly suggestive.[857-859] The estimated strain energy is 85 kcal/mol: equivalently, 12 kcal/mol per carbon atom and 9–10 kcal/mol per bond. These values correspond to those values given for bicyclo[1.1.1]pentane.[853] As such, this propellane represents an eminently reasonable species, although of course, this does not mean synthesis and isolation will prove easy. An organometallic analog with the "1" bridge replaced by platinum, i.e., an olefin–platinum π complex **363**, has been isolated.[329b]



363

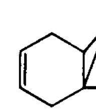
We remember that the original Walsh model for cyclopropane described this species as a complex of ethylene and CH_2 (see section III.D where this approach is cited, but left undiscussed and apparently obsoleted by the more "usual" pictures). This suggests a possible correlation between cyclopropanes such as the propellane of interest and olefin–platinum complexes. It has been found that both $\Delta^{1,4}$-bicyclo[2.2.0]hexene (**78**) and cyclopropane give stronger π complexes with platinum than does ethylene.[329b] Owing to the absence of thermochemical data on **78**, we cannot discuss the strength of the π complex with CH_2 from ethylene to cyclopropene (exothermic, i.e., cyclopropane + cyclopropane → ethylene + bicyclobutane), and we conclude such a relative stability correlation cannot be dismissed.

Let us now turn to the [3.2.1]propellane and its derivatives.[849,857-861] As earlier noted, the crystal structure of only the 8,8-dichloro derivative has been determined,[849] and the expected structural features have been found. Despite a strain energy in excess of 60 kcal/mol,[858] the half-life for decomposition in diphenyl ether at 195 °C is 20 h.[858,860b] Multiple reasons for this surprisingly high thermal (kinetic) stability have been given:[860b] "Fragmentation of the cyclobutane ring to two double bonds in a concerted process is electronically forbidden [while] because of the rigid structure involving first the central bond would probably have the electronic characteristics of a concerted process. Similarly, cleavage of the central bond to a diradical cannot be followed by a hydrogen migrations found with most cyclopropanes because this will lead to a double bond at the bridgehead. Cleavage of one of the other cyclopropane bonds would have to be followed by an alkyl shift and such shifts are not common in free radical reactions". In accord with this, [3.2.1]propellane thermally polymerizes in the liquid state.[860b] In the vapor it is forced to decompose intramolecularly and the "forbidden" product, 1,3-dimethylenecyclohexane, is formed.[862] Exemplary of the thermodynamic instability of this species is the spontaneous reaction with oxygen to form a copolymer[860c] and rapid reaction with bromine even at −60 °C.[861a] The hetero analog, 8-oxa[3.2.1]propellane has likewise been reported to be highly thermally stable.[860a] Few reactions have been described, but like other epoxides formed from tetrasubstituted olefins it is highly resistant to reductions: after 12 days of reaction with $LiAlH_4$ in ether, only a 41% yield of alcohol was formed.[860a] A 1,3-ethano bridged [3.2.1]propellane (**364**) has recently been



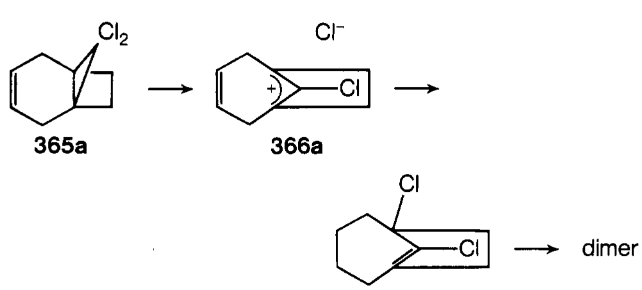
364

reported[862] as has the 9-oxa analog.[328] While they may also be formally described as methano[4.2.1]propellanes as well, their reactivity coincides more with what may be expected of "[2½.2.1]propellanes".[863] As *n* gets larger, we may expect [*n*.2.1]propellanes to be decreasingly reactive. However, these compounds remain bicyclo[2.1.0]pentane derivatives (strain energy bicyclo[2.1.0]pentane) = 57 kcal/mol; see Table IV). As such, it is not unexpected that the olefinic [4.2.1]propellane **365** reacts three times more rapidly at the bridging C–C bond than at the double bond.[864] More surprising is the spontaneous rearrangement of the dichloro analog of **365**, **365a**, to the



365

bridgehead olefin **366** via the doubly-Bredt-violating alkyl cation **366a**.[865] The authors estimated this rearrangement is exother-



365a **366a**

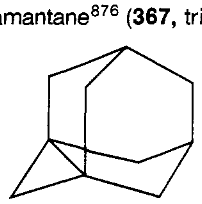
366

mic by ca. 10 kcal/mol even though **366** is highly strained and immediately dimerizes under the reaction conditions.

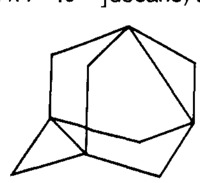
Let us now consider [*n*.2.2]propellanes and commence with $n = 2$. The earlier cited bond stretch isomerism for these species[850,851,866] remains unproven but seems a good explanation for the failures in the isolation[867–869] of this propellane. The 2-carboxamido derivative of [2.2.2]propellane has recently been isolated,[870] but no systematics of the role of substituents on propellane stability has been reported. While tribenzo-[2.2.2] propellane (dehydrotryptycene) remains unsynthesized,[871,872] we hesitate to predict whether the annelated benzene rings on [2.2.2]propellane are stabilizing or destabilizing. Nonetheless, the isolation of tryptycene in this case and the general formation of the "saturated" bicycloalkane instead of paddlanes suggests a regularity. Most of the experiments in this subsection involved electrochemical or alkali metals reduction of dihalo derivative of the saturated bicycloalkane. We suspect, as did many of the original authors, that the propellane is indeed initially produced but subsequently reduced. It may appear surprising to find C–C bonds between saturated carbons cleaved. However, it is to be noted that the intermediate radical anion is isoelectronic with the much studied and usually stabilized radical cation of bicyclic diamines such as 1,4-diazabicyclo[2.2.2]-octane.[873] From our knowledge of such species, we still know of no means to prevent this further reduction in propellanes of interest. While as such, electrochemical or alkali metal reduction suggest a "simple" synthesis of small propellanes (suggested in ref 856), we are somewhat doubtful of success.

In contrast to the above complications on [2.2.2]propellanes and derivatives, the [3.2.2] and [4.2.2]propellanes are isolable, and indeed the Diels–Alder adduct of **78** and cyclopentadiene has been isolated and so constitutes a "2½.2.2" propellane[874] stable to air (though not to Br_2). Unsaturated analogs of [*n*.2.2]propellanes may be recognized as Dewar valence isomers of [*n*]paracyclophanes (see section IX). In particular, compounds **141** and **142** correspond to $n = 3$ and 5, respectively. The $n = 3$ diene also appears in a simultaneously exotic and messy photoderivative of a tyrosine analog.[875]

As may be expected [*n*.3.1]propellanes are more "normal" as the minimum value for *n* is 3. We recognize 1,2-didehydroadamantane[876] (**367**, tricyclo[$3.3.1.1^{1,5}.0^{3,7}$]decane) as such

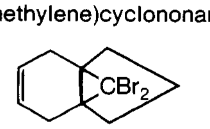


367

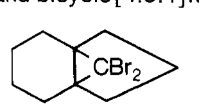


368

a [3.3.1]propellane, and thus we are unsurprised by relative stability to air (half-life = 6 h). As the strain energy is nearly identical with that of cyclopropane,[876c] it does not decompose at 100 °C, but reaction with Br_2 is rapid at −70 °C.[877] Crystallographic studies have been performed on the cyano derivative[878] (apparently more kinetically stable than other derivatives[876c]) and confirmed the qualitatively expected structure. Quantitatively, the "exotic" C–C bond length is 1.643 Å. However, the tetra-dehydro compound **368** has evaded synthesis to date;[879] the reader is advised to compare this species with its isomer, **354**, which although strained, contains no deformed quaternary carbons. Relatively little can be said about higher [*n*.3.1]propellanes. Both the dibromo[4.3.1]propellanes **369**[880,881] and **370**[880,881] rearrange to form derivatives of 4-(bromomethylene)cyclononanone and bicyclo[4.3.1]nonane.



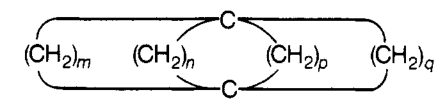
369



370

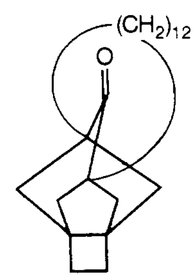
Turning to [*n*.4.1]- and [*n*.4.2]propellanes, we find they are relatively common. Compounds **181** and **185** are examples of the first class while **183**, **186**, and **360** are examples of the second. We refer the reader to our earlier section (X.B) for further discussion of most of these species. The major unique feature of these compounds appears to be the norcaradine–cycloheptatriene equilibrium. As this is essentially independent to propellane chemistry, we so conclude our discussion of propellanes.

We now consider "paddlane" (**371**)[882] which may be characterized as two quaternary carbons joined by four polymethylene chains of varying lengths.[883] Although the original authors

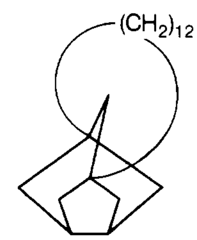


371

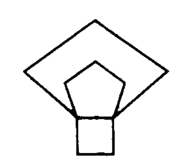
failed at the synthesis of a [12.2.2.2.]paddlane derivative, their "double paddlanes" [882] may alternatively be described as a [32.2.2.2]paddlane (i.e., tetracyclo[$32.2.2.2^{1,34}$]tetracontane. Generalized, but smaller, [n.2.2.2]paddlanes had been earlier suggested[860a] as possible approaches to planar tetracoordinate carbon (see section XVII.C). We note there are examples of other paddlanes in the literature. Through Diels–Alder reactions on the cyclophane analogs of anthracene and[884a] furan[884b] (see section XIII.C), [8.2.2.1]paddlanes were synthesized while from a cyclopentadienone a [12.2.2.1]paddlane was formed.[885] We recall that [6]paracyclophane (**288**) has been synthesized,[678] and a [5]metacyclophane (**300**) (cf. furan or cyclopentadienone) has been observed as transient intermediate.[707] This strongly



372



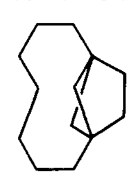
372a



372b

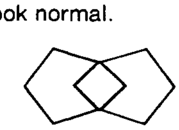
suggest that [6.2.2.1]- and [5.2.2.1]paddlanes are synthesizable.[886] A [12.3.3.1]paddlane has earlier been synthesized,[887] **372**, which may additionally be described as a [3.3.2]propellane.

As with propellanes, paddlanes also appear in hidden form elsewhere in our article. For example, the dibenzoequinene **357a** may be reformulated as a derivative of [7.1.2.1]paddlane, **373.**

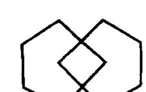


373

Paddlanes are sufficiently unsystematically studied that we cannot deduce the limits of *m, n, p,* and q or even their interrelations. For example, the [3.3.1.1]- and [4.4.1.1]paddlanes **374** and **375** look normal.

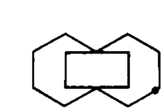
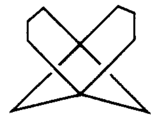
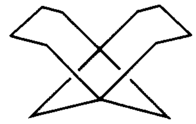


374

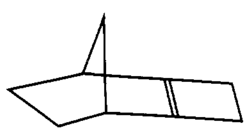


375

In contrast, the "larger" [4.2.4.2]paddlane **376** appears considerably more strained as do the [3.3.1.1]- and [4.4.1.1]paddlanes **374a** and **375a.** We may, however, gain insight by considering alternate archetypes and conceptual hierarchies (although the warning in section XV applies here as


376

374a

375a

well). The first realization is that a [*m.n.p*.0]paddlane is synonymous with a [*m.n.p*]propellane. In turn, a [*m.n*.0]propellane corresponds to a [*m.n*.0]bicycloalkene where the bridghead carbons are additionally joined by a double bond, $m = n = 2$ (**78**) the smallest known member. (We would think $m = n = 2$ is smaller than $m = 4$, $n = 1$, in compound **79**.) If we now consider [*m*.0.0.0]paddlanes or [*m*.0.0]propellanes, we have cycloalkynes, already chronicled in section XII. We remind the reader that $m = 8$, **237**, is the smallest isolated unsubstituted compound, while **240** with $m = 7$ is the smallest isolated cycloalkyne of any type. While direct size and reactivity comparisons among paddlanes, propellanes, bicyclic olefins, and cycloalkynes evades us, we note that the olefin, **377** corresponding to the [2½.2.1]propellane **364** is[888] more reactive to atmospheric oxygen than the propellane itself.

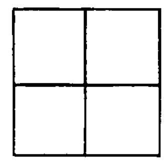
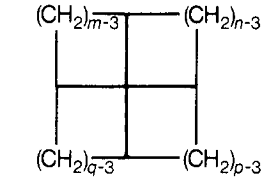

377

The second picture show paddlanes as two methanes bridged by four polymethylene chains. This suggests we investigate the bridging of simple alkanes or cycloalkanes.[889] For example, the above recipe for paddlanes also yields such spiro compounds as **50.** Likewise, bridging cycloalkanes with a bridge for each carbon yield the rotanes **63, 64,** and **65.** We may even view adamantane **10** as cyclooctane with two bridges. Considerable mathematical[890] and chemical research remains to be done on paddlanes and propellanes.

C. Planar Methane and Its Derivatives [84t]

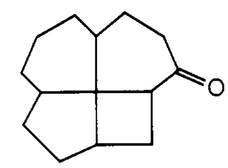
Despite our seeming ignorance of the origin of tetrahedral geometry for methane (section XVII.A), we intuitively sense tetracoordinate (CX_4) carbon is always essentially tetrahedral. (Recall the term "inverted tetrahedron" in the previous subsection.) We usually scoff or perhaps superciliously sympathize with a student who persists in drawing and visualizing methane as though it had all five atoms in a plane and all four hydrogens in a square around the central carbon. Nevertheless, planar methane "merely" has another deformed (carbon) geometry and so is worthy of analysis in our study. While numerous theoretical studies have been made on planar methane, we will consider the numerical results of only the most rigorous.[895,896] Palalikit, Hariharan, and Shavitt[895] and Schleyer, Collins, Dill, Apeloig, and Pople[896] found that the square-planar conformer of methane was less stable then the normal tetrahedral one by ca. 160 kcal/mol. As this value exceeds the C–H bond strength in methane, planar methane itself may be disregarded. However, this does not preclude the possibility of suitable derivatives, and the rest of this subsection will chronicle the largely qualitative studies of such species.

As unlikely as success is,[897] such compounds were proposed and justified by both orbital symmetry analyses and semiempirical quantum chemical calculations.[891] While it would be highly desirable to calibrate these calculations with the rigorous ones[895,896] cited above, this is, unfortunately, nearly undoable. Almost all of the compounds (or racemization reaction intermediates) of interest involve either aromatic ring systems and/or extensively substituted derivatives. As such, they cannot be treated by most of the conceptual apparatus used elsewhere in our review. If we limit ourselves to strained polycyclic hydrocarbons, we come across the most intriguing "fenestrane", **378a,** tetracyclo[3.3.1.0^{3,9}.0^{7,9}]nonane.[898] While this compound


378a


378b

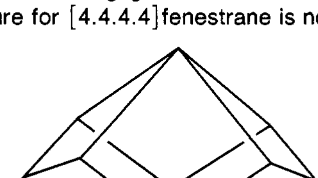
remains unknown, it suggests a class of compounds, **378b,** which we will label [*m.n.p.q*]fenestranes wherein *m, n, p, q* are the ring sizes.[899] Small "fenestranes" such as **378a** involve a symmetric bending mode ($\alpha > 109.5°$) of the central carbon (spiropentane, $\alpha < 109.5°$).[841] Bicyclo[1.1.1]pentane has an umbrella made of distortion at the bridgehead carbon ($\alpha > 109.5°$), while the umbrella distortion in [2.2.2]propellane has ($\alpha < 109.5°$).[841] We thus label **379,** used as a model for fenestrane (i.e., [4.4.4.4]fenestrane) synthesis, a [6.6.5.4]fenestrane derivative.[898,900] (While the parent hydrocarbon



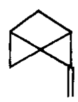
379

[5.5.5.5]fenestrane is unknown to us, 1,4,7,10-tetraazatetracyclo[5.5.1.0^{4,13}.0^{10,13}]tridecane has been synthesized and has been shown to "undergo a remarkable series of degenerate prototropic and conformational equilibria".[901]

Strain energies, calculated or experimental, remain unevaluated for any [*m.n.p.q*]fenestrane derivative. As such, we cannot deduce whether the most desired and initially cited [4.4.4.4]fenestrane is isolable or even if it is stable to spontaneous homolytic C–C bond cleavage. However, several qualitative conclusions may be deduced for this and related species from the results of the more rigorous calculations. First of all, square-planar methane is found to be unstable relative to the square-pyramidal form by ca. 26 kcal/mol.[895,902] The deviation from planarity is a nonnegligible 32°[895] and suggests that the correct structure for [4.4.4.4]fenestrane is not **378a** but **380.**


380

If we excuse the oddity of square-pyramidal carbon, this species does not appear exceptionally strained beyond four cyclobutanes. Admittedly, most interested in this area have tacitly assumed planar tetracoordinate carbon rather than the square pyramid. Insufficient data are known about planar tetracoordinate carbon to evaluate if the isoelectronic equality in planar vs. tetrahedral geometry differences is meaningful: $(CH_2)_2N(CH_2)_2{}^+(CH_2)_2C(CH_2)_2 = NH_4{}^+ - CH_4$ (data from ref 896). We note that the energy needed to flatten spiropentane (**20**) was calculated to be some 80 kcal/mol less than for CH_4.[896] While this indicates that planar spiropentane would be unstable relative to the diradical formed from C–C bond cleavage, it nonetheless suggests an extension of the fenestrane concept. We may define a hierarchy where C–CH_2 bonds are sequentially cut and replaced by C–H bonds. The [*m*]-, [*m.n*]-, and [*m.n.p*]fenestranes, which may be spoken of as "broken windows", have precedent absent for the smaller [*m.n.p.q*]fenestranes. The [*m*] and [*m,n*] members are easily shown to be cycloalkanes and spiroalkanes (sections IV and VI.D, respectively.) Some of the [*m.n.p*] series have already been mentioned in this review but in a different context: compounds **66** and **67** are both [3.5.3]-fenestranes. Compound **236** is a [6.4.4] derivative. Additionally, the hypothetical compounds described by structure **44** would be considered ($n + 2$, 3, $m + 2$) derivatives, while **381**, recently postulated in the literature,[905] is a [3.4.3] derivative.



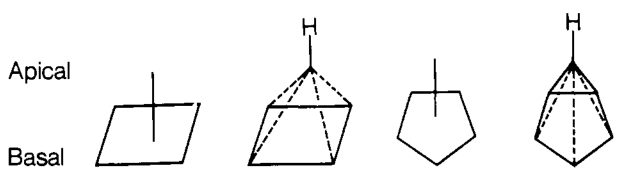
381

We finally note that in strictly square-planar or square-pyramidal tetracoordinate carbon there is an "unused" lone pair.[891,895] This suggests the possibility of Lewis or Bronsted basicity and pentacoordinate carbon, the topic of the next and final subsection on structural pathologies.

D. Five- and Six-Coordinate Carbon

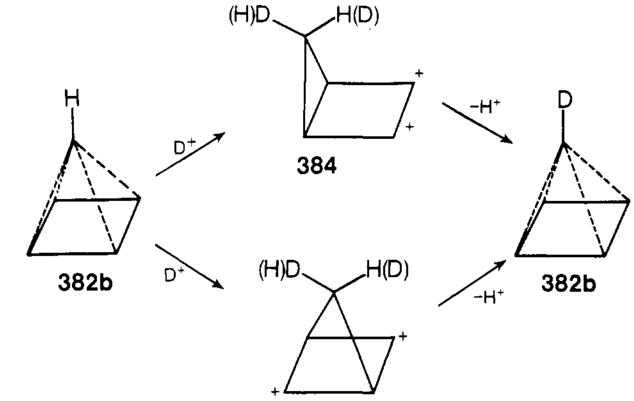
Intermediates or transition states with five-coordinate carbon have long been postulated in connection with S_N2[60] and S_G2[906] reactions. Indeed, they are essentially inherent in the definition of these classes of reaction.[907] In addition, surprisingly stable species containing five- and/or six-coordinate carbon have also been chronicled among the carboranes.[908] Among these compounds are to be found octahedral and icosahedral structures (e.g., $B_{10}C_2H_{12}$), the two remaining platonic solids (regular polyhedra) needed to complete the story in section XIV. Although of considerable interest, we will largely neglect them here as they have too few carbon atoms to be treated in this review.[909]

Numerous highly stable carbonium ions have been observed for which five-coordinate carbon has been fervently suggested.[905,910] Let us limit our discussion to those species which may be visualized as polyhedra with a carbon atom having at least four "bonds" to other carbon atoms. To date, there are but two observed polyhedral frameworks or structures that fit our criterion, the square and pentagonal pyramids **382** and **383**, respectively.



382a **382b** **383a** **383b**

The square pyramid, for which $C_5H_5^+$ is the archetypal species, has stimulated extensive theoretical interest[911–913] and indeed was proposed[911] before any experimental studies were described. Alternative structures, such as the planar pentagon, cannot be dismissed.[912,913] Experimentally it is found that the precise structure is determined by the substituents. The unsubstituted species[914] and the pentachloro[915a,b] and pentaphenyl[915b,c] derivatives are found to be pentagonal: for completeness, the unsubstituted[914] and pentachloro compounds[915a,b] are ground-state triplets while the pentaphenyl[915b,c] and other pentaaryl derivatives[916] are ground-state singlets. In contrast, derivatives containing neither lone pairs nor multiple bonds appear to be square pyramidal in general. For example, the dimethyl[917] and various bishomo derivatives[918–920] appear to be square pyramidal.[921] Likewise, some derivatives of the trishomocyclopropenyl cation have been reformulated[919,920,922] as square-pyramidal $C_5H_5^+$ derivatives. Before leaving substituted $C_5H_5^+$ ions, we remind the reader of the connection between fenestranes and the square-pyramidal ions. Experiments designed to test this have not yet been performed. We note that bishomo derivatives[919] do not exchange the apical hydrogen in FSO_3D.[923] While it is not unexpected that FSO_3^- is too weak a base to abstract the proton, it also suggests that homocylobutadiene dications (**384** and **385**) are either unstable[924] and/or do not circumambulate.[925] Less information is known about



derivatives of the six-carbon $C_6H_6^{2+}$. It has been found that the hexamethyl species has the pentagonal-pyramidal geometry[926] while the hexachloro compound has the hexagonal geometry.[927] Both results are compatible with the substituent effects in the $C_5H_5^+$ case and with the finding that $C_4B_2H_6$ has a pentagonal-pyramidal geometry while $(CH)_4(BF)_2$ has a quinone-like hexagonal geometry.[928,929] While it may simply be argued that fluorine stabilizes the vacant p orbital on boron,[928] insufficient information is available to predict with any certainty when a given $C_6R_6^{2+}$ or $C_4B_2R_6$ species will be a pentagonal pyramid or a planar hexagon. While $(CH)_4(BF)_2$ cannot be a regular hexagon, we note that this is the geometry chosen by the triplet $C_6Cl_6^{2+}$.[927]

The monocation $C_6Cl_6^+$, in contrast, is not a regular hexagon,[927] but Jahn–Teller reasoning simply explains this. No case is known where a $C_6R_6^+$ cation is a pentagonal-pyramid in its ground-state conformation.[930] Following the general logic presented in section XIII.D, we expect that $C_6R_6^+$ should mimic the corresponding anion, in this case neutral C_6R_6.[929] While the most stable form for neutral C_6R_6 is hexagonal, we remind the reader of the benzvalene valence isomer[931] (see section IX), which may be viewed as a distorted pyramid (i.e., not fivefold symmetry). We conclude by noting square-pyramidal $C_5H_5^+$ can be viewed as a combination of CH^+ and the antiaromatic C_4H_4[911,919] and that the pentagonal pyramidal $C_6H_6^{2+}$ likewise can be viewed as a combination of $C_5H_5^+$ and CH^+.[919,926a,c] This suggests that trigonal-pyramidal C_4H_4, i.e., tetrahedrane, "can be viewed as the covalent representation of the product from $HC{:}^+$ and the antiaromatic cyclopropenyl anion".[931] One may further deduce from "the simplest Huckel model, the stability order will be $(CH)_6^{2+} > (CH)_5^+ > (CH)_4$".[931,932] This returns us to three-coordinate carbon and normal chemical experience, although tetrahedrane would scarcely be considered normal otherwise (see section VII). We hope that such analogies will prove useful in the understanding of more general strained molecules.[933]

XVIII. Conclusion

In conclusion, we have chronicled a multitude of strained species and tried to organized them in terms of general structural features. In an attempt to present quantitative thermochemical data, we have included results from both experimental calorimetry and theoretical "molecular mechanics". We have also suggested interrelationships both between and within classes of molecules using conceptual insights gained from chemical and mathematical reasoning. Despite the above, a major problem remains: While it is easy to look at a molecule and conclude it is strained, a simple and unified understanding of strain still evades us.

XIX. Addendum

This section summarizes some contributions to the field of strained organic molecules appearing in the literature during the period from June through December 1975. These publications will be cited in an order consistent with that of the main body of this review.

Some points have been made concerning the possibility of calculating erroneously symmetric molecules using force field methods if due caution is not exercised.[934] To compensate for the absence of sufficiently accurate vibrational data,[935] ab initio force fields have been computed for ethane to facilitate molecular mechanics calculations.[936] Corresponding studies on propane would be useful in order to provide information on C–C–C distortions.

The entropy term $T\Delta S$ (section II.A) appears to be a significant cause of the low quantum yield of the chemiluminescent thermally induced rearrangement of Dewar benzenes to benzene derivatives and the high quantum yield of the thermally induced cycloreversion of 1,2-dioxetanes.[937] The infrared spectrum of the twist-boat conformation of cyclohexane has been obtained by the clever strategem of heating the compound to 800 K (at which the entropy term favoring the twist-boat is significant) and immediately transferring it to a cell at 10 K (where the rate of conformational conversion to the chair is slow).[938]

A relatively high-yield directed synthesis of triamantane from a diamantane derivative holds the promise of obtaining "legitimate" members of the tetramantane group and higher adamantoids.[939] Recent experimental determinations of the heats of formation of some adamantoids show that the Schleyer and Allinger force fields both slightly overestimate thermodynamic stability in this series.[940] An experimentally obtained heat of formation of bicyclo[3.3.3]undecane (manxane) is lower by 11–14 kcal/mol than that calculated by the above methods.[941] The photoelectron spectrum of 1-azabicyclo[3.3.3]undecane (manxine) indicates coplanarity at the nitrogen bridgehead, consistent with high p character of the lone pair and presumed increased basicity; however, increased strain in manxinium ion dominates the hybridization effect and causes manxine to have a lower gas-phase proton affinity than tri-*n*-propylamine.[942] We recall a study of deformed hydrocarbons and the corresponding carbanions.[943] The $^{13}C-^{13}C$ coupling constant between the bridgehead carbons of a bicyclobutane, enriched in ^{13}C at these positions, is in excellent agreement with theory in contrast with an earlier study which relied upon natural isotopic abundances.[944]

An interesting group of ab initio calculations (including theoretical thermochemical data) on C_4 hydrocarbons including tetrahedranes, methylenecyclopropene, cyclobutadiene, cyclobutyne, and $\Delta^{1,3}$-bicyclo[1.1.0]butene has appeared.[945] The first simple alkyl methylenecyclopropenes (see ref 320) have been generated and observed via NMR at -55 °C.[946] The compound 2-carbonyloxirane has been generated and trapped with ethanol.[947] The methylenecyclopropane rearrangement has been monitored in a clever manner which sheds light on the energy difference between the corresponding, substituted singlet trimethylenemethanes. In agreement with most recent calculations (see ref 405 and references cited), the orthogonal singlet appears to be more stable than the planar singlet (by ca. 2–3 kcal/mol).[948] Another derivative of $\Delta^{1,2}$-bicyclo[4.1.0]heptene (see compound **217**) has been generated.[949] Perfluoromethylcyclobutadiene has been generated (possibly via the corresponding tetrahedrane) and the syn dimer isolated.[950] The activation parameters for the synchronous face-to-face dimerization of tri-*tert*-butylcyclobutadiene are very interesting and may support arguments made in section XIII.D which suggest secondary orbital stabilization of [4*n*.4*n*]cyclophanes. The entropy of activation for this dimerization is -47 ± 3 eu, consistent with a severely sterically hindered activated complex, but the enthalpy of activation is only 7.2 ± 0.9 kcal/mol, implying the presence of favorable electronic factors.[951]

The intermediacy of dibenzobicyclo[4.1.0]heptatriene (see the monochloro derivative **86**) has been established.[952] Butalene, a 1,4-dehydrobenzene, has been generated and trapped at low temperature.[953] This species exhibits chemistry distinct from that exhibited by a 1,4-dehydrobenzene generated at elevated temperature which is thought to be benzenediyl[953] (**88a** or **88c**?). It can be noted that retro-Diels–Alder reaction of **140** might yield dibenzobutalene and anthracene. Huckel molecular orbital calculations indicate that the binding energy per π electron in an infinite linear acene (fused six-membered rings, e.g., naphthalene, anthracene) is less than that for the corresponding infinite linear fused four-membered ring (butalene is the first member).[954] The compound 2,3,5,6-tetramethylenebicyclo[2.2.1]heptane has been obtained.[955] X-Ray crystallography indicates that hexamethyl[6]radialene has the shape of a chair almost as puckered as cyclohexane, largely due to nonbonded repulsions.[956] Spiro[4.3]octa-1,3,5-triene, a potential precursor of a $(2\pi,4\pi)$ spiroaromatic system, has a half-life in solution of 90 min at -4.5 °C and perhaps reacts via a zwitterion having both allylic carbonium ion and cyclopentadienide character.[957] The first member of the $[2\pi,6\pi]$spirene series has been reported.[958] The study of rearrangements of benzene valence isomers continues to be an area of interest and controversy.[959-963]

An excellent review of the methods for preparation of bridgehead olefins has appeared.[964] In contrast to the relative thermal stability of 9,9-dibromotricyclo[$4.3.1.0^{1,6}$]decane, increased strain causes 9,9-dichlorotricyclo[$4.2.1.0^{1,6}$]non-3-ene to thermally isomerize to the bridgehead olefin 6,9-dichlorobicyclo[4.2.1]nona-1(9),3-diene, which has been trapped with furan.[965] The enormously strained tricyclo[$3.2.1.0^{4,6}$]octa-2,5-(8)-diene appears to have a transient existence prior to rearranging to 5-ethynyl-1,3-cyclohexadiene.[966] When tricoordinate nitrogen is in the 2 position of a 1-halobicyclo[2.2.2]octyl system, resonance stabilization of the bridgehead carbonium ion produces a *net* 10^5-fold increase in solvolysis rate (a 10^5-fold decrease would normally be attributed to nitrogen's inductive effect).[967] This agrees with the results obtained for the 1-azabicyclo[2.2.2]oct-2-yl cation,[968] which is more stabilized than the 1-azabicyclo[2.2.1]hept-2-yl cation.[969] A 2,3-benzo-2-*cis*-4-*trans*-cyclooctadienone has been isolated.[970] The compound *syn*-1,6:8,13-bismethane[14]annulene is aromatic in spite of nonbonded repulsions between inner bridge hydrogens.[971]

The conformation of 1,2,6-cyclononatriene in solution appears to be the twist-boat-chair near room temperature.[972] Dimers of 1,2,5-cycloheptatriene[973] and 1,2,4,6-cyclooctatetraene[974] have been obtained. Molecular mechanics has been applied to obtain structures and energies of cycloalkynes.[975] The calculated heats of hydrogenation (gas phase) agree with experimental heats of hydrogenation (solution) for the 8–10-membered cycloalkynes: the strain in cycloheptyne is calculated at about 31 kcal/mol.[975] Norbornyne (a "4½- or 5-(−)-cycloalkyne" if cyclopentyne is a "5-cycloalkyne") can be generated from 2-chlorobicyclo[2.2.1]hept-2-ene through use of *n*-butyllithium[976] but, surprisingly, not by methyllithium.[977] The compound 1,5-cyclooctadiyne (**242**) is remarkably stable considering that the (C≡C—C) angles are less than 160° and the two π systems are closer (2.60 Å) than in any known cyclophanes, although not quite so close as those in compound **151** (2.42 Å).[978]

A force-field treatment of out-of-plane deformations of benzene rings has appeared.[979] Benzocyclopropene (**255**) has been shown to have markedly different $^{13}C-^{13}C$ coupling constants from those of the higher benzocycloalkanes and *O*-diethylbenzene.[980] The compound cyclopropa[4.5]benzocyclobutene has been isolated (it exhibits a greater bathochromic shift than does benzocyclopropene)[981,982] as has a derivative of dicyclobuta[*a,d*]benzene[983] (only one derivative of benzocyclobutadiene has been characterized[638]). The first example of a spirocyclopropabenzene has been obtained.[984] Interestingly, despite the anticipated electron withdrawal of the benzene ring, 7,7-difluorobenzocyclopropene has a much higher dipole moment than other geninal difluoro compounds.[985] This result was attributed to a large resonance contribution of the ionic structure: 7-fluorobenzocyclopropenium fluoride[985] (the ionic chloride of **261** has been isolated). Dipole moments of difluoro derivatives of the above benzocycloalkenes and *o*-diethylbenzene remain unmeasured. Recent examination of the hyperfine[986] splittings of the radical anions of 1,3,6,8-tetra-*tert*-butylnaphthalene (**138**) and 1,3,8-tri-*tert*-butylnaphthalene have indicated an outer plane distortion of the *peri-tert*-butyl-bearing carbons to be about 20°. Analogous studies of other sterically hindered aromatic species would be of interest: do the geometries of the neutral hydrocarbons and their radical anions correspond?[987]

Although section XIII.C indicates that the borderline between stability and instability of the [*n*]metacyclophanes occurs at *n* = 5, the smallest known unsubstituted member of this series had been until recently [8]metacyclophane. Now, [7]metacyclophane and [6]metacyclophane have been isolated, are aromatic, but show bathochromic shifts relative to larger metacyclophanes.[988] Compelling evidence for the generation of [5]paracyclophane (**289**) from its Dewar isomer **142** has been presented: most striking is the fact that **142** is *less* stable than the more highly strained trimethylene-bridged homologue, since the latter might be expected to yield the impossibly strained [3]paracyclophane.[989] Attempts to reduce 1(4)-pentamethylenecyclooctatetraene to the corresponding bridged 10π dianion have failed thus far.[990] A spectacular cyclophane composed of two propeller-like triphenylmethyl units which are mutally displaced has been characterized and is one of the very few known compounds of D_3 symmetry.[991] The "super" cyclophanes [2.2](2,7)pyrenophane and its related diene have been reported.[992] While the parallel rings of cyclophanes have often been used as models for the interaction of aromatic compounds, recently convincing evidence has been presented[993] that shows that gaseous benzene dimer has the two rings perpendicular. While these authors precedent their findings by citing the orientation of benzene molecules in condensed phases, this logic has seemingly not been incorporated in studies of the cyclophanes. A systematic study of the photoelectron spectra of the helicenes from benzene, naphthalene, and phenanthrene (i.e., [1]-, [2]-, and [3]helicene) through [14]helicene has been reported[994] with explicit interest in σ and π-orbital mixing and transannular ring effects. The middle benzene ring in 7*bH*-indeno[1,2,3-*jk*]fluorene is distorted and undergoes relatively facile Diels–Alder reactions.[995]

A theoretical study of dodecahedrane has appeared in which there is discussion of the molecule's symmetry-related properties.[996] In section XIV it was noted that there is a 45-kcal/mol discrepancy between the heats of formation calculated by the Schleyer and Allinger force fields for dodecahedrane. An experimental thermochemical study appears to favor the lower value calculated by the Schleyer group.[998] The heat of formation of perhydroquinacene (dodecahedrane may be viewed topologically as a fusion of three perhydroquinacene units) is lower than Schleyer's calculated result by about 3 kcal/mol and lower than Allinger's result by over 16 kcal/mol.[997] *dl*-"Bivalvane" is only five C–C bonds short of dodecahedrane and has all of the requisite carbons; preliminary evidence suggests that it may be "locked" into a favorable conformation for this transformation.[998] Additional syntheses of iceane (wurtzitane) have been reported.[999] Noriceane and pentacyclo[5.3.1.0^{2,6}.0^{3,5}.0^{4,9}]-undecane,[1000] hexacyclo[5.4.0.0^{2,6}.0^{4,11}.0^{5,9}.0^{8,10}]undecane,[1001] and lepidopterene (which contains a 1.64-Å carbon–carbon bond)[1002] are four new highly strained polycyclic hydrocarbons. Tricyclo[7.3.0.0^{4,12}]dodecane is a new member of the $(CH)_{12}$ manifold which is capable of structurally degenerate Cope rearrangements, which are, however, slow on the NMR time scale at 140 °C presumably because of the absence of strain-inducing cyclopropane rings.[1003] A potential precursor of another $(CH)_{12}$ tricyclo[4.2.2.2^{2,5}]dodeca-3,7,9,11-tetraene (a benzene dimer) has been obtained, but the desired molecule has eluded synthesis.[1004]

Investigations into the utility of the "maxiring" hierarchy (section XV) as thermochemical reference states have been simplified by a new definition of molecular branching[1005] and new algorithms for identifying subrings[1006,1007] and an acyclic backbone;[1008] in multiring species still another conceptual approach has been suggested, the use of "maximally covering subgraphs".[1009]

Although benzene has a C–C(H)–C angle of 120°,[148] substituted benzenes have C–C(X)–C angles between 115 and 125°.[1010] Explanations based on VSEPR[28] or hybridization[873] were offered, but the problems encountered are suggestive of complications in predicting the molecular geometries and energetics of substituted cyclophanes, helicenes, etc. Additional thermochemical and structural data on strained fluorocarbons are desirable. For example, the stabilizing perfluoroalkyl effect[437] might not be universal but may depend upon patterns of substitution.[1011]

Molecular mechanics calculations on tetraphenylmethane have confirmed that the local geometry around the central carbon is not tetrahedral.[1012] Although [2.2.1]propellane (**362**) remains unreported, the geometry of its platinum analogue **363** has been published.[1013] The "pyramidal cations" $C_5H_5^+$ (**382**) and $C_6H_6^{+2}$ (**383**) continue to be of interest and the chemistry of these and related species was recently reviewed.[1014] Two of the three possible isomers of spiro[5,5]undeca-5,11-(propan-2-one)-2,8-dione, a potential precursor of the benzo-[*d*]naphthalene cation potentially containing a planar tetracoordinate carbon,[1015] have been reported.[1016]

Acknowledgments. One of us (J.F.L.) wishes to acknowledge the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We wish to thank Professors I. J. Borowitz, B. B. Jarvis, A. Liberles, P. H. Mazzocchi, R. M. Pollack, M. Pomerantz, S. W. Staley, V. P. Vitullo, D. L. Whalen, and most of all Professor P. v. R. Schleyer (Princeton) and Dr. E. J. Domalski (National Bureau of Standards) for their suggestions and shared insights. However, we imply no unanimity except between the authors. We also express our gratitude to all those individuals, admittedly already cited in the references, for providing us with unpublished data and often partially formulated conclusions. Finally, we thank Ms. Deborah Van Vechten and Ms. Susan J. Greenberg for their editorial and typing assistance, respectively, and a fortiori for their tolerance as understanding spouses while we were writing this article.

XX. *References and Notes*

(1) (a) University of Maryland–Baltimore County; (b) Frostburg State College.
(2) (a) G. W. Wheland, "Advanced Organic Chemistry", 3d ed., Wiley, New York, N.Y., 1960; (b) W. J. le Noble, "Highlights of Organic Chemistry", Marcel Dekker, New York, N.Y., 1974.
(3) K. B. Wiberg, "Determination of Organic Structures by Physical Methods", Vol. 3, F. C. Nachod and J. J. Zuckerman, Ed., Academic Press, New York, N.Y., 1971, p 207.
(4) J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds", Academic Press, London, 1970.
(5) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds", Wiley, New York, N.Y., 1969.
(6) "Selected Values of Properties of Hydrocarbons", American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1953.
(7) This value is taken from ref 4 which will be our standard source when

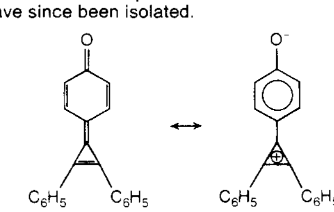
none is explicitly cited. The precise number, admittedly, varies from reference to reference.
(8) G. J. Janz, "Estimation of Thermodynamic Properties of Organic Compounds", Academic Press, New York, N.Y., 1958.
(9) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968. For a new scheme, see S. W. Benson and M. Luria, *J. Am. Chem. Soc.*, **97,** 704 (1975).
(10) Cox and Pilcher[4] present several variants of these fundamental schemes. See also G. R. Somayajuly and B. J. Zwolinski, *J. Chem. Soc., Faraday Trans. 2,* 973 (1974).
(10a) For discussion of the interrelationship of bond dissociation energies, and contributing bond energies, see R. T. Sanderson, *J. Am. Chem. Soc.*, **97,** 1367 (1975).
(11) P. v. R. Schleyer, J. E. Williams, Jr., and K. R. Blanchard, *J. Am. Chem. Soc.*, **92,** 2377 (1970).
(12) E. M. Engler, J. D. Andose, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95,** 8005 (1973).
(13) N. L. Allinger, M. T. Tribble, M. A. Miller, and D. W. Wertz, *J. Am. Chem. Soc.*, **93,** 1637 (1971).
(14) S.-J. Chang, D. McNally, S. Shary-Tehrany, M. J. Hickey, and R. H. Boyd, *J. Am. Chem. Soc.*, **92,** 3109 (1970).
(15) P. v. R. Schleyer, K. R. Blanchard, and C. D. Woody, *J. Am. Chem. Soc.*, **85,** 1358 (1963).
(16) We will use the convention of °K when thermodynamic calculations are performed and °C when more general discussions are being made (e.g., temperature of isolation). In any case, K and °C will be given explicitly and are interrelatable by the simple formula: K = °C + 273.
(17) See any book on group theory, for example, F. A. Cotton, "Chemical Applications of Group Theory", 2nd ed, Interscience, New York, N.Y., 1971.
(18) For the specialist or impatient reader, see E. M. Engler, L. Chang, and P. v. R. Schleyer, *Tetrahedron Lett.*, 2525 (1972).
(19) S. W. Benson, ref 9, pp 37–39; he defines symmetry number rigorously as "the total number of *independent* permutations of identical atoms (or groups) in a molecule that can be arrived at by simple rigid rotations of the entire molecule.
(20) O. K. Rice, "Statistical Mechanics, Thermodynamics and Kinetics", W. H. Freeman, San Francisco, Calif., 1967, pp 49–55, 60–63, 144–52, 559–60.
(21) Equilibration can be either chemical or conceptual. In the first case of the bicyclooctanes and the current one, actual interconversions of the species were done. In other cases such as the earlier mentioned rhetorical question about propane and ethane + methane, no such process is known. However, despite the obvious preference for the first approach, both are equally good for our purposes.
(22) D. E. Johnston, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 29 (1972).
(23) The rotational barrier around the C–O bond is unknown for both isomers. Intuitively, it is highly doubtful that it is considerably different from that in CH_3–OH, 1.07 ± 0.02 kcal/mol: J. P. Lowe *Progr. Phys. Org. Chem.*, **6,** 1 (1968). On that assumption, we would appear to be in the appropriate temperature range (ref 20, pp 60–63), and thus the symmetry number of 3 is appropriate.
(24) K. Mislow, "Introduction to Stereochemistry", W. A. Benjamin, New York, N.Y., 1966, pp 6–23.
(25) Reference 23; this reference contains very good literature compendia up to the time of publication, but an update is sorely lacking.
(26) J. P. Lowe, *Science*, **179,** 527 (1973), presents a comparison of the explanations for ethane.
(27) M. S. Gordon, *J. Am. Chem. Soc.*, **91,** 3122 (1969). However, see J. P. Lowe, *ibid.*, **96,** 3759 (1974).
(28) R. J. Gillespie, *J. Chem. Educ.*, **40,** 295 (1963).
(29) L. S. Bartell, *J. Chem. Educ.*, **45,** 754 (1968).
(30) E. J. Jacob, H. B. Thompson, and L. S. Bartell, *J. Chem. Phys.*, **47,** 3736 (1967).
(31) S. Wolfe, *Acc. Chem. Res.*, **5,** 102 (1970).
(32) R. Hoffmann, C. C. Levin, and R. A. Moss, *J. Am. Chem. Soc.*, **95,** 629 (1973).
(33) (a) N. D. Epiotis, *J. Am. Chem. Soc.*, **95,** 3087 (1973); (b) N. D. Epiotis, D. Bjorkquist, L. Bjorkquist, and S. Sarkanen, *J. Am. Chem. Soc.*, **95,** 7558 (1973).
(34) A. Liberles, A. Greenberg, and J. E. Eilers, *J. Chem. Educ.*, **50,** 676 (1973).
(35) P. Kollman, *J. Am. Chem. Soc.*, **96,** 4363 (1974).
(36) The C–CH_2–C angle for the idealized strain-free alkanes is not 109° but 112°. For example, see D. R. Lide, Jr., *J. Chem. Phys.*, **33,** 1514 (1960), for the structure of propane.
(37) However, consider a "hot" or vibrationally excited ethane molecule with an excitation energy of 3 kcal/mol. The bond length of this excited state is not 1.70 Å but rather the carbons are vibrating between 1.4 and 1.7 Å (1.54 ± 0.15 Å). Thus 1.7 Å constitutes the "classical" maximum or turning point of the motion. Indeed, if we look for the average position of the nuclei (as defined by the expectation value of the internuclear distance), the value is close to, but not exactly, 1.54 Å. Had the interatomic potential been that of a classical spring, i.e., had the energy varied with the square of the distortion, the average bond length would have remained absolutely unchanged regardless of the excitation.
(38) Let us consider an AX_2 molecule or skeleton, e.g., the C–C–C framework of propane. We wish to contrast the increase in energy associated with stretching of the A–X bond with that from increasing the X–A–X angle. For simplicity, we will assume X is structureless, i.e., there is no rearrangement or change in the geometry of the X group upon molecular distortion. We may thus further assume that for a given distance between the two X groups there is a unique energy of interaction. Let us designate the A–X bond length as r, the X–X distance as R, and the X–A–X angle as θ. It is easily seen that if R is changed to $R + \Delta R$, then r must be changed to $r(1 + \Delta R/R)$. Using a somewhat subtle argument, we find $\Delta R = (r \cos(\theta/2))\Delta\theta$, for small changes in R and in θ. Letting r be 1.54 Å and θ be 1.91 radians (109.5°), then $\Delta R = 1.54 \cos(109.5°/2)\Delta\theta = 0.89\Delta\theta$. From the bond stretching and angle deforming expressions of ref 12, we find for the energy expenditures, $E(r) = 0.5(4.4)^2(\Delta R)^2$ and $E(\theta) = 0.5(0.57)^2(\Delta\theta)^2$. Substituting $\Delta R = 0.89\Delta\theta$, we find $E(r)/E(\theta) = (4.4)^2(0.89)^2/(0.57)^2 = 47$. Equivalently, the bond angle may be opened considerably wider and the X groups still further separated without exceeding the A–X bond stretching energies. We remind the reader that the above relation $\Delta R = (r \cos(\theta/2))\Delta\theta$ is only true for small ΔR and $\Delta\theta$. The first-order corrected expression is $\Delta R = (r \cos(\theta/2))\Delta\theta - (r \sin(\theta/2))(\Delta\theta/2)^2$. For the r and θ values of interest, a change in θ of 20% results in a change of ΔR of only about 5%, and a change in R itself of only about 1%. As such, the correction term is rather irrelevant.
(39) Clearly, we cannot stretch physically the C–C bond in ethane or in any other molecule. As such, we cannot determine the rotational barrier or magnitudes of torsional or other nonbonded repulsions as a function of the C–C bond length from experiment. Quantum chemical calculations are eminently suited for this type of problem. Professor J. Lowe (personal communication) performed extended Huckel calculations on distorted ethanes where, for simplification, all angles were taken as tetrahedral and the C–H bond lengths were locked at 1.1 Å. The following values of the rotational barriers were obtained: R_{C-C} = 1.3 Å, V_3 = 7.751 kcal/mol; 1.5, 3.553; 1.7, 1.615; 1.9, 0.724; 2.1, 0.319; 2.3, 0.138; 2.5, 0.058; 2.7, 0.024. Several derived quantities may be given. First, we find V_3 = 3.0 kcal/mol at the experimental bond distance of ethane, in close agreement with experiment (2.75 kcal/mol, see ref 25 and 26). Second, $(\partial V_3/\partial R_{C-C})_q = -12.5$ kcal/mol. This means, for example, stretching the C–C bond from 1.54 to 1.60 Å decreases the rotational barrier or torsional repuions by only about 1 kcal/mol. Alternatively, changing the C–C bond length from 1.54 to 1.7 Å decreases the rotational barrier by 1.4 kcal/mol, considerably smaller than the 3 kcal/mol needed to stretch the bond (see ref 37). Finally, it is seen that for values beyond 2.5 Å the barrier is negligible. As such, we are thus safe in looking at parts of a large molecule of interest independently. (For completeness, we cite $K = 1.75$. H: $\zeta = 1.2$, $\alpha = -13.6$ eV; C: 2s, $\zeta = 1.625$, $\alpha = -19.44$ eV; 2p, $\zeta = 1.625$, $\alpha = -10.67$ eV.)
(40) H. Lee and M. Stiles, cited as footnote 3 in our ref 41a.
(41) (a) H. B. Burgi and L. S. Bartell, *J. Am. Chem. Soc.*, **94,** 5236 (1972); (b) L. S. Bartell and H. B. Burgi, *ibid.*, **94,** 5239 (1972).
(42) Reference 12, p 8015.
(43) G. A. Olah, G. Liang, P. v. R. Schleyer, E. M. Engler, M. J. S. Dewar, and R. C. Bingham, *J. Am. Chem. Soc.*, **95,** 6829 (1973).
(44) T. J. Katz, *J. Am. Chem. Soc.*, **82,** 3784 (1960).
(45) An analogous case is found in O^{2-} where formation of the octet is to be so balanced. In the absence of solvent or neighboring cations for stabilization, O^{2-} is unbound relative to O^- and a free electron: W. K. Stucky and R. W. Kiser, *Nature (London)*, **211,** 963 (1966).
(46) D. Bastiansen, K. Hedberg, and L. Hedberg, *J. Chem. Phys.*, **27,** 1311 (1957).
(47) On the assumption that this species has a regular octagonal geometry (cf. ref 44), this angle is found by simple arithmetic.
(48) L. N. Ferguson, "Highlights of Alicyclic Chemistry", Part 1, Franklin Publishing Co., Palisades, N.J., 1973, Chapter 3.
(49) Reference 9, p 204.
(50) O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17,** 538 (1964).
(51) W. J. Jones and B. P. Stoicheff, *Can. J. Phys.*, **42,** 2259 (1964).
(52) D. R. Lide, Jr., *J. Chem. Phys.*, **33,** 1514 (1960).
(53) T. Shimanouchi, "Tables of Molecular Vibrational Frequencies", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, 39 (1972).
(54) It is well established that there is a difference between 3d and higher orbitals used in the valence scheme and those used as polarization functions to correct for deficiencies in the original basis set. However, it is rarely obvious when these orbitals are needed. We cite both the hypervalent logic of Musher [J. I. Musher, *Angew. Chem., Int. Ed. Engl.*, **8,** 54 (1969)] and the ab initio results of Wolfe on sulfur-containing compounds [F. Bernardi, I. G. Csizmadia, A. Mangini, H. B. Schlegel, M.-H. Whangbo, and S. Wolfe, *J. Am. Chem. Soc.*, **97,** 2209 (1975)].
(55) CH_2: G. F. Bender, H. F. Schaeffer III, D. R. Franceschetti, and L. C. Allen, *J. Am. Chem. Soc.*, **94,** 6888 (1972).
(56) CH_3^+ and CH_3^-: R. E. Kari and I. G. Czismadia, *J. Chem. Phys.*, **50,** 1443 (1969).
(57) (a) "C_1 and C_2 carbonium ions": P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14,** 385 (1972). (b) "Small neutral hydrocarbons": P. C. Hariharan and J. A. Pople, *ibid.*, **16,** 217 (1972).
(58) W. A. Lathan, L. Radom, P. C. Hariharan, W. J. Hehre, and J. A. Pople, *Top. Curr. Chem.*, **40,** 1 (1973), cite 17 calculations on cyclopropane other than their own.
(59) Reference 58, pp 4 and 43.
(60) R. J. Gillespie, *J. Chem. Soc.*, 1002 (1952).
(61) R. J. Gillespie, *J. Chem. Phys.*, **21,** 1893 (1953).
(62) R. F. W. Bader, A. J. Duke, and R. R. Messer, *J. Am. Chem. Soc.*, **95,** 7715 (1973).
(63) (a) L. Pauling, *Proc. Natl. Acad. Sci. U.S.A.*, **44,** 211 (1958); (b) "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, pp 126–8, 143.
(64) J. Jarvie, W. Willson, J. Doolittle, and C. Edminston, *J. Chem. Phys.*, **59,** 3020 (1973).
(65) C. A. Coulson, "Valence", 2nd ed, Oxford University Press, London, 1961, Chapter 8.
(66) O. Martensson and Y. Öhrn, *Theor. Chim. Acta*, **9,** 133 (1967/8).
(67) C. A. Coulson and R. J. White, *Mol. Phys.*, **18,** 577 (1970).
(68) R. H. Hughes, *J. Chem. Phys.*, **24,** 131 (1956).
(69) It is obvious that ozone has open-chain and closed-ring forms, while it would appear that cyclopropane is limited to the latter. In fact, trimeth-

ylene diradical (open-chain form) has been postulated in numerous thermal rearrangements of cyclopropanes (cf. ref 9, p 82). There is also the possibility of open-chain dipolar forms for unsymmetrically substituted cyclopropanes.

(70) R. J. Buenker and S. D. Peyerimhoff, *Theor. Chim. Acta,* **24,** 132 (1972).
(71) R. J. Buenker and S. D. Peyerimhoff, *Chem. Rev.,* **74,** 127 (1974).
(72) (a) C. A. Coulson and W. E. Moffitt, *J. Chem. Phys.,* **15,** 151 (1947); (b) *Philos. Mag.,* **40,** 1 (1949).
(73) D. Peters, *Tetrahedron,* **19,** 1539 (1963).
(74) Theoretical arguments have been given that show that the X–H bonds in H_2O and NH_3 are similarly bent (L. Burnelle and C. A. Coulson, *Trans. Faraday Soc.,* **53,** 403 (1956)).
(75) (a) L. C. Allen, personal communication; (b) G. H. Stewart and H. Eyring, *J. Chem. Educ.,* **35,** 550 (1958), had earlier suggested a similar analysis, but emphasized the orbital's kinetic energy. Despite the appeal of minimum bonding of orbitals, little subsequent work has been done with this approach (see section IV.A).
(76) W. A. Bernett, *J. Chem. Educ.,* **44,** 17 (1967).
(77) D. A. Matthews, G. D. Stucky, and P. Coppens, *J. Am. Chem. Soc.,* **94,** 8001 (1972). Strictly speaking, these authors studied tetracyanoethylene oxide, but the theory is analogous. This article was singled out among many in that accurate diffraction data were used in conjunction with the calculations and bent bonds were directly observed.
(78) R. M. Stevens, E. Switkes, E. A. Laws, and W. N. Lipscomb, *J. Am. Chem. Soc.,* **93,** 2603 (1971).
(79) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.,* 2851 (1962); errata, 3161 (1963).
(80) A. Veillard and G. Del Re, *Theor. Chim. Acta,* **2,** 55 (1964).
(81) (a) M. Randić and Z. P. Maksić, *Theor. Chim. Acta,* **3,** 59 (1965); (b) L. Klasinc, Z. B. Maksić, and M. Randić, *J. Chem. Soc. A,* 755 (1966); (c) M. Randić and Z. B. Maksić, *Chem. Rev.,* **72,** 43 (1972); (d) Z. B. Maksić and M. Randić, *J. Am. Chem. Soc.,* **95,** 6522 (1973).
(82) Stevens, Switke, Laws, and Lipscomb[78] report that the C–C overlap in cyclopropane is 20% less than in ethane.
(83) J. J. Kaufman, *Int. J. Quantum Chem., Symp.,* **No. 1,** 485 (1967).
(84) F. S. Mortimer, *Adv. Chem. Ser.,* **No. 54,** 39 (1968).
(85) R. Manne, *Int. J. Quantum Chem.,* **2,** 69 (1968).
(86) This limitation is largely a computational one and in any case has been, in principle, lessened by the publication of the following extensive numerical compilation: E. A. Boudreaux, L. C. Cusachs, and L. Dureau, "Numerical Tables of Two-Center Overlap Integrals", W. A. Benjamin, New York, N.Y., 1970.
(87) L. Pauling, *J. Am. Chem. Soc.,* **53,** 1347 (1931).
(88) C. A. Coulson and E. T. Stewart in "The Chemistry of the Alkenes", Part 1, S. Patai, Ed., Interscience, New York, N.Y., 1964, discuss this model of ethylene.
(89) A. D. Walsh, *Nature (London),* **159,** 165, 712 (1947).
(90) T. M. Sugden, *Nature (London),* **160,** 367 (1947).
(91) A. D. Walsh, *Trans. Faraday Soc.,* **45,** 179 (1949).
(92) R. S. Mulliken, *Phys. Rev.,* **41,** 751 (1932).
(93) W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973, pp 22–3, provides a very good pictorial and verbal discussion of this "synthesis".
(94) "In" and "out" cyclopropane; see ref 93.
(95) "Internal" and "external" cyclopropane and related heterocycles: H. Basch, M. B. Robin, N A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.,* **51,** 52 (1969).
(96) "In" and "peripheral" cyclobutane: R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.,* **93,** 5699 (1971).
(97) "Inside" and "outside" general cycloalkanes and related heterocycles: P. E. Peterson, *J. Org. Chem.,* **37,** 4180 (1972). Peterson presents rather remarkable alternation data for properties with ring size odd-and-even alternation. Thermochemical justification appears desirable.
(98) "Radial" and "tangential" benzene: V.-Ö. Jonsson and E. Lindholm, *Chem. Phys. Lett.,* **1,** 501 (1967).
(99) "Horizontal" and "vertical wave" cyclohexanes: R. Hoffmann, P. D. Mollière, and E. Heilbronner, *J. Am. Chem. Soc.,* **95,** 4860 (1973).
(100) Bicyclobutane: M. Pomerantz and E. W. Abrahamson, *J. Am. Chem. Soc.,* **88,** 3970 (1966).
(101) Spiropentane: see ref 76, 89, and 91.
(102) (a) Quadricyclane: H. D. Martin, C. Heller, E. Haselbach, and Z. Lanyjova, *Helv. Chim. Acta,* **57,** 465 (1974); (b) Barbaryl cation: R. Hoffmann and W. D. Stohrer, *Bull. Chem. Soc. Jpn.,* **45,** 2513 (1972).
(103) Uniqueness is here taken to mean that we are not merely redrawing a set of degenerate orbitals. See Hoffmann and Davidson's (ref 96) discussion of cyclobutane orbitals. Such a case of nonunique orbitals is discussed in ref 100.
(104) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963, Chapter 2.
(105) Reference 104, pp 30–32.
(106) Heat of formation of cyclopropenium cation: F. P. Lossing, *Can. J. Chem.,* **50,** 3973 (1972).
(107) Reference 9, p 51.
(108) Reference 93, Chapter 1, is the general reference for this method, while cyclopropane is discussed on pp 19–21.
(109) M. Charton in "The Chemistry of Alkenes", Vol. 2, J. Zabicky, Ed., Interscience, New York, N.Y., 1970.
(110) H. C. Allen and E. K. Pyler, *J. Am. Chem. Soc.,* **80,** 2673 (1958).
(111) Reference 9, pp 50–51.
(112) G. Herzberg and J. Shoosmith, *Can. J. Phys.,* **34,** 523 (1956).
(113) This value is the average of those given by A. J. C. Nicholson, *J. Chem. Phys.,* **43,** 1171 (1965); and A. D. Baker, C. Baker, C. R. Brundle, and D. W. Turner, *Int. J. Mass Spectrom. Ion Phys.,* **1,** 285 (1968).
(114) W. C. Price and W. T. Tutte, *Proc. R. Soc. London, Ser. A,* **174,** 207 (1940).
(115) The reader is directed to J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions", *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.,* **26** (1969), for more recent confirmatory results.
(116) G. Herzberg, *Can. J. Phys.,* **39,** 1511 (1961).
(117) W. C. Price, *Phys. Rev.,* **47,** 444 (1935).
(118) G. Herzberg and J. W. C. Johns, *Astrophys. J.,* **158,** 399 (1969).
(119) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Am. Chem. Soc.,* **93,** 808 (1971).
(120) The ionization potential of cyclopropane is known only as an upper bound: H. Basch, M. D. Robin, N. A. Kuebler, C. Baker, and D. W. Turner, *J. Chem. Phys.,* **51,** 52 (1969). The citation of an upper bound means we cannot even tell how much this stabilization is but it may be determined to be at least 10 kcal/mol.
(121) J. M. Schulman and G. J. Fisanick, *J. Am. Chem. Soc.,* **92,** 6653 (1970).
(122) M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.,* **94,** 767 (1972).
(123) Reference 48, pp 52–3, 101–5.
(124) D. J. Patel, M. E. H. Howden, and J. D. Roberts, *J. Am. Chem. Soc.,* **85,** 3218 (1963).
(125) D. M. Graham and C. E. Holloway, *Can. J. Chem.,* **41,** 2114 (1963).
(126) D. Peters, *Tetrahedron Suppl. 2,* **19,** 143 (1963).
(127) E. Clementi and H. Popkis, *J. Am. Chem. Soc.,* **94,** 4057 (1972). These authors quantum chemically analyzed methane and concluded the hybridization is about $s^{1.5}p^{2.5}$ rather than sp^3 as conventional reading would suggest. An analogous but less rigorous calculation has been reported on CH_4, CH_3F, CH_2F_2, and CHF_3 (T.-K. Ha, *J. Mol. Struct.,* **11,** 179 (1972)).
(128) P. Kollman, *J. Am. Chem. Soc.,* **96,** 4363 (1974). In this paper an analysis of "nonbonded attraction" (see ref 33a and 33b in particular) was given and a comparison of the amount of s and p character in the various bonds of ethylene, 1,1-difluoroethylene, and quantum chemical analogs was presented.
(129) We used the calculational results of ref 121 and 122 and arithmetically obtained the percent s character. We derive for the carbons in ethane, 23.6 and 26.4%, and for the carbons in cyclopropane, 29.5 and 32.5%. There are admitted complications regarding the nonorthogonality of the orbitals used for the calculation of percent s character. For a rigorous theoretical and calculational treatment of strained organic molecules, see M. D. Newton, in "Modern Theoretical Chemistry. Volume II. Electronic Structure *Ab Initio* Methods", H. F. Schaefer III, Ed., Plenum Press, New York, N.Y., 1976. We thank Dr. Newton for making his manuscript available to us prior to publication.
(130) M. Pomerantz and D. F. Hilderbrand, *J. Am. Chem. Soc.,* **95,** 5809 (1973), ref 23. See also M. Pomerantz and J. F. Liebman, *Tetrahedron Lett.,* 2385 (1975).
(131) G. Karabatsos and C. E. Orzech, Jr., *J. Am. Chem. Soc.,* **86,** 3574 (1964).
(132) For example, bent bonds hybridization and maximum overlap logic, ref 80, 81b,c; and Y. Kovacević, M. Eckert-Maksić, and Z. B. Maksić, *J. Mol. Struct.,* **21,** 335 (1974); R. Pasternak and A. Mayer, *ibid.,* **13,** 201 (1972); Walsh picture, ref 96 and 97; delocalized molecular orbitals from group orbitals, ref. 108, pp 26–7. The precise comparison of cyclobutane with ethylene will be made later in this section. We now note that the reaction of two ethylene molecules to form one of cyclobutane is exothermic. However, this reaction does not proceed at a measurable rate at ambient conditions as it is an almost archetypal symmetry forbidden reaction: R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, pp 18–22.
(133) K. B. Wiberg, K. C. Bishop, III, and R. B. Davidson, *Tetrahedron Lett.,* 3169 (1973), and references cited therein.
(134) P. Bruckmann and M. Klessinger, *Angew. Chem. Int. Ed. Engl.,* **11,** 524 (1972).
(135) Reference 48, p 94. Although we believe there are conceptual problems with this statement (see section III.G and XVI), we nonetheless believe it is a good, general but empirical, regularity to be used with appropriate caution.
(136) We mean here both C–C and C–H bond repulsions. Across the ring C–C repulsions have rarely been considered in strain energy analyses but have been documented by both theoretical and experimental studies of cyclobutane: L. Salem and J. S. Wright, *J. Am. Chem. Soc.,* **91,** 5447 (1969); and F. Bischof, E. Haselbach, and E. Heilbronner, *Angew. Chem. Int. Ed. Engl.,* **9,** 952 (1970), respectively.
(137) Geometry of cyclobutane itself: A. Almenningen and O. Bastiansen, *Acta Chem. Scand.,* **15,** 711 (1961).
(138) (a) F. A. Cotton and B. A. Frenz, *Tetrahedron,* **30,** 1587 (1974); (b) W. J. Lafferty, in "Critical Evaluation of Chemical and Physical Structural Information", National Academy of Sciences, Washington, D.C., 1974; (c) R. M. Moriarty, in "Topics in Stereochemistry", Vol. 8, E. L. Eliel and N. L. Allinger, Ed., Wiley, New York, N.Y., 1974. (d) C. Cistaro, G. Fronza, R. Mondelli, S. Bradamante, and L. A. Pagini, *J. Magn. Reson.,* **15,** 367 (1974), presents a compendium of NMR coupling constants for four-membered rings.
(139) (a) L. S. Bartell and B. Andersen, *J. Chem. Soc., Chem. Commun.,* 789 (1973); (b) P. Pasternak and A. Y. Meyer, *J. Mol. Struct.,* **20,** 351 (1974).
(140) T. Shimanouchi, *J. Chem. Phys.,* **26,** 594 (1957), had earlier utilized a similar approach to understand the vibrational spectrum of ethylene or cycloethane. Application to cyclopropane and other deformed molecules would be of interest.
(140a) J. W. Beran, A. C. Legon, and D. J. Miller, *J. Chem. Soc., Chem. Commun.,* 658 (1974), applied this approach to the structure of trimethylene sulfoxide.
(141) Geometry of cyclopentane itself: W. J. Adams, H. J. Geise, and L. S. Bartell, *J. Am. Chem. Soc.,* **92,** 5013 (1970).
(142) (a) C. Altona, in "Conformational Analysis, Scope and Present Limitations", G. Chiurdoglu, Ed., Academic Press, New York, N.Y., 1971; (b) R. L. Lipnick, *J. Mol. Struct.,* **21,** 411, 423 (1974).
(143) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, N.Y., 1965. We note that other

references gave different but comparable numbers.
(144) Geometry of cyclohexane itself: M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963).
(145) (a) M. J. O. Anteunis, "Some Results and Limitations in Conformational Studies of Six-Membered Heterocycles", in ref 142a; (b) D. H. R. Barton and O. Hassel, "for their contributions to the development of the concept of conformation and its applications in chemistry" in "Nobel Lectures in Chemistry 1963–1970", Elsevier, Amsterdam, 1972; (c) "Conformational Analysis—The Fundamental Contributions of D. H. R. Barton and O. Hassel" in "Topics in Stereochemistry", Vol. 6, N. L. Allinger and E. L. Eliel, Ed., Wiley, New York, N.Y., 1971; (d) E. L. Eliel, "Stereochemistry of Carbon Compounds", McGraw-Hill, New York, N.Y., 1962, Chapter 8; (e) ref 143, Chapter 2; (f) E. W. Garbisch, Jr., B. L. Hawkins, and K. D. Mackay, "Applicability of the Temperature Dependence of Intensive Parameters for Quantitative Conformational Analysis—Conformational Analysis of Methyl Cyclohexane", ref 142a; (g) M. Hanack, "Conformation Theory", Academic Press, New York, N.Y., 1965, Chapter 2; (h) F. R. Jensen and C. H. Bushweller in "Advances in Alicyclic Chemistry", Vol. 3, H. Hart and G. J. Karbatsos, Ed., Academic Press, New York, N.Y., 1971. (i) G. M. Kellie and F. G. Riddell, "Nonchair Conformations of Six Membered Rings", in ref 138c, 1974; (j) J. Reisse, "Quantitative Conformational Analysis of Cyclohexane Systems", in ref 142a; (k) M. J. T. Robinson, *Tetrahedron*, **30**, 1971 (1974); (l) R. D. Stolow, "Recent Applications of Nuclear Magnetic Resonance Spectrometry in Conformational Studies of Cyclohexane Derivatives", in ref 142a; (m) K. B. Wiberg and A. Shrake, *Spectrochim. Acta, Part A*, **29**, 583 (1973).
(146) (a) E. J. Corey and W. T. Wipke, *Science*, **166**, 178 (1969); (b) E. J. Corey, W. T. Wipke, R. D. Cramer III, and W. J. Howe, *J. Am. Chem. Soc.*, **94**, 431 (1972).
(147) C. A. Coulson and S. L. Altmann, *Trans. Faraday Soc.*, **48**, 283 (1952).
(148) Geometry of benzene: A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, **39**, 350 (1957).
(149) I. Tukui, T. Fukuyama, and K. Kuchitsu, *J. Mol. Struct.*, **23**, 33 (1974), discuss the geometry of simple compounds containing the C=C group and C=O analogs.
(150) (a) F. A. L. Anet, "Nuclear Magnetic Resonance Studies of the Conformers and Conformational Barriers in Cyclic Molecules", in ref 142a; (b) M. S. Baird, in "Alicyclic Compounds", W. Parker, Ed., in the MTP International Review of Science, Butterworth, London, 1963; (c) J. D. Dunitz, in "Perspectives in Structural Chemistry", Vol. 2, J. D. Dunitz and J. A. Ibers, Ed., New York, N.Y., 1968; (d) ref 145d, pp 252–265; (e) ref 143, pp 206–223; (f) ref 145g, pp 158–166; (g) W. D. Ollis, J. F. Stoddart, and I. O. Sutherland, *Tetrahedron*, **30**, 1903 (1974); (h) J. Sicher in "Progress in Stereochemistry", Vol. 3, P. B. D. de la Mare and W. Klyne, Ed., Butterworths, London, 1962; (i) H. H. Westen, "Conformational Aspects of the Reactions of 1-Methylcyclodecane-1,6-diols with Acid" in ref 142a.
(151) (a) Theoretical studies ("molecular mechanics" or "empirical force field calculations") provide a procedure by which considerable structural and thermodynamic information on strained compounds may be obtained in principle and in fact. These studies, and therefore references, are not limited in cycloalkanes. (b) See our ref 12, 13, 14, and 30, and earlier articles by these authors. (c) G. Buemi, F. Zuccanelli, and G. Favini, *J. Mol. Struct.*, **21**, 41 (1974), and earlier articles of these authors cited therein; (d) E. Ehmer and S. Lifson, *J. Am. Chem. Soc.*, **95**, 4121 (1973), and earlier articles of these authors cited therein; (e) J. B. Hendrickson, R. K. Boeckman, Jr., J. D. Glickson, and E. Grunwald, *J. Am. Chem. Soc.*, **95**, 494 (1973), and earlier articles of these authors cited therein; (f) F. H. Westheimer, "Calculation of the Magnitude of Steric Effects" in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, N.Y., 1956; (g) K. B. Wiberg, *J. Am. Chem. Soc.*, **87**, 1070 (1965); (h) J. E. Williams, Jr., P. J. Stang, and P. v. R. Schleyer, in "Annual. Review of Physical Chemistry", Vol. 19, H. Eyring, C. J. Christensen, and H. S. Johnston, Ed., Annual Reviews, Inc., Palo Alto, Calif., 1968. This article provides an extensive description of the mathematical and calculational machinery of molecular mechanics and empirical force field calculations.
(152) We noted earlier the 1,3 nonbonded repulsion in cyclobutane and higher cycloalkanes. This is strictly an example of intra-ring effects, but the term is usually applied to formally more separate groups, e.g., the 1 and 6 positions of cyclodecane. For numerous examples of transannular phenomena see ref 150c–h and 48 (pp 150–160), and references cited therein.
(153) The most recent review on adamantane and related compounds: E. M. Engler and P. v. R. Schleyer, *MTP Int. Rev. Sci., Org. Chem. Ser. One*, **5**, 239 (1973).
(154) S. Landa and V. Machácek, *Collect. Czech. Chem. Commun.*, **5**, 1 (1933).
(155) V. Prelog and R. Seiwerth, *Chem. Ber.*, **74**, 1644, 1769 (1941).
(156) P. v. R. Schleyer and M. M. Donaldson, *J. Am. Chem. Soc.*, **82**, 4645 (1960).
(157) W. Norwacki and K. Hedberg, *J. Am. Chem. Soc.*, **70**, 1497 (1948).
(158) J. Donohue and S. H. Goodman, *Acta Crystallogr.*, **22**, 342 (1967).
(159) I. Hargittai and K. Hedberg, *J. Chem. Soc., Chem. Commun.*, 1499 (1971).
(160) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *J. Am. Chem. Soc.*, **90**, 1199 (1968).
(161) H. W. Whitlock, *J. Am. Chem. Soc.*, **84**, 3412 (1962).
(162) (a) C. Cupas, P. v. R. Schleyer, and D. J. Trecker, *J. Am. Chem. Soc.*, **87**, 917 (1965); (b) T. M. Gund, E. Osawa, V. Z. Williams, Jr., and P. v. R. Schleyer, *J. Org. Chem.*, **39**, 2979 (1974).
(163) V. Z. Williams, Jr., P. v. R. Schleyer, G. J. Gleicher, and L. B. Rodewald, *J. Am. Chem. Soc.*, **88**, 3862 (1966).
(164) P. v. R. Schleyer, E. Osawa, and M. G. B. Drew, *J. Am. Chem. Soc.*, **90**, 5034 (1968).
(165) H. W. Whitlock, Jr., and M. W. Siefken, *J. Am. Chem. Soc.*, **90**, 4929 (1968).
(166) D. Lenoir, D. J. Raber, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 2149 (1974).
(167) (a) E. M. Engler, M. Farcasiu, A. Sevin, J. M. Cense, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5769 (1973); (b) T. M. Gund, P. v. R. Schleyer, P. H. Gund, and W. T. Wipke, *ibid.*, **97**, 743 (1975).
(168) T. Clark, D. E. Johnston, H. Mackle, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 1042 (1972).
(169) E. Boelema, J. Strating, and H. Wynberg, *Tetrahedron Lett.*, 1175 (1972).
(170) W. D. Graham and P. v. R. Schleyer, *Tetrahedron Lett.*, 1179 (1972).
(171) W. D. Graham, P. v. R. Schleyer, E. Hagaman, and E. Wenkert, *J. Am. Chem. Soc.*, **95**, 5785 (1973).
(172) Review articles relevant to section VI.A: (a) K. B. Wiberg in "Advances in Alicyclic Chemistry", Vol. 2, H. Hart and G. Karabatsos, Ed., Academic Press, New York, N.Y., 1968; (b) J. Meinwald and Y. C. Meinwald in "Advances in Alicyclic Chemistry", Vol. 1, H. Hart and G. Karabatsos, Ed., Academic Press, New York, N.Y., 1966.
(173) K. B. Wiberg and G. J. Burgmaier, *J. Am. Chem. Soc.*, **94**, 7396 (1972).
(174) K. B. Wiberg, *Rec. Chem. Prog.*, **26**, 143 (1965).
(175) K. B. Wiberg and H. P. Ciula, *J. Am. Chem. Soc.*, **81**, 5261 (1959).
(176) D. M. Lemal, F. Menger, and G. W. Clark, *J. Am. Chem. Soc.*, **85**, 2529 (1963).
(177) K. B. Wiberg and G. M. Lampman, *Tetrahedron Lett.*, 2173 (1963).
(178) K. B. Wiberg, *Tetrahedron*, **24**, 1083 (1968).
(179) M. D. Harmony and K. W. Cox, *J. Am. Chem. Soc.*, **88**, 5049 (1966).
(180) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).
(181) R. D. Bertrand, D. M. Grant, E. L. Allred, J. C.Hinshaw, and A. B. Strong, *J. Am. Chem. Soc.*, **94**, 997 (1972).
(182) K. B. Wiberg, G. M.Lampman, R. P. Ciula, D. S. Connor, P. Schertler, and J. Lavanish, *Tetrahedron*, **21**, 2749 (1965).
(183) M. Pomerantz, *J. Am. Chem. Soc.*, **88**, 5349 (1966).
(184) M. Pomerantz, G. W. Gruber, and R. N. Wilke, *J. Am. Chem. Soc.*, **90**, 5040 (1968).
(185) M. Pomerantz and R. N. Wilke, *Tetrahedron Lett.*, 463 (1969).
(186) M. Pomerantz, R. N. Wilke, G. W. Gruber, and U. Roy, *J. Am. Chem. Soc.*, **94**, 2752 (1972).
(187) R. Criegee and A. Rimmelin, *Chem. Ber.*, **90**, 414 (1957).
(188) R. K. Bohn and Y. H. Tai, *J. Am. Chem. Soc.*, **92**, 6447 (1970).
(189) (a) R. D. Suenram and M. D. Harmony, *J. Chem. Phys.*, **56**, 3837 (1972). (b) We have been informed by a referee that the latter result is more nearly correct.
(190) P. G. Gassman, *Acc. Chem. Res.*, **4**, 128 (1971).
(191) (a) P. G. Gassman, K. T. Mansfield, and T. J. Murphy, *J. Am. Chem. Soc.*, **90**, 4746 (1968); (b) *ibid.*, **91**, 1684 (1969).
(192) P. G. Gassman and G. D. Richman, *J. Am. Chem. Soc.*, **92**, 2090 (1970).
(193) R. L. Cook and T. B. Malloy, Jr., *J. Am. Chem. Soc.*, **96**, 1703 (1974).
(194) K. B. Wiberg, D. S. Connor, and G. M. Lampman, *Tetrahedron Lett.*, 531 (1964).
(195) J. F. Chiang, S. H. Bauer, and H. Simon, *J. Am. Chem. Soc.*, **92**, 1614 (1970).
(196) A. Almenningen, B. Anderden, and B. A. Nyhus, *Acta Chem. Scand.*, **25**, 1217 (1971).
(197) M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.*, **94**, 773 (1972)
(198) (a) J. C. Coll, D. R. Crist, M. d. C. G. Barrio, and N. J. Leonard, *J. Am. Chem. Soc.*, **94**, 7092 (1972); (b) A. H.-J. Wang, R. J. Missavage, S. R. Byrn, and I. C. Paul, *ibid.*, **94**, 7100 (1972).
(199) 1-Chlorobicyclo[3.3.3]undecane solvolyzes more readily than *tert*-butyl chloride because of the *decrease* in strain in forming the coplanar bridgehead carbonium ion: (W. Parker, R. L. Tranter, C. I. F. Watt, L. W. K. Chang, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 7121 (1974)).
(200) C. H. Park and H. E. Simmons, *J. Am. Chem. Soc.*, **94**, 7184 (1972); see also ref 201.
(201) P. G. Gassman and R. P. Thummel, *J. Am. Chem. Soc.*, **94**, 7183 (1972).
(202) H. E. Simmons and G. H. Park, *J. Am. Chem. Soc.*, **90**, 2428, 2429, 2431 (1968).
(203) Tricyclo[3.1.0.$0^{2,6}$]hexane: J. Meinwald, C. Swithenbank, and A. Lewis, *J. Am. Chem. Soc.*, **85**, 1880 (1963).
(204) Tricyclo[2.1.1.$0^{2,5}$]hexane: D. M. Lemal and K. S. Shim, *J. Am. Chem. Soc.*, **86**, 1550 (1964). Related ketone: C.-Y. Ho and F. T. Bond, *ibid.*, **96**, 7355 (1974).
(205) Tricyclo[4.1.0.$0^{3,7}$]heptane: H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963).
(206) S. Winstein, A. H. Lewin, and K. C. Pande, *J. Am. Chem. Soc.*, **85**, 2324 (1963).
(207) Tricyclo[1.1.1.$0^{4,5}$]pentane system: G. L. Closs and R. B. Larrabee, *Tetrahedron Lett.*, 287 (1965).
(208) Y. Hosokawa and I. Moritani, *Chem. Commun.*, 905 (1970).
(209) S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964).
(210) W. Von E. Doering and M. Pomerantz, *J. Am. Chem. Soc.*, **86**, 961 (1964).
(211) H. Ona, H. Yamaguchi, and S. Masamune, *J. Am. Chem. Soc.*, **92**, 7495 (1970).
(212) W. D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94**, 1661 (1972).
(213) A. Padwa and W. Eisenberg, *J. Am. Chem. Soc.*, **92**, 2590 (1970).
(214) Tricyclo[3.3.0.$0^{2,6}$]octane: (a) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 4923 (1961); (b) *ibid.*, **85**, 819 (1963).
(215) W. Funke, *Angew. Chem., Int. Ed. Engl.*, **8**, 70 (1969).
(216) P. S. Portoghese and D. T. Sepp, *Tetrahedron*, **29**, 2253 (1973).
(217) A. A. Dudinskaya, L. I. Khmelnitski, I. D. Petrova, E. B. Baryshnikova, and S. S. Novikov, *Tetrahedron*, **27**, 4053 (1971).
(218) D. H. Aue, H. Iwahashi, and D. F. Shellhamer, *Tetrahedron Lett.*, 3719 (1973).
(219) Tricyclo[3.1.0.$0^{2,4}$]hexane: E. L. Allred and J. C. Hinshaw, *J. Am. Chem. Soc.*, **90**, 6885 (1968).
(220) Tricyclo[4.1.0.$0^{2,5}$]heptane: H. Tanida, S. Terataka, Y. Hata, and M. Watanabe, *Tetrahedron Lett.*, 5345 (1969).
(221) Tricyclo[4.2.0.$0^{2,5}$]octane: M. Avram, I. G. Dinulescu, E. Marica, G.

Mateescu, E. Sliam, and C. D. Nenitzescu, *Chem. Ber.*, **97**, 382 (1964).
(222) J. M. Harless and S. A. Monti, *J. Am. Chem. Soc.*, **96**, 4714 (1974).
(223) S. Cremer and R. Srinivasan, *Tetrahedron Lett.*, 24 (1960).
(224) R. Srinivasan, *J. Am. Chem. Soc.*, **83**, 2590 (1961).
(225) K. B. Wiberg, B. R. Lowery, and T. H. Colby, *J. Am. Chem. Soc.*, **83**, 3998 (1961).
(226) M. Doyle, W. Parker, P. A. Gunn, J. Martin, and D. D. MacNicol, *Tetrahedron Lett.*, 3619 (1970).
(227) N. J. Leonard and J. C. Coll, *J. Am. Chem. Soc.*, **92**, 6685 (1970).
(228) R. C. Fort, Jr., and P. v. R. Schleyer in ref 172b.
(229) R. C. Fort, Jr., in "Carbonium Ions," Vol. 4, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1973.
(230) P. v. R. Schleyer in ref 142a.
(231) R. B. Bingham and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 3189 (1971); see also: J. L. Fry, E. M. Engler, and P. v. R. Schleyer, *ibid.*, **94**, 4628 (1972).
(232) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **93**, 6873 (1971).
(233) G. A. Olah, D. P. Kelly, and R. G. Johanson, *J. Am. Chem. Soc.*, **92**, 4137 (1970).
(234) P. v. R. Schleyer, R. C. Fort, Jr., W. E. Watts, M. B. Comisarow, and G. A. Olah, *J. Am. Chem. Soc.*, **86**, 4195 (1964).
(235) G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **95**, 194 (1973).
(236) G. A. Olah, G. Liang, J. R. Wiseman, and J. A. Chong, *J. Am. Chem. Soc.*, **94**, 4927 (1972).
(237) (a) P. G. Gassman, *Chem. Commun.*, 793 (1967); (b) P. G. Gassman and F. J. Williams, *J. Am. Chem. Soc.*, **93**, 2704 (1971).
(238) J. V. Paukstelis and J. Kao, *J. Am. Chem. Soc.*, **94**, 4783 (1972).
(239) P. G. Gassman, F. J. Williams, and J. Seter, *J. Am. Chem. Soc.*, **90**, 6893 (1968).
(240) W. Kirmse and C. Hause, *Angew. Chem., Int. Ed. Engl.*, **7**, 891 (1968).
(241) (a) K. B. Wiberg and A. de Meijere, *Tetrahedron Lett.*, 519 (1969); (b) K. B. Wiberg, *Angew. Chem., Int. Ed. Engl.*, **11**, 332 (1972).
(242) A. J. Ashe, III, *Tetrahedron Lett.*, 523 (1969).
(243) P. G. Gassman, J. Seter, and F. J. Williams, *J. Am. Chem. Soc.*, **93**, 1673 (1971).
(244) W. H. Pirkle and W. B. Lunsford, *J. Am. Chem. Soc.*, **94**, 7201 (1972).
(245) A. C. Cope and J. K. Hecht, *J. Am. Chem. Soc.*, **85**, 1780 (1963).
(246) E. J. Corey and J. I. Schulman, *Tetrahedron Lett.*, 3655 (1968).
(247) C. H. DePuy and J. L. Marshall, *J. Org. Chem.*, **33**, 3326 (1968).
(248) G. Moshuk, G. Petrowski, and S. Winstein, *J. Am. Chem. Soc.*, **90**, 2179 (1968).
(249) See footnote 6 in ref 237b of this paper.
(250) See D. E. Applequist, G. F. Fanta, and B. W. Henrikson, *J. Org. Chem.*, **23**, 1715 (1958), and references cited therein.
(251) G. Dallinga, P. K. Van der Draai, and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **87**, 897 (1968).
(252) M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 5550 (1961).
(253) J. C. Gilbert, *Tetrahedron*, **25**, 1459 (1969).
(254) J. J. Gajewski and L. T. Burka, *J. Am. Chem. Soc.*, **94**, 8857, 8860, 8865 (1972).
(255) D. E. McGreer, *Can. J. Chem.*, **38**, 1638 (1960).
(256) B. Winstein, A. H. Fenselav, and J. G. Thorpe, *J. Chem. Soc.*, 2281 (1965).
(257) J. M. Denis, C. Girard, and J. M. Conia, *Synthesis*, 549 (1972).
(258) P. Binger, *Angew. Chem., Int. Ed. Engl.*, **11**, 433 (1972).
(259) W. R. Roth and M. Martin, *Tetrahedron Lett.*, 4695 (1967).
(260) L. Fitjer and J. M. Conia, *Angew. Chem., Int. Ed. Engl.*, **12**, 761 (1973).
(261) E. Buchta and W. Merk, *Justus Liebigs Ann. Chem.*, **716**, 106 (1968).
(262) J. R. Salaün and J. M. Conia, *Chem. Commun.*, 1579 (1971).
(263) J. K. Crandall and D. R. Paulson, *J. Org. Chem.*, **33**, 991 (1968).
(264) J. K. Crandall and D. R. Paulson, *Tetrahedron Lett.*, 2751 (1969).
(265) B. M. Trost and M. J. Bogdanowicz, *J. Am. Chem. Soc.*, **95**, 5311 (1973).
(266) J. K. Crandall and H. W. Connor, *J. Chem. Soc., Chem. Commun.*, 33 (1973).
(267) (a) J. K. Crandall, W. H. Machleder, and S. A. Sojka, *J. Org. Chem.*, **38**, 1149 (1973); (b) J. K. Crandall, W. H. Machleder, and M. J. Thomas, *J. Am. Chem. Soc.*, **90**, 7346 (1968).
(268) (a) R. L. Lambert and D. Seyferth, *J. Am. Chem. Soc.*, **94**, 9246 (1972); (b) D. Seyferth and D. C. Annarelli, *ibid.*, **97**, 2273 (1975).
(269) J. M. Denis and J. M. Conia, *Tetrahedron Lett.*, 461 (1973).
(270) L. Fitjer and J. M. Conia, *Angew. Chem., Int. Ed. Engl.*, **12**, 334 (1973).
(271) J. M. Conia and J. M. Denis, *Tetrahedron Lett.*, 3545 (1969).
(272) P. Le Perchec and J. M. Conia, *Tetrahedron Lett.*, 587 (1970).
(273) J. L. Ripoll and J. M. Conia, *Tetrahedron Lett.*, 979 (1969).
(274) J. L. Ripoll, J. C. Limassett, and J. M. Conia, *Tetrahedron*, **27**, 2431 (1971).
(275) L. Skattebol, *J. Org. Chem.*, **31**, 2789 (1966).
(276) M. S. Baird, *J. Chem. Soc., Chem. Commun.*, 197 (1974).
(277) (a) N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, **89**, 3966 (1967); (b) *J. Chem. Phys.*, **50**, 1262 (1969); (c) N. C. Baird, *Tetrahedron*, **26**, 2185 (1970).
(278) J. M. Schulman and T. J. Venanzi, *J. Am. Chem. Soc.*, **96**, 4739 (1974).
(279) L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972).
(280) M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, N.Y., 1967.
(281) G. Maier, *Angew. Chem., Int. Ed. Engl.*, **13**, 425 (1974).
(282) R. J. Buenker and S. D. Peyerimhoff, *J. Am. Chem. Soc.*, **91**, 4342 (1969).
(283) R. F. Peterson, Jr., R. T. K. Baker, and R. L. Wolfgang, *Tetrahedron Lett.*, 4749 (1969).
(284) H. Ona, H. Yamaguchi, and S. Masamune, *J. Am. Chem. Soc.*, **92**, 7495 (1970).
(285) P. B. Shevlin and A. P. Wolf, *J. Am. Chem. Soc.*, **92**, 406, 5291 (1970).
(286) L. B. Rodewald and H.-K. Lee, *J. Am. Chem. Soc.*, **95**, 623, 3084 (1973).
(287) I. H. Hillier and V. R. Saunders, *J. Chem. Soc., Chem. Commun.*, 1233 (1970).
(288) J. S. Wright, *J. Am. Chem. Soc.*, **96**, 4753 (1974).
(289) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3d ed, Interscience, New York, N.Y., 1972.
(290) G. C. Pimentel and R. D. Spratley, "Understanding Chemistry", Holden-Day, San Francisco, Calif., 1971.
(291) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 112.
(292) J. Simpson, *MTP Int. Rev. Sci., Inorg. Chem., Ser. One*, **1**, 221 (1973).
(293) E. L. Muetterties, "The Chemistry of Boron and Its Compounds", Wiley New York, N.Y., 1967, pp 364–366.
(294) (a) S. Masamune and M. Kato, *J. Am. Chem. Soc.*, **87**, 4190 (1965); (b) *ibid.*, **88**, 610 (1966).
(295) E. H. White, G. E. Maier, R. Graeve, U. Zirngibl, and E. W. Friend, *J. Am. Chem. Soc.*, **88**, 611 (1966).
(296) H. A. Staab, E. Wehninger, and W. Thorwart, *Chem. Ber.*, **105**, 2290 (1972).
(297) C. Y. Lin and A. Krantz, *J. Chem. Soc., Chem. Commun.*, 1111 (1972).
(298) S. Masamune, M. Suda, H. Ona, and L. M. Leichter, *J. Chem. Soc., Chem. Commun.*, 1268 (1972).
(299) O. L. Chapman, C. L. McIntosh, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 614 (1973).
(300) O. L. Chapman, D. De La Cruz, R. Roth, and J. Pacansky, *J. Am. Chem. Soc.*, **95**, 1337 (1973).
(301) G. Maier and B. Hoppe, *Tetrahedron Lett.*, 861 (1973).
(302) A. Krantz, C. Y. Lin, and M. D. Newton, *J. Am. Chem. Soc.*, **95**, 2744 (1973).
(303) G. Maier an A. Alźrreca, *Angew. Chem., Int. Ed. Engl.*, **12**, 1015 (1973).
(304) R. Gompper and G. Seybold, *Angew. Chem., Int. Ed. Engl.*, **7**, 824 (1968).
(305) H. Kimling and A. Krebs, *Angew. Chem., Int. Ed. Engl.*, **11**, 932 (1972).
(306) S. Masamune, N. Nakamura, M. Suda, and H. Ona, *J. Am. Chem. Soc.*, **95**, 8481 (1973). X-Ray crystallography on a relatively unperturbed cyclobutadiene suggests that the ground state of [4]annulene is a rectangular singlet: L. T. J. Delbaere, M. N. G. James, N. Nakamura, and S. Masamune, *ibid.*, **97**, 1973 (1975).
(307) G. L. Closs in ref 172b, p 53.
(308) (a) Most recent microwave data on cyclopropene: W. M. Stigliani, V. W. Laurie, and J. C. Li, *J. Chem. Phys.*, **62**, 1890 (1975). (b) Microwave data on 1-methylcyclopropene: M. K. Kemp and W. H. Flygare, *J. Am. Chem. Soc.*, **91**, 3163 (1969).
(309) E. Schmitz, "XXIIIrd International Congress of Pure and Applied Chemistry", Vol. 2, Butterworths, London, 1971, p 283.
(310) (a) A. H. Laufer and H. Okabe, *J. Am. Chem. Soc.*, **93**, 4137 (1971); (b) *J. Phys. Chem.*, **76**, 3504 (1972).
(311) For example, see G. Smolinsky, *J. Am. Chem. Soc.*, **83**, 4483 (1961).
(312) N. L. Allinger and J. T. Sprague, *J. Am. Chem. Soc.*, **94**, 5734 (1972).
(313) J. Meinwald and F. Uno, *J. Am. Chem. Soc.*, **90**, 800 (1968).
(314) F. T. Bond and L. Scerbo, *Tetrahedron Lett.*, 2789 (1968).
(315) K. B. Wiberg and R. W. Ubersox, *Tetrahedron Lett.*, 3063 (1968).
(316) H. E. Zimmerman and R. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960).
(317) R. F. Bleiholder and H. Schechter, *J. Am. Chem. Soc.*, **86**, 5032 (1964).
(318) E. A. Dorko, *J. Am. Chem. Soc.*, **87**, 5519 (1965).
(319) P. A. Waitkus, L. I. Peterson, and G. W. Griffith, *J. Am. Chem. Soc.*, **88**, 181 (1966).
(320) Note that the parent compound, methylenecyclopropene, has not yet been characterized. The first substituted derivative to be prepared was i: A. S. Kende, *J. Am. Chem. Soc.*, **85**, 1882 (1963). Numerous other derivatives, all of which possess considerable cyclopropenium character, have since been isolated.



i

(321) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 846 (1966).
(322) (a) For discussions of the intramolecular interactions of "ethylene" or "1,3-butadiene" with "cyclobutane" or "bicyclobutane", see W. L. Jorgenson and W. T. Borden, *J. Am. Chem. Soc.*, **95**, 6649 (1973); (b) W. L. Jorgensen and W. T. Borden, *Tetrahedron Lett.*, 223 (1975); (c) P. Th. van Duijnen, P. van der Ploeg, H. Hogeveen, and W. F. J. Huurdeman, *ibid.*, 573 (1975); (d) W. L. Jorgensen, *J. Am. Chem. Soc.*, **97**, 3082 (1975).
(323) S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, W. H. Flygare, and J. E. Baldwin, *J. Am. Chem. Soc.*, **92**, 5250 (1970).
(324) E. Vogel, *Chem. Ber.*, **85**, 25 (1952).
(325) J. Sauer, B. Schroeder, and R. Wiemer, *Chem. Ber.*, **100**, 306 (1967).
(326) J.-L. Ripoll, *Tetrahedron Lett.*, 1665 (1974).
(327) W. Kirmse and K. H. Pook, *Angew. Chem., Int. Ed. Engl.*, **5**, 594 (1966).
(328) D. H. Aue and R. N. Reynolds, *J. Am. Chem. Soc.*, **95**, 2027 (1973).
(329) (a) K. B. Wiberg, G. J. Burgmaier, and P. Warner, *J. Am. Chem. Soc.*, **93**, 246 (1971); (b) M. E. Jason, J. A. McGinnety, and K. B. Wiberg, *ibid.*, **96**, 6531 (1974); (c) C. J. Casanova and H. R. Rogers, *J. Org. Chem.*, **39**, 3803 (1974); (d) K. B. Wiberg, W. F. Bailey, and M. E. Jason, *ibid.*, **39**, 3803 (1974).
(330) G. L. Closs and W. A. Böll, *J. Am. Chem. Soc.*, **85**, 3904 (1963).
(331) G. L. Closs, W. A. Böll, H. Heyn, and V. Dev, *J. Am. Chem. Soc.*, **90**, 173 (1968).
(332) R. Breslow, J. Posner, and A. Krebs, *J. Am. Chem. Soc.*, **85**, 234 (1963).
(333) R. Breslow, L. J. Altman, A. Krebs, E. Mohacsi, I. Murata, R. A. Peterson, and J. Posner, *J. Am. Chem. Soc.*, **87**, 1326 (1965).
(334) M. Suda and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 504 (1974).

(335) A. S. Kende and E. R. Riecke, *J. Chem. Soc., Chem. Commun.*, 383 (1974).
(336) J. A. Berson, R. J. Bushby, J. M. McBride, and M. Tremelling, *J. Am. Chem. Soc.*, **93**, 1544 (1971).
(337) W. E. Billups, L. P. Lin, and W. Y. Chow, *J. Am. Chem. Soc.*, **96**, 4026 (1974).
(338) See footnote 1 in ref 337. Also see R. L. Tyner, W. M. Jones, Y. Öhrn, and J. R. Sabin, *J. Am. Chem. Soc.*, **96**, 3765 (1974), and references cited therein.
(339) H. Hopf, *Chem. Ber.*, **104**, 1499 (1971).
(340) R. G. Bergman, *Acc. Chem. Res.*, **6**, 27 (1973).
(341) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1003 (65).
(342) R. S. Berry, J. Clardy, and M. E. Schafer, *Tetrahedron Lett.*, 1011 (1965).
(343) H. E. Bertorello, R. A. Rossi, and R. H. de Rossi, *J. Org. Chem.*, **35**, 3332 (1970).
(344) D. L. Wilhite and J. L. Whitten, *J. Am. Chem. Soc.*, **93**, 2858 (1971).
(345) (a) M. J. S. Dewar and W.-K. Li, *J. Am. Chem. Soc.*, **96**, 5569 (1974); (b) W. N. Washburn, *ibid.*, **97**, 1615 (1975).
(346) (a) An excellent treatise on all aspects of aromaticity: P. J. Garratt, "Aromaticity", McGraw-Hill, London, 1971. (b) A review of recent studies of small-ring aromatics and antiaromatics: D. Lloyd, *MTP Int. Rev. Sci., org. Chem., Ser. One*, **3**, 779 (1973); (c) See also article entitled "Symmetry, Topology, and Aromaticity", M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 6193 (1971).
(347) R. Breslow, *Pure Appl. Chem.*, **28**, 111 (1971).
(348) (a) R. Breslow, J. T. Groves, and G. Ryan, *J. Am. Chem. Soc.*, **89**, 5048 (1967); (b) R. Breslow and J. T. Groves, *ibid.*, **92**, 984 (1970).
(349) R. Breslow and M. Douek, *J. Am. Chem. Soc.*, **90**, 2698 (1968).
(350) R. Breslow, *Angew. Chem., Int. Ed. Engl.*, **8**, 565 (1969).
(351) G. A. Olah, J. M. Bollinger, and A. M. White, *J. Am. Chem. Soc.*, **91**, 3667 (1969).
(352) G. A. Olah and G. D. Mateescu, *J. Am. Chem. Soc.*, **92**, 1430 (1970).
(353) J. S. McKennis, L. Brener, J. R. Schweiger, and R. Pettit, *J. Chem. Soc., Chem. Commun.*, 365 (1972).
(354) R. N. McDonald and P. A. Schwab, *J. Am. Chem. Soc.*, **86**, 4866 (1964).
(355) J. K. Stille and D. D. Whitehurst, *J. Am. Chem. Soc.*, **86**, 4871 (1964).
(356) F. G. Csizmadia, J. Font, and O. P. Strausz, *J. Am. Chem. Soc.*, **90**, 7360 (1968).
(357) D. E. Thornton, R. K. Gosavi, and O. P. Strausz, *J. Am. Chem. Soc.*, **92**, 1768 (1970).
(358) G. Frater and O. P. Strausz, *J. Am. Chem. Soc.*, **92**, 6654 (1970).
(359) J. Fenwick, G. Frater, K. Ogi, and O. P. Strausz, *J. Am. Chem. Soc.*, **95**, 124 (1973).
(360) I. G. Csizmadia, H. E. Gunning, R. K. Gosavi, and O. P. Strausz, *J. Am. Chem. Soc.*, **95**, 133 (1973).
(361) D. J. Anderson, T. L. Gilchrist, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 147 (1969).
(362) T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1519 (1971).
(363) O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Am. Chem. Soc.*, **89**, 4805 (1967); see also ref 364.
(364) H. Kato, M. Kawamura, T. Shiba, and M. Ohta, *J. Chem. Soc., Chem. Commun.*, 959 (1970).
(365) L. A. Carpino and H.-W. Chen, *J. Am. Chem. Soc.*, **93**, 785 (1971).
(366) R. Breslow and G. Ryan, *J. Am. Chem. Soc.*, **89**, 3073 (1967).
(367) R. Breslow, G. Ryan, and J. T. Groves, *J. Am. Chem. Soc.*, **92**, 988 (1970).
(368) R. Breslow and M. Oda, *J. Am. Chem. Soc.*, **94**, 4787 (1972).
(369) J. Ciabattoni and E. C. Nathan, III, *J. Am. Chem. Soc.*, **91**, 4766 (1969).
(370) B. A. Hess, Jr., L. J. Schaad, and C. W. Holyoke, Jr., *Tetrahedron*, **28**, 5299 (1972).
(371) R. C. Benson, W. H. Flygare, M. Oda, and R. Breslow, *J. Am. Chem. Soc.*, **95**, 2772 (1973).
(372) We thank Professor Ronald H. Levin for discussion of unpublished carbon-13 NMR data on cyclopropenones.
(372a) D. Eggerding and R. West, *J. Am. Chem. Soc.*, **97**, 207 (1975).
(373) G. Köbrich and H. Heinemann, *Angew. Chem., Int. Ed. Engl.*, **4**, 594 (1965).
(374) E. A. Dorko, *J. Am. Chem. Soc.*, **87**, 5519 (1965).
(375) P. A. Waitkus and L. I. Peterson, *J. Am. Chem. Soc.*, **85**, 2268 (1963).
(376) (a) G. W. Griffin and L. I. Peterson, *J. Am. Chem. Soc.*, **85**, 2268 (1963). (b) The crystal structure of perchloro[4]radialene shows this compound to be highly puckered in order to relieve nonbonded interactions between chlorine atoms. The results, of course, cannot be extrapolated to the parent system; see F. P. van Remoortere and F. P. Boer, *ibid.*, **92**, 3355 (1970).
(377) Corannulene (**319a**) may be considered to be a [5]radialene.
(378) H. Hopff and A. K. Wick, *Helv. Chim. Acta*, **44**, 380 (1961).
(379) M. J. S. Dewar, *Chem. Soc., Spec. Publ.*, **No. 21**, 177 (1967).
(380) V. H. Dietrich, *Acta Crystallogr., Sect. B*, **26**, 44 (1970).
(381) R. C. Cass, H. D. Springall, and P. G. Quincey, *J. Chem. Soc.*, 1188 (1955).
(382) H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89**, 5208 (1967).
(383) R. Hoffmann, A. Imamura, and G. D. Zeiss, *J. Am. Chem. Soc.*, **89**, 5219 (1967).
(384) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1970, p 461.
(385) M. F. Semmelhack and R. J. DeFranco, *J. Am. Chem. Soc.*, **94**, 8838 (1972).
(386) L. A. Hulshof and H. Wynberg, *J. Am. Chem. Soc.*, **96**, 2191 (1974).
(387) (a) M. F. Semmelhack, J. S. Foos, and S. Katz, *J. Am. Chem. Soc.*, **94**, 8638 (1972); (b) *ibid.*, **95**, 7325 (1973).
(388) H. Dürr, B. Ruge, and H. Schmitz, *Angew. Chem., Int. Ed. Engl.*, **12**, 577 (1973).
(389) M. F. Semmelhack, R. J. DeFranco, Z. Margon, and J. Stock, *J. Am. Chem. Soc.*, **95**, 426 (1973).
(390) C. F. Wilcox, Jr. and R. R. Craig, *J. Am. Chem. Soc.*, **83**, 4258 (1961).
(391) R. A. Clark and R. A. Fiato, *J. Am. Chem. Soc.*, **92**, 4736 (1970).
(392) R. Gleiter, E. Heilbronner, and A. de Meijere, *Helv. Chim. Acta*, **54**, 1029 (1971).
(393) J. F. Chiang and C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **95**, 2885 (1973).
(394) R. D. Miller, M. Schneider, and D. L. Dolce, *J. Am. Chem. Soc.*, **95**, 8468 (1973).
(395) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1971.
(396) J. P. Chesick, *J. Am. Chem. Soc.*, **85**, 2720 (1963).
(397) J. J. Gajewski, *J. Am. Chem. Soc.*, **90**, 7178 (1968).
(398) J. C. Gilbert and J. R. Butler, *J. Am. Chem. Soc.*, **92**, 2168 (1970).
(399) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).
(400) M. J. S. Dewar, *J. Am. Chem. Soc.*, **93**, 3081 (1971).
(401) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).
(402) P. Dowd and K. Sachdev, *J. Am. Chem. Soc.*, **89**, 715 (1967).
(403) F. Weiss, *Q. Rev., Chem. Soc.*, **24**, 278 (1970).
(404) P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972).
(405) D. R. Yarkony and H. F. Schaefer, III, *J. Am. Chem. Soc.*, **96**, 3754 (1974); see also W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2906 (1975).
(406) J. J. Gajewski and C. N. Shih, *J. Am. Chem. Soc.*, **89**, 4532 (1967).
(407) W. von E. Doering and W. R. Dolbier, Jr., *J. Am. Chem. Soc.*, **89**, 4534 (1967).
(408) W. R. Dolbier, Jr., K. Akiba, J. M. Riemann, C. A. Harmon, M. Bertrand, A. Bezaquet, and M. Santelli, *J. Am. Chem. Soc.*, **93**, 3933 (1971).
(409) (a) C.-S. Chang and N. C. Bauld, *J. Am. Chem. Soc.*, **94**, 7593 (1972); (b) N. C. Bauld and C.-S. Chang, *ibid.*, **94**, 7595 (1972).
(410) N. J. Turro, *Acc. Chem. Res.*, **2**, 25 (1969).
(411) N. J. Turro, R. B. Gagosian, S. S. Edelson, T. R. Darling, and W. B. Hammond, *Trans. N.Y. Acad. Sci.*, **33**, 396 (1971).
(412) H. H. Wasserman, G. C. Clark, and P. C. Turley, *Top. Curr. Chem.*, **47**, 73 (1974).
(413) M. E. Zandler, C. E. Choc, and C. K. Johnson, *J. Am. Chem. Soc.*, **96**, 3317 (1974).
(414) R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).
(415) J. M. Pochan, J. E. Baldwin, and W. H. Flygare, *J. Am. Chem. Soc.*, **91**, 1896 (1969).
(416) R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1302 (1975).
(417) A. Liberles, A. Greenberg, and A. Lesk, *J. Am. Chem. Soc.*, **94**, 8685 (1972).
(418) J. F. Liebman and A. Greenberg, *J. Org. Chem.*, **39**, 123 (1974).
(419) R. L. Camp and F. D. Greene, *J. Am. Chem. Soc.*, **90**, 7349 (1968).
(420) J. K. Crandall and W. H. Machleder, *J. Heterocycl. Chem.*, **6**, 777 (1969).
(421) R. Wheland and P. D. Bartlett, *J. Am. Chem. Soc.*, **92**, 6057 (1970).
(422) W. Adam and R. Rucktäschel, *J. Am. Chem. Soc.*, **93**, 557 (1971).
(423) O. L. Chapman, P. W. Wojkowski, W. Adam, O. Rodriquez, and R. Rucktäschel, *J. Am. Chem. Soc.*, **94**, 1365 (1972).
(424) W. Adam, J.-C. Liu, and O. Rodriquez, *J. Org. Chem.*, **38**, 2269 (1973).
(424a) H. Hiraoka, *J. Chem. Soc., Chem. Commun.*, 1014 (1974).
(425) M. C. Flowers and J. M. Frey, *J. Am. Chem. Soc.*, **94**, 8636 (1972).
(426) J. I. Brauman, W. E. Farneth, and M. B. D'Amore, *J. Am. Chem. Soc.*, **95**, 5043 (1973).
(427) G. D. Andrews, M. Davalt, and J. E. Baldwin, *J. Am. Chem. Soc.*, **95**, 5044 (1973).
(428) N. J. Turro, P. Lechtken, N. E. Schore, G. Schuster, H.-C. Steinmetzer, and A. Yekta, *Acc. Chem. Res.*, **7**, 97 (1974).
(429) E. H. White, J. D. Miano, C. J. Watkins, and E. J. Breaux, *Angew. Chem., Int. Ed. Engl.*, **13**, 229 (1974).
(430) (a) W. Adam and J.-C. Liu, *J. Am. Chem. Soc.*, **94**, 2894 (1972); (b) *Angew. Chem., Int. Ed. Engl.*, **11**, 540 (1972).
(431) W. H. Richardson and H. E. O'Neall, *J. Am. Chem. Soc.*, **94**, 8665 (1972).
(432) E. E. van Tamelen, *Angew. Chem., Int. Ed. Engl.*, **4**, 738 (1965).
(433) H. G. Viehe, *Angew. Chem., Int. Ed. Engl.*, **4**, 746 (1965).
(434) E. E. van Tamelen, *Acc. Chem. Res.*, **5**, 186 (1972).
(435) W. Baker, *Chem. Br.*, **1**, 191 (1965).
(436) J. F. M. Oth, *Angew. Chem., Int. Ed. Engl.*, **7**, 646 (1968); see also W. Adam and J. C. Chiang, *Int. J. Chem. Kinet.*, **1**, 487 (1969).
(437) D. M. Lemal and L. H. Dunlap, Jr., *J. Am. Chem. Soc.*, **94**, 6562 (1972).
(438) N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, **91**, 352 (1969).
(439) G. Berthier, A. Y. Meyer, and L. Praud in *Jerusalem Symp. Quantum Chem. Biochem.*, **3**, 174 (1971).
(440) M. D. Newton, J. M. Schulman, and M. M. Manus, *J. Am. Chem. Soc.*, **96**, 17 (1974).
(441) The simplest reported derivative of 3,3'-bicyclopropenyl is the dimethyl compound: W. H. De Wolf, W. Stol, I. J. Landheer, and F. Bickelhaupt, *Recl. Trav. Chim. Pays-Bas*, **90**, 405 (1971); see also ref 597 for a description of another simple derivative.
(442) R. Weiss and S. Andrae, *Angew. Chem., Int. Ed. Engl.*, **12**, 150, 152 (1973).
(443) B. D. Kybett, S. Carroll, P. Natalis, B. W. Bonnell, J. L. Margrave, and J. L. Franklin, *J. Am. Chem. Soc.*, **88**, 626 (1966).
(444) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **84**, 3789 (1962).
(445) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963).
(446) E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *J. Am. Chem. Soc.*, **93**, 6092 (1971).
(447) H. G. Viehe, R. Merényi, J. F. M. Oth, J. R. Senders, and P. Valange, *Angew. Chem., Int. Ed. Engl.*, **3**, 755 (1964).
(448) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1031 (1967).
(449) D. M. Lemal and J. R. Lokensgard, *J. Am. Chem. Soc.*, **88**, 5934 (1966).
(450) W. Schaefer, R. Criegee, R. Askani, and H. Gruener, *Angew. Chem., Int. Ed. Engl.*, **6**, 78 (1967).
(451) T. J. Katz and N. Acton, *J. Am. Chem. Soc.*, **95**, 2738 (1973).
(452) R. Breslow and P. Gal, *J. Am. Chem. Soc.*, **81**, 4747 (1959).
(453) W. Schaefer, *Angew. Chem., Int. Ed. Engl.*, **5**, 669 (1966).
(454) M. J. Cardillo and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 2399 (1970).

(455) E. M. Arnett and J. M. Bollinger, *Tetrahedron Lett.*, 3803 (1964).
(456) K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *J. Am. Chem. Soc.*, **93**, 1270 (1971).
(457) W. L. Mandella and R. W. Franck, *J. Am. Chem. Soc.*, **95**, 971 (1973).
(458) D. E. Applequist and R. Searle, *J. Am. Chem. Soc.*, **86**, 1389 (1964).
(459) (a) K. Weinges and K. Klessing, *Chem. Ber.*, **107**, 1915 (1974); (b) I. J. Landheer, W. H. de Wolf, and F. Bickelhaupt, *Tetrahedron Lett.*, 2813 (1974); (c) *ibid.*, 349 (1975).
(460) J. A. Barltrop and A. C. Day, *J. Chem. Soc., Chem. Commun.*, 177 (1975). (a) K. E. Wilzbach and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 4004 (1965).
(461) L. Kaplan, J. S. Ritscher, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **88**, 2881 (1966).
(462) J. A. Berson and N. M. Hasty, Jr., *J. Am. Chem. Soc.*, **93**, 1549 (1971).
(463) T. J. Katz, E. J. Wang, and N. Acton, *J. Am. Chem. Soc.*, **93**, 3782 (1971).
(464) L. Kaplan, L. A. Wendling, and K. E. Wilzbach, *J. Am. Chem. Soc.*, **93**, 3821 (1971).
(465) H. R. Ward and J. R. Wishnok, *J. Am. Chem. Soc.*, **90**, 1085 (1968).
(466) L. Kaplan and K. E. Wilzbach, *J. Am. Chem. Soc.*, **90**, 3291 (1968).
(467) D. M. Lemal, J. V. Staros, and V. Austel, *J. Am. Chem. Soc.*, **91**, 3373 (1969).
(468) M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc., Chem. Commun.*, 202 (1969).
(469) (a) E. D. Clifton, W. T. Flowers, and R. N. Haszeldine, *J. Chem. Soc., Chem. Commun.*, 1216 (1969); (b) A.-M. Debbagh, W. T. Flowers, R. N. Haszeldine, and P. J. Robinson, *ibid.*, 323 (1975).
(470) G. D. Burt and R. Pettit, *Chem. Commun.*, 517 (1965).
(471) R. N. McDonald, D. G. Frickley, and G. M. Moschik, *J. Org. Chem.*, **37**, 1304 (1972).
(472) As an intermediate: U. Mende, J. L. Lancaster, and G. W. Griffin, *Tetrahedron Lett.*, 3747 (1970).
(473) T. J. Katz and K. C. Nicolaou, *J. Am. Chem. Soc.*, **96**, 1948 (1974).
(474) C. G. Allison, R. D. Chambers, Y. A. Cheburkov, J. A. H. McBride and W. K. R. Musgrave, *J. Chem. Soc., Chem. Commun.*, 1200 (1969).
(475) R. D. Chambers, W. K. R. Musgrave, and K. C. Srivastana, *J. Chem. Soc., Chem. Commun.*, 264 (1970).
(476) R. N. Haszeldine, M. G. Barlow, and J. G. Dingall, *J. Chem. Soc., Chem. Commun.*, 1580 (1970).
(477) K. E. Wilzbach and D. J. Rauch, *J. Am. Chem. Soc.*, **92**, 2178 (1970).
(478) J. A. Barltrop, K. Dawes, A. C. Day, and A.-J. H. Summers, *J. Chem. Soc., Chem. Commun.*, 1240 (1972).
(479) J. W. Pavlik and E. L. Clennan, *J. Am. Chem. Soc.*, **95**, 1697 (1973).
(480) (a) P. Lechtken, R. Breslow, A. H. Schmidt, and N. J. Turro, *J. Am. Chem. Soc.*, **95**, 3025 (1973); (b) C. A. Renner, T. J. Katz, J. Pouliquen, N. J. Turro, and W. H. Waddell, *ibid.*, **97**, 2568 (1975).
(481) N. C. Yang, R. V. Carr, E. Li, J. K. McVey, and S. A. Rice, *J. Am. Chem. Soc.*, **96**, 2297 (1974).
(482) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **12**, 464 (1973).
(483) Corrections for nonperfect overlap of simple p orbitals may be found in J. D. Roberts, "Notes on Molecular Orbital Calculations", W. A. Benjamin, New York, N.Y., 1961.
(484) N. M. Weinshenker and F. D. Greene, *J. Am. Chem. Soc.*, **90**, 506 (1968).
(485) R. L. Viavattene, F. D. Greene, L. D. Cheung, R. Majeste, and L. M. Trefonas, *J. Am. Chem. Soc.*, **96**, 4342 (1974).
(486) A. Almenningen, I. M. Anfinsen, and A. Haaland, *Acta Chem. Scand.*, **24**, 43 (1970).
(487) (a) O. Ermer and S. Lifson, *J. Am. Chem. Soc.*, **95**, 4121 (1973); (b) *Tetrahedron*, **30**, 2425 (1974).
(488) Cf. ref 312, explanation on p 5737.
(489) G. J. Abruscato and T. T. Tidwell, *J. Am. Chem. Soc.*, **92**, 4125 (1970).
(490) G. J. Abruscato, R. G. Binder, and T. T. Tidwell, *J. Org. Chem.*, **37**, 1787 (1972).
(491) G. J. Abruscato and T. T. Tidwell, *J. Org. Chem.*, **37**, 4151 (1972).
(491) (a) An unsuccessful attempt at tetra-*tert*-butylethylene through an extrusion reaction has been reported recently: D. H. R. Barton, F. S. Guziec, Jr., and I. Shahak, *J. Chem. Soc., Perkin Trans. 1*, 1794 (1974); (b) T. G. Back, D. H. R. Barton, M. R. Britten-Kelly, and F. S. Guziec, Jr., *J. Chem. Soc., Chem. Commun.*, 539 (1975).
(492) G. D. Mendenhall and K. U. Ingold, *J. Am. Chem. Soc.*, **95**, 3422 (1973).
(493) P. D. Bartlett and T. T. Tidwell, *J. Am. Chem. Soc.*, **90**, 4421 (1968).
(494) (a) J. H. Wieringa, J. Strating, H. Wynberg, and W. Adam, *Tetrahedron Lett.*, 169 (1972); (b) S. C. Swen-Walstra and G. J. Visser, *Chem. Commun.*, 82 (1971).
(495) (a) A. Nierth, H. M. Ensslin, and M. Hanack, *Justus Liebigs Ann. Chem.*, **733**, 187 (1970); (b) T. Teraji, I. Moritani, E. Tsuda, and S. Nishida, *J. Chem. Soc. C*, 3252 (1971); (c) R. F. Langler and T. T. Tidwell, *Tetrahedron Lett.*, 777 (1975); (d) D. S. Bomse and T. H. Morton, *ibid.*, 781 (1975).
(496) D. Mootz, *Acta Crystallogr., Sect. B*, **24**, 839 (1968).
(497) S. C. Nyburg, *Acta Crystallogr., Sect. B*, **7**, 779 (1954).
(498) (a) N. A. Bailey and S. E. Hull, *J. Chem. Soc., Chem. Commun.*, 960 (1971); (b) H. L. Ammon and G. L. Wheeler, *J. Am. Chem. Soc.*, **97**, 2326 (1975), cited in Table III as N. A. Bailey, personal communication.
(499) I. R. Gault, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., Chem. Commun.*, 269 (1970).
(500) I. Agranat, M. Rabinovitz, and A. Weitzen-Dagan, *J. Chem. Soc., Chem. Commun.*, 732 (1972).
(501) M. Rabinowitz, I. Agranat, and A. Weitzen-Dagan, *Tetrahedron Lett.*, 1241 (1974).
(502) V. Mark, *Tetrahedron Lett.*, 333 (1961).
(503) H. L. Ammon, G. L. Wheeler, and I. Agranat, *Tetrahedron*, **29**, 2695 (1973).
(504) See footnote 1 of ref 10.
(505) E. Harnik and G. M. J. Schmidt, *J. Chem. Soc.*, 3295 (1954).
(506) R. Korenstein, K. A. Muszkat, and S. Sharafy-Ozeri, *J. Am. Chem. Soc.*, **95**, 6177 (1973).
(507) G. L. Buchanan, *Chem. Soc. Rev.*, **3**, 41 (1974).
(508) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Am. Chem. Soc.*, **87**, 934 (1965).
(509) P. C. Manor, D. P. Shoemaker, and A. S. Parkes, *J. Am. Chem. Soc.*, **92**, 5260 (1970).
(510) (a) R. M. Cavin, Jr. and Z. F. Wang, *J. Am. Chem. Soc.*, **95**, 1425 (1973); (b) O. Ermer, *Angew. Chem., Int. Ed. Engl.*, **13**, 604 (1974); (c) H. Traetteberg, *Acta Chem. Scand., Ser. B*, **29**, 29 (1975). The olefinic bond is shorter than that in ethylene. The author explains this by a weakened π bond more than compensated for by a strengthened σ framework.
(511) A. C. Cope, G. R. Ganellin, and H. W. Johnson, Jr., *J. Am. Chem. Soc.*, **84**, 3191 (1962).
(512) A. Moscowitz and K. Mislow, *J. Am. Chem. Soc.*, **84**, 4605 (1962).
(513) A. C. Cope, G. R. Ganellin, H. W. Johnson, J. V. Van Anken, and H. J. S. Winkler, *J. Am. Chem. Soc.*, **85**, 3276 (1963).
(514) P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **86**, 2087 (1964).
(515) E. J. Corey, M. Tada, R. La Mahieu, and L. Libit, *J. Am. Chem. Soc.*, **87**, 2051 (1965).
(516) P. E. Eaton and K. Lin, *J. Am. Chem. Soc.*, **87**, 2052 (1965).
(517) A. C. Cope and C. L. Bumgardner, *J. Am. Chem. Soc.*, **78**, 2812 (1956).
(518) E. Vedejs and P. L. Fuchs, *J. Am. Chem. Soc.*, **93**, 4070 (1971). (The first substituted *cis,trans*-1,4-cyclooctadienes were reported in M. S. Baird and C. B. Reese, *Chem. Commun.*, 1644 (1970).)
(519) A. C. Cope, C. F. Howell, and A. Knowles, *J. Am. Chem. Soc.*, **84**, 3190 (1962).
(520) A. C. Cope, C. F. Howell, J. Bowers, R. C. Lord, and G. M. Whitesides, *J. Am. Chem. Soc.*, **89**, 4024 (1967).
(521) G. M. Whitesides, G. L. Goe, and A. C. Cope, *J. Am. Chem. Soc.*, **89**, 7136 (1967).
(522) I. Haller and R. Srinivasan, *J. Am. Chem. Soc.*, **88**, 5084 (1966).
(523) J. Meinwald and H. Tsuruta, *J. Am. Chem. Soc.*, **92**, 2579 (1970).
(524) G. L. Lange and E. Neidert, *Tetrahedron Lett.*, 1349 (1972).
(525) K. Kraft and G. Koltzenberg, *Tetrahedron Lett.*, 4357, 4723 (1967).
(526) H. E. Zimmerman and H. Iwamura, *J. Am. Chem. Soc.*, **92**, 2015 (1970).
(527) E. H. White, E. W. Friend, Jr., R. L. Stern, and H. Maskill, *J. Am. Chem. Soc.*, **91**, 523 (1969).
(528) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968).
(529) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *J. Am. Chem. Soc.*, **92**, 7002 (1970).
(530) (a) A. R. Brember, A. A. Gorman, and J. B. Sheridan, *Tetrahedron Lett.*, 475 (1973); (b) M. Christl and G. Brüntrup, *Angew. Chem., Int. Ed. Engl.*, **13**, 208 (1974).
(531) S. W. Staley and T. J. Henry, *J. Am. Chem. Soc.*, **91**, 7787 (1969).
(532) A. G. Anastassiou and R. C. Griffith, *J. Am. Chem. Soc.*, **93**, 3083 (1971).
(533) J. A. Deyrup and M. F. Betkouski, *J. Org. Chem.*, **40**, 284 (1975).
(534) J. A. Marshall and H. Faubl, *J. Am. Chem. Soc.*, **89**, 5965 (1967).
(535) J. R. Wiseman, *J. Am. Chem. Soc.*, **89**, 5966 (1967).
(536) J. R. Wiseman, H.-F. Chan, and C. J. Ahola, *J. Am. Chem. Soc.*, **91**, 2812 (1969).
(537) P. M. Lesko and R. B. Turner, *J. Am. Chem. Soc.*, **90**, 6888 (1968).
(538) J. Bredt, *Justus Liebigs Ann. Chem.*, **437**, 1 (1924).
(539) V. Prelog, *J. Chem. Soc.*, 420 (1950), and references cited.
(540) F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950).
(541) E. Vogel, W. Wiedemann, H. D. Roth, J. Eimer, and H. Guenther, *Justus Liebigs Ann. Chem.*, **759**, 1 (1972).
(542) G. Maier, *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967).
(543) L. A. Paquette and J. C. Phillips, *Chem. Commun.*, 680 (1969).
(544) E. Vogel, *Chem. Soc., Spec. Publ.*, **No. 21**, 113 (1967).
(545) W. Bremser, R. Hagen, E. Heilbronner, and E. Vogel, *Helv. Chim. Acta*, **52**, 418 (1969).
(546) R. Bianchi, A. Mugnoli, and M. Simonetta, *J. Chem. Soc., Chem. Commun.*, 1073 (1972).
(547) E. Vogel, W. Maier, and J. Eimer, *Tetrahedron Lett.*, 655 (1966).
(548) W. Carruthers and M. I. Qureshi, *Chem. Commun.*, 832 (1969).
(549) C. B. Quinn and J. R. Wiseman, *J. Am. Chem. Soc.*, **95**, 1342 (1973).
(550) C. B. Quinn and J. R. Wiseman, *J. Am. Chem. Soc.*, **95**, 6120 (1973).
(551) H. O. Krabbenhoft, J. R. Wiseman, and C. B. Quinn, *J. Am. Chem. Soc.*, **96**, 258 (1974).
(552) M. Toda, Y. Hirata, and S. Yamamura, *Chem. Commun.*, 1597 (1970).
(553) J. R. Wiseman and W. A. Pletcher, *J. Am. Chem. Soc.*, **92**, 956 (1970).
(554) J. R. Wiseman and J. A. Chong, *J. Am. Chem. Soc.*, **91**, 7775 (1969).
(555) J. A. Chong and J. R. Wiseman, *J. Am. Chem. Soc.*, **94**, 8627 (1972).
(556) B. L. Adams and P. Kovacic, *J. Am. Chem. Soc.*, **95**, 8206 (1973).
(557) C. B. Reese and M. R. D. Stebles, *J. Chem. Soc., Chem. Commun.*, 1231 (1972).
(558) P. Warner, R. La Rose, C.-M. Lee, and J. C. Clardy, *J. Am. Chem. Soc.*, **94**, 7607 (1972).
(559) K. Taguchi and F. H. Westheimer, *J. Am. Chem. Soc.*, **95**, 7413 (1973).
(560) H. H. Grootveld, C. Blomberg, and F. Bickelhaupt, *J. Chem. Soc., Chem. Commun.*, 542 (1973).
(561) A. D. Wolf and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 8209 (1973).
(562) (a) D. Grant, M. A. McKervey, J. J. Rooney, N. G. Samman, and G. Step, *J. Chem. Soc., Chem. Commun.*, 1186 (1972); (b) W. Burns and M. A. McKervey, *ibid.*, 858 (1974).
(563) D. Lenoir, *Tetrahedron Lett.*, 4049 (1972).
(564) J. E. Gano and L. Eizenberg, *J. Am. Chem. Soc.*, **95**, 972 (1973).
(565) M. Farcasiu, D. Farcasiu, R. T. Conlin, M. Jones, Jr., and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8207 (1973).
(566) (a) R. Keese and E. P. Krebs, *Angew. Chem., Int. Ed. Engl.*, **10**, 262 (1971); (b) *ibid.*, **11**, 518 (1972).
(567) S. F. Campbell, J. M. Leach, J. C. Tatlow, and K. N. Wood, *J. Fluorine Chem.*, **1**, 103 (1971).
(568) C. B. Quinn, J. R. Wiseman, and J. C. Calabrese, *J. Am. Chem. Soc.*, **95**, 6121 (1973).
(569) W. G. Dauben and J. Ipaktschi, *J. Am. Chem. Soc.*, **95**, 5088 (1973).
(570) H. Pracejus, M. Kehlen, H. Kehlen, and M. Matschiner, *Tetrahedron*, **21**, 2257 (1965).

(571) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **80**, 6412 (1958).
(572) M. Tichy and J. Sicher, *Tetrahedron Lett.*, 4609 (1969). (Twisting in the analogous amide is evident through examination of its infrared spectrum; see M. Tichy, E. Duskova, and K. Blaha, *Tetrahedron Lett.*, 237 (1974).)
(573) W. R. Moore and R. C. Bertelson, *J. Org. Chem.*, **27**, 4182 (1962).
(574) L. Skattebol, *Acta Chem. Scand.*, **17**, 1683 (1963).
(575) (a) L. Skattebol, *Chem. Ind. (Berlin)*, 2146 (1962); (b) L. Skattebol, *J. Org. Chem.*, **31**, 2789 (1966).
(576) See footnote 44a in ref 482.
(577) G. Köbrich and M. Baumann, *Angew. Chem., Int. Ed. Engl.*, **11**, 52 (1972).
(578) F. Toda and K. Akagi, *Chem. Commun.*, 764 (1970).
(579) A. T. Bottini, F. P. Corson, R. Fitzgerald, and K. A. Frost, Jr., *Tetrahedron Lett.*, 4757 (1970).
(580) J. P. Visser and J. E. Ramakes, *J. Chem. Soc., Chem. Commun.*, 178 (1972).
(581) G. Wittig and P. Fritze, *Angew. Chem., Int. Ed. Engl.*, **5**, 846 (1966).
(582) G. Wittig, H. L. Dorsch, and J. Meske-Schuller, *Justus Liebigs Ann. Chem.*, **711**, 55 (1968).
(583) G. Wittig and J. Meske-Schuller, *Justus Liebigs Ann. Chem.*, **711**, 76 (1968).
(584) (a) W. R. Moore and W. R. Moser, *J. Am. Chem. Soc.*, **92**, 5469 (1970); (b) *J. Org. Chem.*, **35**, 908 (1970).
(585) P. W. Dillon and G. R. Underwood, *J. Am. Chem. Soc.*, **96**, 779 (1974).
(586) G. W. Klumpp and P. M. van Dijk, *Recl. Trav. Chim. Pays-Bas*, **90**, 381 (1971).
(587) R. G. Bergman and V. J. Rajadhyaksha, *J. Am. Chem. Soc.*, **92**, 2163 (1970).
(588) R. A. LaBar and W. M. Jones, *J. Am. Chem. Soc.*, **96**, 3645 (1974).
(589) E. V. Dehmlow and G. C. Ezimora, *Tetrahedron Lett.*, 4047 (1970).
(590) (a) M. B. D'Amore and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 5694 (1969); (b) M. B. D'Amore, R. G. Bergman, M. Kent, and E. Hedaya, *J. Chem. Soc., Chem. Commun.*, 49 (1972).
(591) L. Skattebol and S. Solomon, *J. Am. Chem. Soc.*, **87**, 4506 (1965).
(592) A. D. Ketley, *Tetrahedron Lett.*, 1687 (1964).
(593) (a) R. A. Moss and J. R. Whittle, *Chem. Commun.*, 341 (1969); (b) R. A. Moss, U.-H. Dolling, and J. R. Whittle, *Tetrahedron Lett.*, 931 (1971).
(594) R. Breslow, W. Washburn, and R. G. Bergman, *J. Am. Chem. Soc.*, **91**, 196 (1969).
(595) N. L. Bauld, C. E. Dahl, and Y. S. Rim, *J. Am. Chem. Soc.*, **91**, 2787 (1969).
(596) M. P. Cava, K. Narasimham, W. Zieger, L. J. Radonovich, and M. D. Glick, *J. Am. Chem. Soc.*, **91**, 2379 (1969).
(597) For a similarly strained unit that has been isolated, see R. L. Cargill and A. B. Sears, *Tetrahedron Lett.*, 3555 (1972).
(598) R. W. Hoffmann, "Dehydrobenzene and Cycloalkynes", Academic Press, New York, N.Y., 1967.
(599) A. T. Blomquist and L. H. Liu, *J. Am. Chem. Soc.*, **75**, 2153 (1953).
(600) R. B. Turner, A. D. Jarrett, P. Goebel, and B. J. Mallon, *J. Am. Chem. Soc.*, **95**, 790 (1973).
(601) (a) G. Wittig, A. Krebs, and R. Pohlke, *Angew. Chem.*, **72**, 324 (1960); (b) G. Wittig and A. Krebs, *Chem. Ber.*, **94**, 3268 (1961).
(602) A. Krebs and H. Kimlimg, *Angew. Chem., Int. Ed. Engl.*, **10**, 509 (1971).
(603) (a) A. Krebs and H. Kimlimg, *Tetrahedron Lett.*, 761 (1970); (b) J. Haase and A. Krebs, *Z. Naturforsch. A*, **27**, 624 (1972).
(604) (a) F. Scardiglia and J. D. Roberts, *Tetrahedron*, **13**, 343 (1957); (b) L. K. Montgomery and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 4750 (1960); (c) L. K. Montgomery, F. Scardiglia, and J. D. Roberts, *ibid.*, **87**, 1917 (1965).
(605) H. Schmidt, A. Schweig, and A. Krebs, *Tetrahedron Lett.*, 1471 (1974).
(606) E. Kloster-Jensen and J. Wirz, *Angew. Chem., Int. Ed. Engl.*, **12**, 671 (1973).
(607) G. Seitz, L. Pohl, and R. Pohlke, *Angew. Chem., Int. Ed. Engl.*, **8**, 447 (1969).
(608) A. Krebs, *Angew. Chem., Int. Ed. Engl.*, **4**, 953 (1965).
(609) H. N. C. Wong, P. J. Garratt, and F. Sondheimer, *J. Am. Chem. Soc.*, **96**, 5604 (1974).
(610) G. Wittig and H. Heyn, *Chem. Ber.*, **97**, 1609 (1964).
(611) W. Draber, *Angew. Chem., Int. Ed. Engl.*, **6**, 75 (1967).
(612) W. Tochtermann, K. Oppenländer, and M. N.-D. Hoang, *Justus Liebigs Ann. Chem.*, **701**, 117 (1967).
(613) W. R. Moore and T. M. Ozretich, *Tetrahedron Lett.*, 3205 (1967).
(614) W. R. Roth and G. Erker, *Angew. Chem., Int. Ed. Engl.*, **12**, 505 (1973).
(615) W. Grimme and H.-J. Rother, *Angew. Chem., Int. Ed. Engl.*, **12**, 505 (1973).
(616) T. Negi, T. Kaneda, Y. Sakata, and S. Misumi, *Chem. Lett.*, 703 (1972).
(617) O. L. Chapman, K. Mattes, C. L. McIntosh, J. Pacansky, G. V. Calder, and G. Orr, *J. Am. Chem. Soc.*, **95**, 6134 (1973).
(618) H. M. Rosenstock, J. T. Larkins, and J. A. Walker, *Int. J. Mass Spectrom. Ion Phys.*, **11**, 309 (1973).
(619) W. H. Mills and I. G. Nixon, *J. Chem. Soc.*, 2510 (1930).
(620) J. Vaughan, G. J. Welch, and G. J. Wright, *Tetrahedron*, **21**, 1665 (1965).
(621) R. Taylor, G. J. Wright, and A. J. Homes, *J. Chem. Soc. B*, 780 (1967).
(622) A. Streitweiser, Jr., G. R. Ziegler, P. J. Mowery, A. Lewis, and R. G. Lawler, *J. Am. Chem. Soc.*, **90**, 1357 (1968).
(623) B. Holton, *Chem. Rev.*, **73**, 113 (1973).
(624) R. Anet and F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 525 (1964).
(625) E. Vogel, W. Grimme, and S. Korte, *Tetrahedron Lett.*, 3625 (1965).
(626) E. F. Ullman and E. Buncel, *J. Am. Chem. Soc.*, **85**, 2106 (1963).
(627) W. E. Billups, W. Y. Chow, K. H. Leavell, E. S. Lewis, J. L. Margrave, R. L. Sass, J. J. Shieh, P. G. Werness, and J. L. Wood, *J. Am. Chem. Soc.*, **95**, 7878 (1973).
(628) E. Carstensen-Oeser, B. Muller, and H. Dürr, *Angew. Chem., Int. Ed. Engl.*, **11**, 422 (1972).
(629) C. S. Cheung, M. A. Cooper, and S. L. Manatt, *Tetrahedron*, **27**, 101 (1971).
(630) M. A. Cooper and S. L. Manatt, *J. Am. Chem. Soc.*, **92**, 1605 (1970).
(631) (a) M. P. Cava and D. R. Napier, *J. Am. Chem. Soc.*, **78**, 500 (1956); (b) M. P. Cava and A. A. Deana, *ibid.*, **81**, 4266 (1959).
(632) G. L. Hardgrove, L. K. Templeton, and D. H. Templeton, *J. Phys. Chem.*, **72**, 668 (1968).
(633) M. P. Cava, A. A. Deana, and K. Muth, *J. Am. Chem. Soc.*, **82**, 2524 (1960).
(634) (a) S. G. G. MacDonald, J. L. Lawrence, and M. P. Cava, *Chem. Ind. (London)*, 86 (1965); (b) J. L. Lawrence and S. G. G. MacDonald, *Acta Crystallogr., Sect. B*, **25**, 978 (1969).
(635) J. K. Fawcett and J. Trotter, *Acta Crystallogr.*, **20**, 87 (1966).
(636) A. Yokozeki, C. F. Wilcox, Jr., and S. H. Bauer, *J. Am. Chem. Soc.*, **96**, 1026 (1974).
(637) B. Holton, A. D. Woodhouse, H. M. Hugel, and D. P. Kelly, *J. Chem. Soc., Chem. Commun.*, 247 (1974).
(638) H. Straub, *Angew. Chem., Int. Ed. Engl.*, **13**, 405 (1974).
(639) M. P. Cava and J. A. Kuczkowski, *J. Am. Chem. Soc.*, **92**, 5800 (1970).
(640) R. W. Hoffmann and W. Sieber, *Angew. Chem., Int. Ed. Engl.*, **4**, 786 (1965).
(641) D. C. DeJongh and G. N. Evenson, *Tetrahedron Lett.*, 4093 (1971).
(642) V. Balasubramaniyan, *Chem. Rev.*, **66**, 567 (1966).
(643) A strain energy of 6–7 kcal/mol for **268** has also been calculated: H. H. Boyd, R. L. Christensen, and R. Pua, *J. Am. Chem. Soc.*, **87**, 3554 (1965).
(644) W. D. Good, *J. Chem. Thermodyn.*, **5**, 715 (1973).
(645) G. L. Simmons and E. C. Lingafelter, *Acta Crystallogr.*, **14**, 872 (1961).
(646) U. Krüerke, C. Hoogzand, and W. Hübel, *Chem. Ber.*, **94**, 2817 (1961).
(647) C. Hoogzand and W. Hübel, *Angew. Chem.*, **73**, 680 (1961).
(648) E. M. Arnett and M. E. Strem, *Chem. Ind. (London)*, 2008 (1961).
(649) L. R. C. Barclay, N. D. Hall, and J. W. MacClean, *Tetrahedron Lett.*, 243 (1961).
(650) C. Hoogzand and W. Hübel, *Tetrahedron Lett.*, 637 (1961).
(651) E. M. Arnett, M. E. Strem, and R. A. Friedel, *Tetrahedron Lett.*, 658 (1961).
(652) A. W. Burgstahler and M. O. Abdel-Rahman, *J. Am. Chem. Soc.*, **85**, 173 (1963).
(653) E. M. Arnett, J. C. Sanda, J. M. Bollinger, and M. Barber, *J. Am. Chem. Soc.*, **89**, 5389 (1967).
(654) A. van Bruijnsvoort, C. Eilermann, H. van der Meer, and C. H. Stam, *Tetrahedron Lett.*, 2527 (1968).
(655) E. M. Arnett, J. M. Bollinger, and J. C. Sanda, *J. Am. Chem. Soc.*, **87**, 2050 (1965).
(656) M. D. Jameson and B. R. Penfold, *J. Chem. Soc.*, 528 (1965).
(657) M. A. Davydova and Yu T. Struchkov, *J. Struct. Chem. (Engl. Transl.)*, **2**, 63 (1961); **3**, 170, 202 (1962); **6**, 98 (1965).
(658) G. Gafner and F. H. Herbstein, *Acta Crystallogr.*, **15**, 1081 (1962).
(659) G. Gafner and F. H. Herbstein, *Nature (London)*, **200**, 130 (1963), and references therein.
(660) G. Ferguson and J. M. Robertson, *Adv. Phys. Org. Chem.*, **1**, 203 (1963).
(661) R. W. Franck and E. G. Leser, *J. Am. Chem. Soc.*, **91**, 1577 (1969).
(662) H. van Bekkum, Th. J. Nieuwstad, and J. van Barneveld, *Recl. Trav. Chim. Pays-Bas*, **88**, 1028 (1969).
(663) D. L. Fields and T. H. Regan, *J. Org. Chem.*, **36**, 2986 (1971).
(664) H. A. Karnes, B. D. Kybett, M. H. Wilson, J. I. Margrave, and M. S. Newman, *J. Am. Chem. Soc.*, **87**, 5554 (1965).
(665) M. S. Newman and R. M. Wise, *J. Am. Chem. Soc.*, **78**, 450 (1956).
(666) M. S. Newman and D. Lednicer, *J. Am. Chem. Soc.*, **78**, 4795 (1956).
(667) (a) R. H. Martin and M. J. Marchant, *Tetrahedron*, **30**, 347 (1974); (b) R. H. Martin, *Angew. Chem., Int. Ed. Engl.*, **13**, 649 (1974).
(668) Ch. Goedicke and H. Stegemeyer, *Tetrahedron Lett.*, 937 (1970).
(669) B. H. Smith, "Bridged Aromatic Compounds", Academic Press, New York, N.Y., 1964.
(670) D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, **4**, 204 (1971).
(671) F. Vögtle and P. Neumann, *Top. Curr. Chem.*, **48**, 67 (1974).
(672) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.*, **76**, 6132 (1954), and references cited therein.
(673) M. F. Bartlett, S. K. Figdor, and K. Wiesner, *Can. J. Chem.*, **30**, 291 (1952).
(674) (a) D. J. Cram and G. R. Knox, *J. Am. Chem. Soc.*, **83**, 2204 (1961); (b) D. J. Cram, C. S. Montgomery, and G. R. Knox, *ibid.*, **88**, 515 (1966).
(675) The 4-carboxylic acid: N. L. Allinger and L. A. Freiberg, *J. Org. Chem.*, **27**, 1490 (1962); and A. T. Blomquist and L. F. Chow, cited in A. T. Blomquist and F. W. Schaefer, *J. Am. Chem. Soc.*, **83**, 4547 (1961).
(676) A. D. Wolf, V. V. Kane, R. H. Levin, and M. Jones, Jr., *J. Am. Chem. Soc.*, **95**, 1680 (1973).
(677) The 3-carboxylic acid: N. L. Allinger and T. J. Walter, *J. Am. Chem. Soc.*, **94**, 9267 (1972).
(678) V. V. Kane, A. D. Wolf, and M. Jones, Jr., *J. Am. Chem. Soc.*, **96**, 2643 (1974).
(679) N. L. Allinger, J. T. Sprague, and T. Lilhefors, *J. Am. Chem. Soc.*, **96**, 5100 (1974).
(680) N. L. Allinger, T. J. Walter, and M. G. Newton, *J. Am. Chem. Soc.*, **96**, 4588 (1974).
(681) We thank Professor Maitland Jones, Jr., for helpful discussion of this compound as well as [6]paracyclophane. Professor Jones informs us that his efforts to obtain [5]paracyclophane, in a manner analogous to that used for the higher homologue, were unsuccessful.
(682) S. W. Benson, F. R. Cruickshank, D. M. Golden, G. R. Haugen, H. E. O'Neal, A. S. Rodgers, H. Shaw, and R. Walsh, *Chem. Rev.*, **69**, 279 (1969).
(683) (a) A. T. Blomquist and B. H. Smith, *J. Am. Chem. Soc.*, **82**, 2073 (1960); (b) A. T. Blomquist, R. E. Dahl, Y. C. Meinwald, and B. H. Smith, *J. Org. Chem.*, **26**, 1687 (1961).
(684) C. J. Brown and A. C. Farthing, *Nature (London)*, **164**, 915 (1949).
(685) C. J. Brown, *J. Chem. Soc.*, 3265 (1953).
(686) K. Lonsdale, H. J. Milledge, and K. W. Krishna Rao, *Proc. R. Soc. London, Ser. A*, **255**, 82 (1960).
(687) H. Hope, J. Bernstein, and K. N. Trueblood, *Acta Crystallogr., Sect. B*,

28, 1733 (1972).
(688) R. H. Boyd, *Tetrahedron,* **22,** 119 (1966).
(689) D. L. Rodgers, E. F. Westrum, Jr., and J. T. S. Andrews, *J. Chem. Thermodyn.,* **5,** 733 (1973).
(690) R. H. Boyd, *J. Chem. Phys.,* **49,** 2574 (1968).
(691) D. T. Longone and L. H. Simanyi, *J. Org. Chem.,* **29,** 3245 (1964).
(692) D. J. Cram, R. C. Helgeson, D. Lock, and L. A. Singer, *J. Am. Chem. Soc.,* **88,** 1324 (1966).
(693) C. Shieh, D. C. McNally and R. H. Boyd, *Tetrahedron,* **25,** 3653 (1969).
(694) K. C. Dewhirst and D. J. Cram, *J. Am. Chem. Soc.,* **80,** 3115 (1958).
(695) R. K. Gantzel and K. N. Trueblood, *Acta Crystallogr.,* **18,** 958 (1965).
(696) D. J. Cram and M. F. Antar, *J. Am. Chem. Soc.,* **80,** 3103 (1958).
(697) N. L. Allinger, L. A. Freiberg, H. B. Herman, and M. A. Miller, *J. Am. Chem. Soc.,* **85,** 1171 (1963).
(698) H. Wynberg, W. C. Nieuwpoort, and H. T. Jonkman, *Tetrahedron Lett.,* 4623 (1973).
(699) M. G. Newton, T. J. Walter, and N. L. Allinger, *J. Am. Chem. Soc.,* **95,** 5652 (1973).
(700) K. N. Trueblood and M. J. Crisp, footnote 17 cited in ref 670 of this paper.
(701) C. L. Coulter and K. N. Trueblood, *Acta Crystallogr.,* **16,** 667 (1963).
(702) A. W. Hanson, *Acta Crystallogr., Sect. B,* **27,** 197 (1971).
(703) (a) W. Rebafka and H. A. Staab, *Angew. Chem., Int. Ed. Engl.,* **12,** 776 (1973); (b) W. Rebafka and H. A. Staab, *ibid.,* **13,** 203 (1974).
(704) V. Prelog and K. Wiesner, *Helv. Chim. Acta,* **30,** 1465 (1947).
(705) V. Prelog, K. Wiesner, W. Ingold, and O. Häfliger, *Helv. Chim. Acta,* **31,** 1325 (1948).
(706) W. E. Parham and J. K. Rinehart, *J. Am. Chem. Soc.,* **89,** 5668 (1967).
(707) W. E. Parham, D. R. Johnson, C. T. Hughes, M. K. Meilahn, and J. K. Rinehart, *J. Org. Chem.,* **35,** 1048 (1970).
(708) R. H. Mitchell and V. Boekelheide, *J. Am. Chem. Soc.,* **96,** 1547 (1974).
(709) (a) V. Boekelheide and J. A. Lawson, *Chem. Commun.,* 1558 (1970); (b) V. Boekelheide and W. Pepperdine, *J. Am. Chem. Soc.,* **92,** 3684 (1970).
(710) (a) V. Boekelheide and R. A. Hollins, *J. Am. Chem. Soc.,* **92,** 3512 (1970); (b) *ibid.,* **95,** 3201 (1973).
(711) R. Boschi and W. Schmidt, *Angew. Chem., Int. Ed. Engl.,* **12,** 405 (1973).
(712) (a) E. A. Truesdale and D. J. Cram, *J. Am. Chem. Soc.,* **95,** 5825 (1973); (b) R. G. Gray and V. Boekelheide, *Angew. Chem., Int. Ed. Engl.,* **14,** 107 (1975).
(713) A. J. Hubert, *J. Chem. Soc. C,* 13 (1967).
(714) E. I. Bagrii, T. N. Dolgopolova, P. I. Sanin, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 2648 (1973); *Chem. Abstr.,* **80,** 59770f (1974).
(715) M. Nakazaki, K. Yamamoto, and S. Tanaka, *Tetrahedron Lett.,* 341 (1971).
(716) Hubert and Hubert, *Tetrahedron Lett.,* 5779 (1966).
(717) R. D. Stephens, *J. Org. Chem.,* **38,** 2260 (1973).
(718) D. T. Longone and H. S. Chow, *J. Am. Chem. Soc.,* **86,** 3898 (1964).
(719) D. T. Longone and H. S. Chow, *J. Am. Chem. Soc.,* **92,** 994 (1970).
(720) T. Otsubo, S. Mizogami, Y. Sakata, and S. Misumi, *Tetrahedron Lett.,* 4803 (1971).
(721) H. Hopf, *Angew. Chem., Int. Ed. Engl.,* **11,** 419 (1972).
(722) T. Otsubo, Z. Tozuka, S. Mizogami, Y. Sakata, and S. Misumi, *Tetrahedron Lett.,* 2927 (1972).
(723) M. Nakazaki, K. Yamamoto, and J. Tanaka, *J. Chem. Soc., Chem. Commun.,* 433 (1972).
(724) T. Umemoto, T. Otsubo, Y. Sakata, and S. Masamune, *Tetrahedron Lett.,* 593 (1973).
(725) D. T. Longone and G. R. Chipman, *Chem. Commun.,* 1358 (1969).
(726) H. Rapoport and G. Smolinsky, *J. Am. Chem. Soc.,* **82,** 1171 (1960).
(727) H. Rapoport and J. Z. Pasky, *J. Am. Chem. Soc.,* **78,** 3788 (1956).
(728) B. L. McDowell, H. Rapoport, and G. Smolinsky, *J. Am. Chem. Soc.,* **84,** 3531 (1962).
(728a) W. E. Barth and R. G. Lawton, *J. Am. Chem. Soc.,* **88,** 380 (1966); (b) *ibid.,* **93,** 1730 (1971); (c) P. J. Jessup and J. A. Reiss, *Tetrahedron Lett.,* 1453 (1975); (d) B. M. Trost and P. L. Kinson, *J. Am. Chem. Soc.,* **92,** 2591 (1970); (e) B. M. Trost, P. L. Kinson, C. A. Maier, and I. C. Paul, *ibid.,* **93,** 7275 (1971); (f) B. M. Trost and P. L. Kinson, *ibid.,* **97,** 2438 (1975); (g) N. K. Hota and D. S. Matteson, *ibid.,* **90,** 3570 (1968); (h) D. S. Matteson and N. K. Hota, *ibid.,* **93,** 2893 (1971).
(729) E. Heilbronner and J. O. Maier, *Helv. Chim. Acta,* **57,** 151 (1974), present a related but more rigorous description for [2.2]paracyclophane with conceptual emphasis on its ionization and substitution. These authors also cited other studies of the orbitals of paracyclophanes.
(730) (a) D. J. Cram, N. L. Allinger, and H. Steinberg, *J. Am. Chem. Soc.,* **76,** 6132 (1954); (b) D. J. Cram and R. H. Bauer, *ibid.,* **81,** 5971 (1959).
(731) W. J. Hehre, *J. Am. Chem. Soc.,* **95,** 5807 (1973).
(732) D. T. Hefelfinger and D. J. Cram, *J. Am. Chem. Soc.,* **93,** 4754 (1971).
(733) D. J. Cram, W. J. Wechter, and R. W. Kierstead, *J. Am. Chem. Soc.,* **80,** 3126 (1958).
(734) [2.2]Paracyclophane undergoes homolytic aromatic substitution more rapidly than benzene: S. C. Dickerman and L. Milstein, *J. Org. Chem.,* **32,** 852 (1967). See also ref 852.
(735) (a) A. Ishitani and S. Nagakura, *Mol. Phys.,* **12,** 1 (1967), investigated [2.2]paracyclophane; (b) F. Gershon and W. B. Martin, Jr., *J. Am. Chem. Soc.,* **91,** 1883 (1969), investigated [2.2]-, [3.3]-, and [4.4]paracyclophane, [2.2]metacyclophane, and acyclic analogs.
(736) J. M. Pearson, D. J. Williams, and M. Levy, *J. Am. Chem. Soc.,* **93,** 5478 (1971); D. J. Williams, J. M. Pearson and M. Levy, *ibid.,* **93,** 5483 (1971). These authors investigated [2.2]paracyclophane and its di- and tetrabenzo analogs (i.e., bridged naphthalene and anthracene), and the open-chain phenyl, 1-naphthyl, 9-anthryl, and 1-pyrenyl derivatives.
(737) This cyclophane dianion must be a singlet if it decomposes to the open-chain dianion by a spin-allowed process. The reader should convince himself that the dianion is predicted to be stabilized by HOMO–LUMO analysis.
(738) (a) D. J. Cram and L. A. Singer, *J. Am. Chem. Soc.,* **85,** 1075 (1963); (b) D. J. Cram and F. L. Harris, Jr., *ibid.,* **89,** 4642 (1967).
(739) B. E. Norcross, D. Becker, R. I. Cukier, and R. M. Schultz, *J. Org. Chem.,* **32,** 220 (1967).
(740) Comparison of amine basicity and hydrocarbon acidity and the role of solvation will be discussed in Section XVI.C.
(741) We doubt that the $6\text{–}7^-$ species intrinsically will be more stable than $6\text{–}7^+$ since 7^- is antiaromatic while 7^+ is aromatic. However, the reduction of $6\text{–}7^+$ to $6\text{–}7^-$ should be considerably easier than that of the one-ring seven-membered compounds. A parallel study of analogs of [*n*]paracyclophane would also be of interest since a corresponding effect is not predicted.
(742) See R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", Academic Press, New York, N.Y., 1970, pp 145–151, for a discussion of this specific type of "steric attraction" and reaction product geometry.
(743) H. P. Schultz, *J. Org. Chem.,* **30,** 1361 (1965).
(744) W. N. Lipscomb, "Boron Hydrides", W. A. Benjamin, New York, N.Y., 1963.
(745) P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.,* **86,** 962 (1964).
(746) P. E. Eaton and T. W. Cole, Jr., *J. Am. Chem. Soc.,* **86,** 3157 (1964).
(747) J. C. Barborak, L. Watts, and R. Pettit, *J. Am. Chem. Soc.,* **88,** 1328 (1966).
(748) C. G. Chin, H. W. Cutts, and S. Masamune, *Chem. Commun.,* 880 (1966).
(749) R. B. Woodward, T. Fukunaga, and R. C. Kelly, *J. Am. Chem. Soc.,* **86,** 3162 (1964).
(750) P. E. Eaton and R. H. Mueller, *J. Am. Chem. Soc.,* **94,** 1014 (1972).
(751) K.-W. Shen, *J. Am. Chem. Soc.,* **93,** 3064 (1971).
(752) G. R. Underwood and B. Ramamoorthy, *Chem. Commun.,* 12 (1970).
(753) L. DeVries and S. Winstein, *J. Am. Chem. Soc.,* **82,** 5363 (1960).
(754) W. G. Dauben and R. L. Cargill, *Tetrahedron,* **15,** 197 (1961).
(755) G. S. Hammond, N. J. Turro, and A. Fischer, *J. Am. Chem. Soc.,* **83,** 4674 (1961).
(756) R. B. Turner, P. Goebel, B. J. Mallon, W. von E. Doering, J. F. Coburn, Jr., and M. Pomerantz, *J. Am. Chem. Soc.,* **90,** 4315 (1968).
(757) P. K. Freeman, D. G. Kuper, and V. N. Mallikarjuna Rao, *Tetrahedron Lett.,* 3301 (1965).
(758) U. Biethan, U. v. Gizycki, and H. Musso, *Tetrahedron Lett.,* 1477 (1965).
(759) A. R. Brember, A. A. Gorman, and J. B. Sheridan, *Tetrahedron Lett.,* 481 (1973).
(760) W. G. Dauben, C. H. Schallhorn, and D. I. Whalen, *J. Am. Chem. Soc.,* **93,** 1446 (1971).
(761) See footnote 1 in ref 760.
(762) E. T. McBee, W. L. Dilling, and H. P. Braendlin, *J. Org. Chem.,* **27,** 2704 (1962). Also see W. G. Dauben and D. L. Whalen, *J. Am. Chem. Soc.,* **93,** 7244 (1971), for references to other bishomocubanes.
(763) H.-M. Hutmacher, H.-G. Fritz, and H. Musso, *Angew. Chem., Int. Ed. Engl.,* **14,** 180 (1975).
(764) G. R. Underwood and B. Ramamoorthy, *Tetrahedron Lett.,* 4125 (1970).
(764a) S. Godleski, P. v. R. Schleyer, E. Osawa, and G. J. Kent, *J. Chem. Soc., Chem. Commun.,* 976 (1974).
(765) L. Cassar, P. E. Eaton, and J. Halpern, *J. Am. Chem. Soc.,* **92,** 6366 (1970).
(766) S. Masamune, H. W. Cutts, and M. G. Hogben, *Tetrahedron Lett.,* 1017 (1966).
(767) W. G. Dauben and D. L. Whalen, *Tetrahedron Lett.,* 3743 (1966).
(768) A. De Meijere, D. Kaufmann, and O. Schallner, *Angew. Chem., Int. Ed. Engl.,* **10,** 417 (1971).
(769) H. Prinzbach and D. Stusche, *Helv. Chim. Acta,* **54,** 755 (1971).
(770) E. L. Allred and B. R. Beck, *J. Am. Chem. Soc.,* **95,** 2393 (1973).
(770a) D. Bosse and A. De Meijere, *Angew. Chem., Int. Ed. Engl.,* **13,** 663 (1974).
(770b) G. E. Cream, L. R. Smith, and J. Meinwald, *J. Org. Chem.,* **39,** 3461 (1974).
(771) (a) C. A. Cupas and L. Hodakowski, *J. Am. Chem. Soc.,* **96,** 4668 (1974); (b) D. P. G. Hamon and G. F. Taylor, *Tetrahedron Lett.,* 155 (1975).
(772) D. Fărcasiu, E. Wiskott, E. Osawa, W. Thielecke, E. M. Engler, J. Slutsky, P. v. R. Schleyer, and G. J. Kent, *J. Am. Chem. Soc.,* **96,** 4669 (1974).
(773) F. P. Bundy and J. S. Kaper, *J. Chem. Phys.,* **46,** 3437 (1967).
(774) D. J. Cram and N. L. Allinger, *J. Am. Chem. Soc.,* **77,** 6289 (1955).
(775) R. J. Lagow, R. B. Badachhape, J. L. Wood, and J. L. Margrave, *J. Am. Chem. Soc.,* **96,** 2628 (1974).
(776) K. I. Harao, T. Iwakuma, M. Taniguchi, E. Abe, O. Yonemitsu, T. Date, and K. Kotera, *J. Chem. Soc., Chem. Commun.,* 691 (1974).
(777) R. R. Sauers and R. A. Parent, *J. Org. Chem.,* **28,** 605 (1963).
(778) P. K. Freeman, V. N. Mallikarjuna Rao, and G. E. Bigam, *Chem. Commun.,* 511 (1965).
(779) T. J. Katz and N. Acton, *Tetrahedron Lett.,* 2601 (1967).
(780) A. C. Udding, J. Strating, H. Wynberg, and J. L. M. A. Schlatmann, *Chem. Commun.,* 657 (1966); see also D. Fărcaşiu and P. v. R. Schleyer, *Tetrahedron Lett.,* 3835 (1973), for a dehydrodiamantane.
(781) H. W. Geluk and Th. J. De Boer, *J. Chem. Soc., Chem. Commun.,* 3 (1972).
(782) Z. Majerski, S. H. Liggero, and P. v. R. Schleyer, *Chem. Commun.,* 949 (1970).
(783) H. Prinzbach and D. Hunkler, *Angew. Chem., Int. Ed. Engl.,* **6,** 247 (1967).
(784) P. K. Freeman and D. M. Balls, *J. Org. Chem.,* **32,** 2354 (1967).
(785) H. H. Wasserman and P. M. Keehn, *J. Am. Chem. Soc.,* **89,** 2770 (1967).
(786) X-Ray Structure: A. V. Fratini, *J. Am. Chem. Soc.,* **90,** 1688 (1968).
(787) (a) S. Winstein and R. L. Hansen, *Tetrahedron Lett.,* 25, 4 (1960); (b) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Am. Chem. Soc.,* **83,** 2938 (1961).
(788) Describing benzene as 1,3,5-cyclohexatriene is complicating enough but tetracyclo[$6.0^{1,2}.0^{3,4}.0^{5,6}$]hexane appears absurd. Specifically, C.-Y. Shieh, N. McNally, and R. H. Boyd, *Tetrahedron,* **25,** 3653 (1969), employed $p\text{-}C_6H_4$ as a group (ΔH_f° = 24.3 kcal/mol) in a study of simple paracyclophanes and their acyclic analogues.

(789) Although this cannot usually be done by inspection, a useful algorithm has been written by W. N. Anderson, Jr., and J. F. Liebman, as yet unpublished.

(790) Ideally, every (carbon) atom in the polycyclic compound is found in this ring. For this to be the case, it is necessary that the acyclic compound have no substituents. That is, it must be a "normal" unbranched alkane. However, the converse is not necessarily true and, indeed, is rarely true. Finding all of the conditions under which every atom in the polycyclic compound is found in the ring may be easily translated into one of the great unsolved problems in mathematics. (See the discussion on "Hamiltonian graphs" in C. Berge, "The Theory of Graphs and Its Applications", Engl. transl., Wiley, New York, N.Y., 1962, pp 107–118, and F. Harary, "Graph Theory", Addison-Wesley, Reading, Mass., 1969, pp 64–79.) Our chemical problem is indubitably considerably more difficult to solve in the general, mathematical sense. However, we are confident that chemical considerations provide simplifications. For example, no carbon atom is bound to no more than four other carbons, and in a $[m.n.p]$bicycloalkane, the maxiring contains $m + n + 2$ carbons. Information about and the generation and use of Hamiltonian graphs have been interrelated with organic nomenclature of polycyclic hydrocarbons: D. Eckroth, *J. Org. Chem.*, **32**, 3362 (1967). The term "polygonal graph", similar to the "maxiring" concept, has been introduced but no extension has been made of it. See L. A. Paquette and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 2584 (1970).

(791) C. R. Somayajulu and B. J. Zwolinski, *J. Chem. Soc., Faraday Trans. 2*, **70**, 973 (1973). We note that almost all interest in substituted compounds, both in this and our other thermochemical references of general nature, have dealt with acyclic species. A notable exception is K. Pihlaja and E. Taskinen, "Some Applications of Thermochemistry to Heterocyclic Chemistry", Vol. VI, A. P. Katritsky, Ed., Academic Press, New York, N.Y., 1971.

(792) For an extensive discussion of the stereochemical and conformational effects on replacing CH_2 by O, see J. Dale, *Tetrahedron*, **36**, 1603 (1973).

(793) See, for example, the equilibration of bicyclooctane derivatives (ref 15) and references cited therein.

(794) Recall the ubiquity of adamantane syntheses from other hydrocarbons (see Section V).

(795) No experimental data are available for most of these species. We thus quote the result of two theoretical studies, both of which rely heavily on and interpret experiment: L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 8193 (1973) (X = H, CH_3, F, OH, and NH_2); J. F. Liebman and A. Greenberg, *J. Org. Chem.*, **39**, 123 (1974) (X = O^-, i.e., cyclopropanone vs. oxyallyl).

(796) J. McBride, *Tetrahedron*, **30**, 2009 (1974).

(797) H. Nakatsuji, T. Kuwata, and A. Yoshida, *J. Am. Chem. Soc.*, **95**, 6894 (1973).

(798) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969, pp 27–40, present a thorough treatment of the C–F bond including a subsection on the CF_3 group and C–CF_3 bonding.

(799) P. Politzer and J. W. Timberlake, *J. Org. Chem.*, **37**, 3557 (1972).

(800) Electron withdrawal by fluorine and accelerated ortho and para electrophilic substitution of fluorobenzene appear contradictory. The reader is encouraged to relook at ref 798 and 799.

(801) W. A. Bernett, *J. Org. Chem.*, **34**, 1772 (1969).

(802) Bernett[801] (ref 11) extensively used hybridization logic to explain numerous aspects of fluorocarbon chemistry. As expressed in section III.G, we are extremely skeptical of hybridization logic. Further reasons for our disbelief will be presented to Section XVI.C.

(803) This phenomenon occurs for numerous unsaturated species that are mostly or exhaustively (i.e., per-) fluorinated, and thus goes under the name "The Perfluoro Effect": C. R. Brundle, M. B. Robin, N. A. Kuebler, and H. Basch, *J. Am. Chem. Soc.*, **94**, 1451 (1972); C. R. Brundle, M. B. Robin and N. A. Kuebler, *ibid.*, **94**, 1466 (1972). However, we believe it is a characteristic of linear or planar species with occupied π orbitals and geminal fluorine substitution (J. F. Liebman and P. Politzer, unpublished results). For example, the π ionization potentials of HF and F_2 are 16.01 and 15.69 eV, respectively: J. Berkowitz, W. A. Chupka, P. Guyon, J. Holloway, and R. Spohr, *J. Chem. Phys.*, **54**, 5165 (1971).

(804) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry", W. A. Benjamin, New York, N.Y., 1969.

(805) R. E. Banks, "Fluorocarbons and the Derivatives", 2d ed, McDonald Technical and Scientific, London, 1970.

(806) R. D. Chambers, "Fluorine in Organic Chemistry", Wiley, New York, N.Y., 1973.

(807) We wish to emphasize that our customary theoretical "apparatus" for the predictions of heats of formation of these species appears inherently inapplicable. Besides the earlier cited ignorance regarding perfluorocycloalkanes, we make mention of R. Shaw in "The Chemistry of the Carbon–Halogen Bond", Part 2, S. Patai, Ed., Wiley, New York, N.Y., 1973, where other unforseen complications are discussed.

(808) K. V. Scherer, Jr., and T. J. Meyers, *J. Am. Chem. Soc.*, **90**, 6253 (1968).

(809) For further information on perhalogenated (i.e., Cl, Br, I) compounds, see R. West, *Acc. Chem. Res.*, **3**, 130 (1970); T. Chivers in "The Chemistry of the Carbon-Halogen Bond", ref 807.

(810) (a) S. W. Tobey and R. West, *J. Am. Chem. Soc.*, **88**, 2478 (1966); (b) S. W. Tobey and R. West, *ibid.*, **86**, 56 (1964); (c) W. R. Moore, S. E. Krikorian, and J. E. LaPrade, *J. Org. Chem.*, **28**, 1404 (1963); (d) W. v. E. Doering, *J. Am. Chem. Soc.*, **80**, 5274 (1958).

(811) For a comparison of the mass spectrum and molecular fragmentation patterns of cyclopropane, hexachlorocyclopropane, and their acyclic propene isomers, see E. K. Fields and S. Meyerson, *J. Org. Chem.*, **28**, 1915 (1963).

(812) (a) Recently, analogous isomerization studies have been made on 1,3,5, 2,4,6-$(CF_3)_3C_6F_3$ (M. G. Barlow, R. N. Haszeldine, and M. J. Kershaw, *J. Chem. Soc., Perkin Trans. 1*, 1736 (1973)) but simple regularities still evade the reviews; (b) J. O. Cheswick, *J. Am. Chem. Soc.*, **88**, 4800 (1966).

(813) This logic was earlier introduced by H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).

(814) G. L. Closs and R. B. Larrabee, *Tetrahedron. Lett.*, 287 (1965).

(815) (a) C_3–C_8 cycloalkanes: A. Streitwieser, Jr., R. A. Caldwell, and W. R. Young, *J. Am. Chem. Soc.*, **91**, 529 (1969); (b) C_9–C_{14} cycloalkanes: A. Streitwieser, Jr., and W. R. Young, *ibid.*, **91**, 529 (1969). (c) "The transition state (of deprotonation) has substantially the structural character of the carbanion intermediate" (ref 815 b).

(816) (a) M. T. Bowers, D. H. Aue, H. M. Webb, and R. T. McIver, Jr., *J. Am. Chem. Soc.*, **93**, 4314 (1971); (b) E. M. Arnett, R. M. Jones, III, M. Taagepera, W. G. Henderson, J. L. Beauchamp, D. Holtz, and R. W. Taft, *ibid.*, **94**, 4724 (1972).

(817) (a) J. P. Briggs, R. Yamdagni, and P. Kebarle, *J. Am. Chem. Soc.*, **94**, 5128 (1972); (b) I. Dzidic, *ibid.*, **94**, 8333 (1972).

(818) Leaving aside amines and hydrocarbons, we note other reversals. For example, in the gas phase C_2H_5OH is a stronger acid than CH_3OH (R. T. McIver, Jr., J. A. Scott, and J. M. Riveros, *J. Am. Chem. Soc.*, **95**, 2706 (1973)) while $C_2H_5FH^+$ is a weaker acid than CH_3FH^+ (J. L. Beauchamp, "Ion Cyclotron Resonance", in *Annu. Rev. Phys. Chem.*, **22**, 527 (1971).

(819) (a) E. M. Arnett, *Acc. Chem. Res.*, **6**, 404 (1973); (b) F. M. Jones, III, and E. M. Arnett, *Prog. Phys. Org. Chem.*, **11**, 263 (1974).

(820) H. C. Brown, "Boranes in Organic Chemistry", Cornell University Press, Ithaca, N.Y., 1972, pp 62, 98.

(821) From ref 819b, we find the following order of pK's: quinuclidine > triethylamine > *N*-ethylpiperidine.

(822) T.-Y. Luh and L. M. Stock, *J. Am. Chem. Soc.*, **96**, 3712 (1974).

(823) (a) A. Streitwieser, Jr., and P. H. Owens, *Tetrahedron Lett.*, 5221 (1973). These authors show % s character and acidity of deformed CH species correlate very well although the precise value of % s character is shown to depend on the precise quantum chemical procedure. In line with our discussion in section III.G, tetrahedral CH_4 does not have precisely sp^3 hybridization. (b) A. Streitwieser, Jr., P. H. Owens, R. A. Wolf, and J. E. williams, Jr., *J. Am. Chem. Soc.*, **96**, 5448 (1974).

(824) Experimentally, *tert*-butyl cation is solvated more strongly than 1-adamantyl by at least 4 kcal/mol: R. D. Wieting, R. H. Staley, and J. L. Beauchamp, *J. Am. Chem. Soc.*, **96**, 7552 (1974); **97**, 924 (1975).

(825) (a) Three recent reviews describe the general role of solvent molecules in organic chemistry: ref. 819b; M. H. Abraham and J. M. Harris, all in "Progress in Physical Organic Chemistry", Vol 11, A. Streitwieser, Jr., and R. W. Taft, Ed., Wiley, New York, N.Y., (1974). (b) This conclusion would appear implicit in the Foote–Schleyer correlation of ketone C═O stretching frequencies and solvolysis of secondary alcohol derivatives: C. S. Foote, *J. Am. Chem. Soc.*, **86**, 1853 (1964); P. v. R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(826) J. Slutsky, R. C. Bingham, P. v. R. Schleyer, W. C. Dickerson, and H. C. Brown, *J. Am. Chem. Soc.*, **96**, 1969 (1974), and references cited therein.

(827) F. P. Lossing, *Can. J. Chem.*, **50**, 3973 (1973). In addition to propane and cyclopropane, 1-butene and methylcyclopropane also yield allyl cation. However, one cannot tacitly assume that the most stable carbonium ion is always formed. For example, Lossing also cited that while 1-butyne yields cyclopropenyl cation, the isomeric propargyl cation is formed from the propargyl radical.

(828) We now present an alternative picture. By analogy to our description of paracyclophanes and related species (section XIII.D) and the five- and six-coordinate carbon containing $C_5R_5^+$ and $C_6R_6^{2+}$ (section XVII.D), we suggest that the dication of interest may also be written as $[C(CH_2)_3]^{2+}$. It may simply be shown that extra stability arises as the dication is the three-dimensional analogue of two dimensional "Y-delocalized" species. (For the initial discussion of "Y-delocalization" and numerous two-dimensional examples, see P. Gund, *J. Chem. Educ.*, **49**, 100 (1972).)

(829) A. Akhrem, T. K. Ustynyuk, and Yu. A. Titov, *Russ. Chem. Rev.*, **39**, 732 (1970).

(830) (a) J. M. Conia and J. Salaün, *Tetrahedron Lett.*, 1175 (1963); (b) J. M. Conia and J. Salaün, *Bull. Soc. Chim. Fr.*, 1957 (1964).

(831) R. T. Conley and S. Ghosh in "Mechanisms of Molecular Migrations", Vol. 4, B. S. Thyagarajan, Ed., Wiley, New York, N.Y., 1971).

(832) This intuitive conclusion is borne out by quantum chemical calculations on the relative ease of distorting HCCH and $HCNH^+$ from linearity: P. A. Kollman and J. F. Liebman, unpublished results.

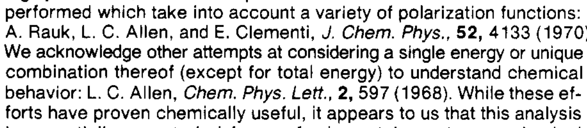
(833) (a) P. Kovacic, J. H. Liu, E. M. Levi, and P. D. Rusk, *J. Am. Chem. Soc.*, **93**, 5801 (1971); (b) S. J. Padegiwias and P. Kovacic, *J. Org. Chem.*, **37**, 2672 (1972).

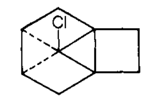
(834) (a) For kinetics comparisons that relate to this general point and compare stabilization of bridgehead carbonium ions by CH_2, NCH_3, S, and O, see H. O. Krabbenoft, J. R. Wiseman, and C. O. Quinn, *J. Am. Chem. Soc.*, **96**, 258 (1974), and references cited therein. (b) Theoretical calculations (P. A. Kollman, W. F. Trager, S. Rothenberg, and J. E. Williams, *J. Am. Chem. Soc.*, **95**, 458 (1973)) show that planar $CH_2NH_2^+$ is stabilized by 96 kcal/mol relative to CH_3^+. As the rotational barrier of $CH_2NH_2^+$ was given as 27 kcal/mol, perpendicular $CH_2NH_2^+$ (i.e., the NH_2 rotated by 90° relative to the CH_2 plane) is thus determined to be $96 - 27 = 69$ kcal/mol stabilized relative to CH_3^+. Analogous results may be deduced for CH_2OH^+ where the perpendicular cation is stabilized by $48 - 17 = 31$ kcal/mol over CH_3^+.

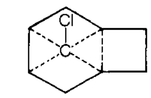
(835) (a) C. C. Lee, "Protonated Cyclopropanes" in *Prog. Phys. Org. Chem.*, **7**, (1970); (b) M. Saunders, P. Vogel, E. L. Hagen, and J. Rosenfeld, *Acc. Chem. Res.*, **6**, 53 (1973).

(836) (a) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 311 (1972); (b) L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, **94**, 5935 (1972).

(837) A. Robbins and G. A. Jeffrey, "Refinement of the Crystal Structure of Tetraphenylmethane", American Crystallographical Association, Ser.

2, Vol. 2, Aug 1974, Abstracts B-11, and personal communications from Drs. A. Robbins and G. A. Jeffrey. It is additionally known that neither $C(HgOOCCF_3)_4$ nor $C(HgOOCCH_3)_4$ has precisely tetrahedral geometry around the carbon, but it is not apparent whether this is due to inter- or intramolecular effects: D. Gardenič, B. Kamenar, B. Korpar-Čolig, M. Sikirica, and G. Jovanoski, *J. Chem. Soc., Chem. Commun.*, 646 (1974).
(838) Substituted tetraphenylmethanes are not simple species stereochemically. (See the analysis of M. G. Hutchings, J. G. Nourse, and K. Mislow, *Tetrahedron,* **30,** 1535 (1974).) We anticipate the crystallographic analyses of such species is likely to be complicated by either disordered crystals or several distinct molecules per unit cell.
(839) C. W. Holt, M. C. L. Gerry, and I. Ozier, *Phys. Rev. Lett.*, **31**, 1033 (1973).
(840) At this time, we feel we should discuss another "myth" concerning the geometry of methane. In elementary discussions of tetracoordinate carbon it is often asserted that a carbon atom "naturally" forms only two bonds since it has the electron configuration $1s^22s^22p^2$ (^3P). In order to be tetracoordinate, one needs to promote and hybridize the carbon atom to $1s^22s^12p^3$ (^5S). We observe that CH_2 is a ground-state triplet (G. Herzberg, "The Spectra and Structures of Free Radicals on Introduction to Molecular Spectroscopy", Cornell University Press, Ithaca, N.Y., 1971, p 140) and thus is "ready" for two more bonds. Equivalently, carbon is "naturally" tetracoordinate although HCF and CF_2 are probably ground-state singlets; G. Herzberg, *ibid.*, pp 123, 167. By the fact that CH_2 is a triplet, in essence, it is already rehybridized.
(841) K. B. Wiberg and G. B. Ellison, *Tetrahedron,* **30,** 1573 (1974).
(842) Highly accurate, all-electron quantum chemical calculations have been performed which take into account a variety of polarization functions: A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, **52,** 4133 (1970)
(843) We acknowledge other attempts at considering a single energy or unique combination thereof (except for total energy) to understand chemical behavior: L. C. Allen, *Chem. Phys. Lett.*, **2,** 597 (1968). While these efforts have proven chemically useful, it appears to us that this analysis is essentially a posteriori from a fundamental quantum mechanical viewpoint: I. Kramer and J. F. Liebman, unpublished results.
(844) G. Snatzke and G. Zanati, *Justus Liebigs Ann. Chem.*, **684,** 62 (1965).
(845) F. Nernd, K. Janowsky, and D. Frank, *Tetrahedron Lett.*, 2979 (1965).
(846) J. Altman, Z. Bad, J. Itzchaki, and D. Ginsburg, *Tetrahedron Suppl.*, **8** (1), 279 (1966).
(847) (a) D. Ginsburg, *Acc. Chem. Res.*, **2,** 121 (1969); (b) *ibid.*, **5,** 249 (1972); (c) *Tetrahedron*, **30,** 1487 (1974).
(848) (a) J. J. Bloomfield and R. E. Moser, *J. Am. Chem. Soc.*, **90,** 5625 (1968); (b) S. C. Neely, C. Fink, D. Van Der Helm, and J. J. Bloomfield, *ibid.*, **93,** 4903 (1971). (c) The pink color has been attributed to inter-ring interactions. Such interactions are rather general in propellane chemistry. See, for example, L. A. Paquette and G. L. Thompson, *ibid.*, **94,** 7118 (1972).
(849) K. B. Wiberg, G. J. Burgmaier, K.-W. Shen, S. J. La Placa, W. C. Hamilton, and M. D. Newton, *J. Am. Chem. Soc.*, **94,** 7402 (1972).
(850) W.-D. Stöhrer and R. Hoffmann, *J. Am. Chem. Soc.*, **94,** 778 (1972).
(851) M. D. Newton and J. M. Schulman, *J. Am. Chem. Soc.*, **94,** 4392 (1972).
(852) J. F. Liebman and J. S. Vincent, *J. Am. Chem. Soc.*, **97,** 1373 (1975).
(853) Newton and Schulman (ref 197) give values of strain energy per bond. The same conclusion may be deduced from strain energy per carbon atom (see section XV for a comparison of the two methods in general). The numerical values, however, markedly differ: bicyclobutane, [1.1.1]propellane, and tetrahedrane—SEb = 13, 15, and 23 kcal/mol, respectively; SEc = 16, 22, and 34 kcal/mol, respectively. Conclusions as to the eventual isolation of [1.1.1]propellane and tetrahedrane differ accordingly.
(854) We estimated the heat of formation of 1,2-dimethylenecyclopropane by the following bond additivity relations (see Table VI):


The value was the higher of the two values just obtained.
(855) Reference 742, pp 76–78.
(856) From ref 855 we find that 2,4-disubstituted bicyclobutanes, either both endo or exo, yield cis-trans 1,4-disubstituted butadienes. This logic has already been employed in explaining the high thermal stability of bicyclobutane so joined by a -CH=CH- group, i.e., benzvalene (see section IX). This suggests that a small [*n*.1.1]propellane may be likewise stabilized with regard to thermal decomposition by connecting the "1" bridges. Doing so trades the "superstrain" in the propellane for a substantial amount in the resultant cis-trans cycloalkadiene. Thermochemical data are unfortunately absent on such species, but we may make reasonable estimates by adding the strain energies of "normal", *cis*-cycloalkenes (Table VI) and *trans*-cycloalkenes (Table VIII). An eminently reasonable compound is [2.1.1]propellane with the "1" bridges joined by $-CH_2-CH_2-$.
(857) C. F. Wilcox, Jr. and C. Leung, *J. Org. Chem.*, **33,** 577 (1968).
(858) M. R. Rifi, *Collect. Czech. Chem. Commun.*, **36,** 932 (1971).
(859) K. B. Wiberg and G. J. Burgmaier, *J. Am. Chem. Soc.*, **94,** 7316 (1972).
(860) The facile synthesis and isolation of the precursor olefin, **78** (ref 329b,c) suggest some new options for [2.2.1]propellane syntheses which are now in progress: K. B. Wiberg, personal communication.
(860) (a) K. B. Wiberg, J. E. Hiatt, and G. J. Burgmaier, *Tetrahedron Lett.*, 5955 (1968); (b) K. B. Wiberg and G. J. Burgmaier, *ibid.*, 317 (1969); (c) K. B. Wiberg, B. C. Lupton, and G. J. Burgmaier, *J. Am. Chem. Soc.*, **91,** 3372 (1969).
(861) (a) P. G. Gassman, A. Topp, and J. W. Keller, *Tetrahedron Lett.*, 1093 (1969); (b) P. G. Gassman and E. A. Armour, *ibid.*, 1431 (1971).
(862) D. H. Aue and R. N. Reynolds, *J. Org. Chem.*, **39,** 2315 (1974).
(863) D. H. Aue, personal communication.
(864) P. Warner and R. LaRose, *Tetrahedron Lett.*, 2141 (1972).
(865) P. Warner, R. LaRose, C.-M. Lee, and J. C. Clardy, *J. Am. Chem. Soc.*, **94,** 7607 (1972). Direct comparison with the saturated and doubly unsaturated (propelladiene) compound would be of interest since the saturated dichloro[3.2.1]propellane appears relatively stable (ref 849). We anticipate that the rearrangement is so rapid because the intermediate cyclopropyl cations are stabilized by interaction with the olefinic π cloud. Furthermore, we may reformulate the cyclopropyl cations as a bishomocyclopropenyl cation, **365b,** or even as a square-pyramidal $C_5H_5^+$ derivative, **365c** (see section XVII.D). As such the monochloro analog of **365** would be of considerable interest.


365b


365c
(866) The more exact calculations of ref 851 decrease the energy barrier between the two isomers of [2.2.2]propellane relative to the value predicted in ref 850. However, the geometric predictions, i.e., the structures of the isomers, are essentially unchanged. In general, predictions of molecular structure are far easier to do and far more reliable than corresponding predictions of energy differences.
(867) K. B. Wiberg and G. A. Epling, *J. Am. Chem. Soc.*, **96,** 912 (1974).
(868) J. J. Dannenberg, T. M. Procliv, and C. Hutt, *J. Am. Chem. Soc.*, **96,** 913 (1974).
(869) J. J. Gajewski, L. K. Hoffman, and C. N. Shih, *J. Am. Chem. Soc.*, **96,** 3705 (1974).
(870) P. E. Eaton and G. H. Temme III, *J. Am. Chem. Soc.*, **95,** 7508 (1973).
(871) G. Märkl and A. Mayl, *Tetrahedron Lett.*, 1817 (1974).
(872) H. Bohm, J. Kalo, C. Varnitzky, and D. Ginsburg, *Tetrahedron*, **30,** 217 (1974).
(873) R. Hoffmann, A. Imamura, and W. J. Hehre, *J. Am. Chem. Soc.*, **90,** 1499 (1968).
(874) E. Heilbroner and K. A. Muszkrat, *ibid.*, **93,** 3818 (1972).
(875) Y. Onemitsu, H. Nakai, Y. Kamaoka, I. L. Karle and B. Witkop, **91,** 4591 (1969).
(876) (a) R. E. Pincock and E. J. Torupka, *J. Am. Chem. Soc.*, **91,** 4593 (1969); (b) R. E. Pincock, J. Schmidt, M. B. Scott, and E. J. Torupka, *Can. J. Chem.*, **50,** 3958 (1972); (c) W. B. Scott and R. E. Pincock, *J. Am. Chem. Soc.*, **95,** 2040 (1973).
(877) From ref 876b, we find that the initial product is the Br_3^- salt of the 3-bromoadamantyl diethyloxonium ion. Warming this isolable product then forms the 1,3-dibromoadamantane, formally produced by Br_2 addition across the "exotic" C–C bond.
(878) C. S. Gibbons and J. Trotter, *Can. J. Chem.*, **51,** 87 (1973).
(879) See ref 876b. Reduction of tetrahaloadamantanes yielded **307** instead of the desired **308.**
(880) D. B. Ledlie, J. Knetzer, and A. Gitterman, *J. Org. Chem.*, **39,** 709 (1974).
(881) P. Warner, J. Fayus, and J. Clardy, *Tetrahedron Lett.*, 4473 (1973).
(882) E. H. Hahn, H. Bohm, and D. Ginsburg, *Tetrahedron Lett.*, 507 (1973).
(883) We note at this time that the set of numbers *m, n, p* and *q* do not define a paddlane uniquely. If *m, n, p,* and *q* are different, then paddlanes may exist with these bridges (*m, n, p, q* and *m, n, q, p*). If $m = n$ and $p = q$, we have (*m, m, p, q*) and (*m, p, m, q*) while if $m = n$ and $p = q$, we have (*m, m, p, p*) and (*m, p, m, p*). The reader may recognize this discussion as analogous, indeed equivalent, to that of the possible number of isomers of variously substituted planar methanes and recall that this provided considerable support for tetrahedral carbon. However, for the paddlane case, we are too ignorant to anticipate the relative stability and interconversion of various isomers or even to quantitatively ascertain the range of possible values for (*m, n, p, q*).
(884) R. Helder and H. Wynberg, *Tetrahedron Lett.*, 4317 (1971). These authors also suggested the possibility of planar tetracoordinate carbon if *n* is small enough.
(885) C. F. H. Allen and J. A. Van Allan, *J. Org. Chem.*, **18,** 882 (1953).
(886) The reaction of [3.2.1]propellanes with species with double or triple bonds would appear to be a possible route to [3.2.1.2]- or [3.2.2.1]paddlanes. However, the reaction of the parent [3.2.1]propellane and the [2½.2.1]propellane, **364,** with dimethyl acetylenedicarboxylate instead yield derivatives of 4-methylene-spiro[2.6]non-1-ene and 1,5-divinylbicyclo[3.2.1]non-6-ene (ref 862). One may not, however, conclude that [3.2.1.2]- or [3.2.2.1]paddlanes are inherently unisolable. The above propellane–acetylene reactions are "forbidden" (2 + 2) cycloaddition reactions between a "free" cyclopropane and an acetylene to yield a cyclopentene: Woodward and Hoffmann, ref 872, pp 12–21). While the "free" cyclopropene–acetylene reaction is highly exothermic (ca. 60 kcal/mol), we cannot estimate the total strain energy change going from the propellane to the paddlane. The analogous reactions of the oxapropellanes with the acetylene would prove of interest since the ring-opened epoxide $^{\delta-}C{=\!=}O^{\delta+}{=\!=}C^{\delta-}$ may add to acetylene in an allowed (4 + 2) reaction (see Woodward and Hoffmann, ref 872, pp 57–58 for discussion of an isoelectronic example of an aziridine–acetylene addition reaction). Admittedly, the ring-opened form of the propellanes would violate Bredt's rule but we are reminded of the cationic rearrangement **365a** → **366a** → **366.** Furthermore, the "doubly Bredt-violating" anion would be relatively stable since carbanions tend to be pyramidal (section XVI.C). As a final suggestion, we recall that ketenes readily add olefins in an "allowed" reaction (Woodward and Hoffmann, ref 872, pp 163–168) and thus suggest the reaction of the above propellanes with ketenes. We conclude by noting that all of our thoughts above apply to any propellane.

(887) H. Nozaki, T. Koyama, and T. Mori, *Tetrahedron*, **25**, 5357 (1961).
(888) D. H. Aue, personal communication. As this is a multiphase reaction, and competitive kinetics were not employed, it cannot provide a quantitative comparison. Nonetheless, the qualitative conclusion remains intact and analogous comparisons between other pairs of compounds in the section would be of interest.
(889) The mathematical analysis, admittedly fraught with unforeseen subtleties, is in progress: D. Houck and J. F. Liebman, unpublished results.
(890) H. J. Monkhorst, *Chem. Commun.*, 1111 (1968).
(891) R. Hoffmann, R. W. Alder, and C. F. Wilcox, *J. Am. Chem. Soc.*, **92**, 4992 (1970).
(892) W. A. Lathan, W. J. Hehre, C. A. Curtiss, and J. A. Pople, *J. Am. Chem. Soc.*, **93**, 6377 (1971).
(893) S. Durmaz, J. N. Murrell, and J. B. Pedley, *J. Chem. Soc., Chem. Commun.*, 933 (1972).
(894) R. A. Firestone, *J. Chem. Soc., Chem. Commun.*, 163 (1973).
(895) S. Palalikit, P. C. Hariharan, and I. Shavitt, unpublished results; personal communication from Dr. Isaiah Shavitt.
(896) P. v. R. Schleyer, J. Collins, J. Dill, Y. Apeloig, and J. A. Pople, unpublished results; P. v. R. Schleyer, personal communication.
(897) A quote seems appropriate at this time: "Attempts to subvert something as basic to organic chemistry as the tetrahedral tetracoordinate carbon atom should perhaps as acts be appropriately described by the Yiddish word *chutzpah* and/or the Greek *hubris*": R. Hoffmann, *Pure Appl. Chem.*, **28**, 181 (1971). This, though the quote and italics are Hoffmann's, did not prevent him from such a theoretical study (see ref 10.)
(898) V. Georgian and M. Saltzman, *Tetrahedron Lett.*, 4315 (1972).
(899) The reader may alternatively recognize this compound as neopentane joined by four methylene chains (cf. our paddlane discussion in the previous subsection) and additionally note that [1]diadamantane (**16**) may also be described in this way.
(900) Appropriately functionalized fenestranes are being synthesized that should allow systematic ring contractions eventually to the desired [4.4.4.4] compound: V. Georgian and M. Saltzman, personal communication.
(901) J. E. Richman and H. E. Simmons, *Tetrahedron*, **30**, 1769 (1974).
(902) This result may be rationalized by noting that the square-planar form corresponds in a valence shell electron pair theory sense[28] to a six-coordinated species, while the square-pyramidal is a not uncommon form of five-coordination. As five is closer to four than six is, square-pyramidal is more "reasonable" than square planar.
(903) This does not mean that corresponding calculations on ethane or other hydrocarbons are easily obtained. While conceptually there is no problem, a quantum chemical "folkrule" says that the financial expense of a calculation (at a given accuracy level) increases as the 4.5th power of the number of electrons. Accordingly, going from CH_4 to C_2H_6 increases the price by $(18/10)^{4.5}$ or ca. 14-fold. Furthermore, geometry searches gain expense even more rapidly as the molecular complexity increases. For example, in an investigation of ethane, one would like to consider the staggered and eclipsed rotamers, one and both carbons "planarized" and their respective rotamers, and even a bridged diborane-like structure. Indeed, the question of when a substituted ethane is bridged parallels the current one of when a substituted methane is planar. We refer the reader to R. Hoffmann and J. E. Williams, Jr. *Helv. Chim. Acta*, **55**, 67 (1972), where such a comparison is made, although at a computational and conceptual level paralleling ref 891 and not ref 895 and 896.
(904) We parenthetically note that the σ^* state of spiropentane has been predicted to be square planar: R. Hoffmann, *Tetrahedron Lett.*, 3819 (1965).
(905) K. J. Drachenberg and H. Hopf, *Tetrahedron Lett.*, 3267 (1974).
(906) G. A. Olah, "Carbocations and Electrophilic Reactions", Wiley, New York, N.Y., 1974.
(907) An alternative possibility of going through ion pairs and triplets was recently discussed and largely dismissed: N. F. Raaen, T. Juhlke, F. J. Brown, and C. J. Collins, *J. Am. Chem. Soc.*, **96**, 5928 (1974).
(908) The literature of these species, the "carboranes", is extensive and we merely cite the following recent and general reviews: G. B. Dunksgard and M. F. Hawthorne, *Acc. Chem. Res.*, **6**, 124 (1973); M. F. Hawthorne, K. R. Callahan, and R. J. Wiersma, *Tetrahedron*, **30**, 1795 (1974). For theoretical systematics of these species, we note K. Wade, *Chem. Commun.*, 792 (1971); R. E. Williams, *Inorg. Chem.*, **10**, 210 (1971); R. W. Rudolph, *ibid.*, **11**, 1974 (1972); K. Wade, *Inorg. Nucl. Chem. Lett.*, **8**, 559 (1972).
(909) This does not mean that no connections can be made. One way contrasts the closo structure of $B_6H_6^{2-}$ (or $B_4C_2H_6$) with the nido structure of $C_5H_5^+$ and $C_6(CH_3)_6^{2+}$ (to be discussed later in this subsection) and the arachno structure of benzvalene (see section IX): K. Wade, *New Sci.*, **62**, 615 (1974), and references cited in ref 908). Application has also been made to metal-hydrocarbon π complexes [K. Wade, *Inorg. Nucl. Chem. Lett.*, **8**, 563 (1972)], but these are admittedly beyond the scope of our review.
(910) We admit sloppiness in the word "carbonium ion" in our writing (see ref 905) but note that it is indeed correct in this context.
(911) See ref 212. In this pioneering study on this species, Stohrer and Hoffmann interrelated $C_5H_5^+$, the related anions $C_5H_5^-$ and $C_5H_5^{3-}$, the boron hydride B_5H_9, and also various derivatives.
(912) (a) H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5834 (1973); (b) W. J. Hebre and P. v. R. Schleyer, *ibid.*, **95**, 5838 (1973).
(913) (a) M. J. S. Dewar and R. C. Haddon, *J. Am. Chem. Soc.*, **95**, 5836 (1973); (b) *ibid.*, **96**, 255 (1974).
(914) M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, Jr., C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *J. Am. Chem. Soc.*, **95**, 3017 (1973).
(915) (a) R. Breslow, R. Hill, and E. Wasserman, *J. Am. Chem. Soc.*, **86**, 5349 (1964); (b) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *ibid.*, **89**, 1112 (1967); (c) R. Breslow, H. W. Chang, and W. A. Yager, *ibid.*, **85**, 2033 (1963).
(916) (a) W. Brosser, H. Kurreck, and P. Siegle, *Chem. Ber.*, **100**, 788 (1967). (b) W. Brosser, P. Siegle, and H. Kurreck, *ibid.*, **101**, 69 (1969). The singlet-triplet energy differences in all of the pentaaryl derivatives presented was <1 kcal/mol.
(917) (a) S. Masamune, M. Sakai, and H. Ona, *J. Am. Chem. Soc.*, **94**, 8955 (1972); (b) S. Masamune, M. Sakai, H. Ona, and A. J. Jones, *ibid.*, **94**, 8966 (1972).
(918) (a) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **94**, 8558 (1972); (b) *Tetrahedron Lett.*, 4123 (1973).
(919) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **96**, 6436 (1974).
(920) (a) S. Masamune, M. Sakai, and A. V. Kemp-Jones, *Can. J. Chem.*, **52**, 588 (1972); (b) S. Masamune, M. Sakai, A. V. Kemp-Jones, H. Ona, A. Venot, and T. Nakashina, *Angew. Chem., Int. Ed. Engl.*, **12**, 769 (1973); (c) A. V. Kemp-Jones, N. Nakamura, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 1001 (1974).
(921) However, contrary to theoretical predictions (ref 912b), apical methyl substitution appears to destabilize the square-pyramidal cation. An analogous conflict of theory and experiment was also found for basal phenyl substitution. These results of Professor Harold Hart and Dr. Masayuki Kuzuya have been simply reconciled by them (personal communication): . . . "replacement of the apical hydrogen . . . by a methyl group, or presumably any electron donor which would increase the amount of positive charge on the apical carbon atom, facilitates cyclobutane ring contraction very much more than it stabilizes the pyramidal structure" (H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **97**, 2459 (1975)). Furthermore, "the phenyl rings must be unable to exert their usual conjugative stabilizing effect and in fact exhibit a destabilizing electron-withdrawing effect . . . and is probably a consequence of twisting of the phenyl rings in a canted face-to-face orientation as a result of steric crowding" (H. Hart and M. Kuzuya, *ibid.*, **97**, 2450 (1975)). We note that these results have been presented in that C_{4v} square-pyramidal $C_5H_5^+$ with an apical, electron-donating substituent O^- is unstable relative to distortion and forms ketohomotetrahedrane, **29** (ref 212). Likewise, we know of no tendency of cyclopentadienones to scramble to aryl substituents through such a C_{4v} intermediate.
(922) R. K. Lustgarten, *J. Am. Chem. Soc.*, **94**, 7602 (1972).
(923) H. Hart and M. Kuzuya, personal communication.
(924) We note that the (mono)homocyclopropenyl cation has only recently been prepared and characterized: (G. A. Olah, J. S. Staral, and G. Liang, *J. Am. Chem. Soc.*, **96**, 6233 (1974). Available comparison of the cyclopropenyl cation and cyclobutadiene dication (**90** and **92**) strongly suggests that the homocyclobutadiene dication will be markedly less stable than the above cited homocyclopropenyl cation.
(925) (a) R. K. Lustgarten, M. Brockhart, and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6350 (1967); (b) *ibid.*, **94**, 2347 (1972).
(926) (a) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1655 (1973); (b) H. T. Jonkman and W. C. Nieuport, *ibid.*, 1671 (1973); (c) H. Hogeveen and P. W. Kwant, *J. Am. Chem. Soc.*, **96**, 2208 (1974).
(927) E. Wasserman, R. S. Hutton, V. J. Kuck, and E. A. Chandross, *J. Am. Chem. Soc.*, **96**, 1965 (1974).
(928) R. L. Timms, *Acc. Chem. Res.*, **6**, 118 (1973).
(929) While we acknowledge comparisons of *o*-, *p*-, and even *m*-quinones [M. J. S. Dewar and G. J. Gleicher, *J. Chem. Phys.*, **44**, 759 (1966)], we know of no study that interrelates these species with other isomers such as the pentagonal pyramid or the α-diketone corresponding to Dewar benzene **132** or benzvalene, **133**.
(930) We quote "The randomization of carbon and hydrogen atoms in benzene which occurs on electron impact is analogous to the numerous skeletal rearrangements in the benzene series that occur on photolysis. The rearrangements of the benzene molecule ion must proceed through structures that are related to known products of benzene photolysis, i.e., benzvalene (**133**), prismane (**134**), Dewar benzene (**132**), and hexadienyne": R. G. Dougherty, *Top. Curr. Chem.*, **45**, 93 (1974). We have taken the liberty of inserting our compound numbers in place of the author's—his were **38, 39,** and **40,** respectively. Dougherty's comparison and generalization interrelates the reactions of radical cations and neutrals while our earlier treatment dealt more with structural and inherent stability considerations.
(931) Reference 919, footnote 6.
(932) Quantitation of this model by more rigorous theory is severely complicated by the large number of orbitals of closely lying energy. These difficulties have been recently resolved and thus a more definitive, quantitative understanding of these ions is in progress: J. F. Harrison and H. Hart, personal communication.
(933) A qualitative model has been devised that explains the geometry of these $(CH)_4$, $(CH)_5^+$ and $(CH)_6^{2+}$ species as well as many of the boron species described in ref 908 and 909, benzvalene (formally $CH^+ + C_5H_5^-$, not C_{5v} symmetry), 7-norbornadienyl cation (formally $CH^+ + C_6H_6$, not C_{6v} symmetry), and barbaryl cation (formally $(CH^+ + C_8H_8$, not C_{8v} symmetry): J. F. Liebman, unpublished results derived from the author's paper, *J. Am. Chem. Soc.*, **96**, 3053 (1974). We note that neither C_{8v} $C_9H_9^+$ nor barbaryl cation is lowest energy isomer but rather a distorted cyclononatetraenyl cation appears to be: M. J. S. Dewar, unpublished results. As noted in ref 866, predictions of energetics seems to require quantitative understanding in great excess of that required for prediction of geometry.
(934) O. Ermer, *Tetrahedron*, **31**, 1849 (1975).
(935) See discussion relating to obstacles introduced in using high-accuracy quantum calculations to obtain thermochemical data: J. S. Binkley, J. A. Pople, and W. J. Hehre, *Chem. Phys. Lett.*, **36**, 1 (1975).
(936) L. S. Bartell, S. Fitzwater, and W. J. Hehre, *J. Chem. Phys.*, **63**, 4750 (1975).
(937) C. L. Perrin, *J. Am. Chem. Soc.*, **97**, 4419 (1975).
(938) M. Aquillacote, R. S. Sheridan, O. L. Chapman, and F. A. L. Anet, *J. Am.*

Chem. Soc., 3244 (1975).
(939) W. Burns, M. A. McKervey, and J. J. Rooney, *J. Chem. Soc., Chem. Commun.*, 965 (1975).
(940) T. Clark, T. M. Knox, H. Mackle, M. A. McKervey, and J. J. Rooney, *J. Am. Chem. Soc.*, **97**, 3836 (1975).
(941) W. Parker, W. V. Steele, W. Stirling, and I. Watt, *J. Chem. Thermodyn.*, **7**, 795 (1975).
(942) D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Am. Chem. Soc.*, **97**, 4136 (1975).
(943) See discussions relating to isoelectronic principles in ref 823a and b.
(944) M. Pomerantz and R. Fink, *J. Chem. Soc., Chem. Commun.*, 430 (1975).
(945) W. J. Hehre and J. A. Pople, *J. Am. Chem. Soc.*, **97**, 6941 (1975).
(946) P. J. Stang and M. C. Mangum, *J. Am. Chem. Soc.*, **97**, 3854 (1975).
(947) H.-D. Becker and B. Ruge, *Angew. Chem., Int. Ed. Engl.*, **14**, 761 (1975).
(948) W. R. Roth and G. Wegener, *Angew. Chem., Int. Ed. Engl.*, **14**, 758 (1975).
(949) W. E. Billups, B. A. Baker, W. Y. Chow, K. H. Leavell, and E. S. Lewis, *J. Org. Chem.*, **40**, 1702 (1975).
(950) (a) T. Kobayashi, I. Kumadaki, A. Ohsawa, Y. Hanzawa, M. Honda, and Y. Iitaka, *Tetrahedron Lett.*, 3001 (1975); (b) T. Kobayashi, I. Kumaki, A. Ohsawa, Y. Hanzawa, and M. Honda, *ibid.*, 3819 (1975).
(951) G. Maier and W. Sauer, *Angew. Chem., Int. Ed. Engl.*, **14**, 648 (1975).
(952) J. P. Mykytka and W. M. Jones, *J. Am. Chem. Soc.*, **97**, 5933 (1975).
(953) R. Breslow, J. Napierski, and T. C. Clarke, *J. Am. Chem. Soc.*, **97**, 6275 (1975) [footnote 9 in R. R. Jones and R. G. Bergman, *ibid.*, **94**, 660 (1972), discusses the apparent diradical nature of the 1,4-dehydrobenzene generated at elevated temperature.]
(954) N. P. Adams, I. Kramer, and J. F. Liebman, unpublished results.
(955) A. Florey and P. Vogel, *Helv. Chim. Acta*, **58**, 1488 (1975).
(956) W. Marsh and J. D. Dunitz, *Helv. Chim. Acta*, **58**, 707 (1975).
(957) R. D. Miller and M. Schneider, *Tetrahedron Lett.*, 1557 (1975).
(958) H. Dürr and B. Weiss, *Angew. Chem., Int. Ed. Engl.*, **14**, 646 (1975).
(959) W. H. deWolf, I. J. Landheer, and F. Bickelhaupt, *Tetrahedron Lett.*, 179 (1975).
(960) J. Barltrop, R. Carder, A. C. Day, J. R. Harding, and C. Samuel, *J. Chem. Soc., Chem. Commun.*, 729 (1975).
(961) R. D. Chambers, K. Middleton, and R. P. Corbally, *J. Chem. Soc., Chem. Commun.*, 731 (1975).
(962) R. Weiss and H. Kölbl, *J. Am. Chem. Soc.*, **97**, 3222, 3224 (1975).
(963) N. J. Turro, G. B. Schuster, R. G. Bergman, K. J. Shea, and J. H. Davis, *J. Am. Chem. Soc.*, **97**, 4758 (1975).
(964) R. Keese, *Angew. Chem., Int. Ed. Engl.*, **14**, 528 (1975).
(965) P. M. Warner, R. C. LaRose, R. F. Palmer, C. Lee, D. O. Ross, and J. C. Clardy, *J. Am. Chem. Soc.*, **97**, 5507 (1975).
(966) M. Christl and M. Lecher, *Angew. Chem., Int. Ed. Engl.*, **14**, 765 (1975).
(967) T. A. Wnuk and P. Kovacic, *J. Am. Chem. Soc.*, **97**, 5807 (1975).
(968) C. A. Grob and A. Sieber, *Helv. Chim. Acta*, **50**, 2531 (1967).
(969) P. G. Gassman, R. L. Cryberg, and K. Shudo, *J. Am. Chem. Soc.*, **94**, 7600 (1972).
(970) H. Hart and M. Suzuki, *Tetrahedron Lett.*, 4327 (1975).
(971) E. Vogel, J. Sombroek, and W. Wagemann, *Angew. Chem., Int. Ed. Engl.*, **14**, 564 (1975).
(972) F. A. L. Anet and I. Yavari, *J. Chem. Soc., Chem. Commun.*, 927 (1975).
(973) W. R. Dolbier, Jr., O. T. Garza, and B. H. Al-Sader, *J. Am. Chem. Soc.*, **97**, 5038 (1975).
(974) M. Oda, Y. Ito, and Y. Kitahara, *Tetrahedron Lett.*, 2587 (1975).
(975) N. L. Allinger and A. Y. Meyers, *Tetrahedron*, **31**, 1807 (1975).
(976) P. G. Gassman and J. J. Valcho, *J. Am. Chem. Soc.*, **97**, 4768 (1975).
(977) P. G. Gassman and T. J. Atkins, *Tetrahedron Lett.*, 3035 (1975).
(978) E. Kloster-Jensen and J. Wirz, *Helv. Chim. Acta*, **58**, 162 (1975).
(979) H. B. Bürgi and E. Shefter, *Tetrahedron*, **31**, 2976 (1975).
(980) H. Günther and W. Herrig, *J. Am. Chem. Soc.*, **97**, 5594 (1975).
(981) D. Davalian and P. J. Garratt, *J. Am. Chem. Soc.*, **97**, 6883 (1975).
(982) C. J. Saward and K. P. C. Vollhardt, *Tetrahedron Lett.*, 4539 (1975).
(983) F. Toda and M. Oshi, *J. Chem. Soc., Chem. Commun.*, 506 (1975).
(984) H. Dürr and H. Schmitz, *Angew. Chem., Int. Ed. Engl.*, **14**, 647 (1975).
(985) R. Pozzi, K. R. Ramaprasad, and E. A. C. Lucken, *J. Mol. Struct.*, **28**, 111 (1975).
(986) I. B. Goldberg, H. R. Crane, and R. W. Franck, *J. Phys. Chem.*, **79**, 1741 (1975).
(987) We note that one may place an aromatic solvent in contact with potassium metal film and addition of crown ether will generate the encapsulated cation and solvated electrons which form radical anions of the aromatic compound; see B. Kempf, S. Raynal, A. Collet, F. Schue, S. Boileau, and J. M. Lehn, *Angew. Chem., Int. Ed. Engl.*, **13**, 611 (1974).
(988) S. Hirano, H. Hara, T. Hiyama, S. Fujita, and H. Nozaki, *Tetrahedron*, **31**, 2219 (1975).
(989) J. W. van Straten, I. J. Landheer, W. H. deWolf, and F. Bickelhaupt, *Tetrahedron Lett.*, 4499 (1975). See ref 5 in this paper in which the authors mention that K. Weiniges et al. have also generated [5]paracyclophane.
(990) See footnote 188 in L. A. Paquette, *Tetrahedron*, **31**, 2285 (1975).
(991) F. Vögtle and G. Hohner, *Angew. Chem., Int. Ed. Engl.*, **14**, 497 (1975).
(992) T. Unemoto, S. Satani, Y. Sakata, and S. Misumi, *Tetrahedron Lett.*, 3159 (1975).
(993) K. C. Janda, J. C. Hemminger, J. S. Winn, S. E. Novick, S. J. Harris, and W. Klemperer, *J. Chem. Phys.*, **63**, 1419 (1975). These authors' proposal is in accord with P. Kollman's model of the directionality of hydrogen bonds [*J. Am. Chem. Soc.*, **94**, 1837 (1972)]; cf. a $C{\equiv}C\cdots H{-}C_6H_5$ hydrogen bond, and our earlier discussion of secondary orbital effects in paracyclophanes (section XIII.D).
(994) S. Obenland and W. Schmidt, *J. Am. Chem. Soc.*, **97**, 6633 (1975).
(995) H. Dietrich, D. Bladauski, M. Grosse, K. Roth, and D. Rewicki, *Chem. Ber.*, **108**, 1807 (1975).
(996) J. M. Schulman, T. Venanzi, and R. L. Disch, *J. Am. Chem. Soc.*, **97**, 5335 (1975).
(997) T. Clark, T. M. Knox, H. Mackle, and M. A. McKervey, *J. Chem. Soc., Chem. Commun.*, 666 (1975).
(998) L. A. Paquette, I. Itoh, and W. Farnham, *J. Am. Chem. Soc.*, **97**, 7280 (1975).
(999) (a) D. P. G. Hamon and G. F. Taylor, *Tetrahedron Lett.*, 155 (1975); (b) H. Tobler, R. O. Klaus, and C. Ganter, *Helv. Chim. Acta*, **58**, 1455 (1975).
(1000) T. Katsushima, R. Yamaguchi, and M. Kawanisi, *J. Chem. Soc., Chem. Commun.*, 692 (1975).
(1001) A. P. Marchand, T.-C. Chou, and M. Barfield, *Tetrahedron Lett.*, 3359 (1975).
(1002) G. Felix, R. Lapouyade, A. Castellan, and H. Bovas-Laurent, *Tetrahedron Lett.*, 409 (1975).
(1003) D. G. Farnum and A. A. Hagedorn, III, *Tetrahedron Lett.*, 3987 (1975).
(1004) N. C. Yang, C. V. Neywick, and K. Srinivasachar, *Tetrahedron Lett.*, 4313 (1975).
(1005) M. Randic, *J. Am. Chem. Soc.*, **97**, 6609 (1975).
(1006) J. B. Hendrickson, *J. Am. Chem. Soc.*, **97**, 5763 (1975).
(1007) A. Esack, *J. Chem. Soc., Perkin Trans. 1*, 1120 (1975).
(1008) E. J. Corey, W. J. Howe, H. Worf, D. A. Pensak, and G. Peterson, *J. Am. Chem. Soc.*, **97**, 6116 (1975).
(1009) D. J. Houck and J. F. Liebman, unpublished results.
(1010) A. Domenico, A. Vaciago, and C. A. Coulson, *Acta Crystallogr., Sect. B*, **31**, 221, 1630 (1975).
(1011) For example, "substitution" of CF_3 for CH_3 in propene shortens and presumably strengthens both the olefinic linkage and the $C_d{-}CX_3$ bond, while "substitution" of geminal CF_3's for the CH_3's in isobutylene lengthens and presumably weakens both bonds; see A. Yokozeki and S. H. Bauer, *Top. Cur. Chem.*, **53**, 71 (1975), for a review of electron diffraction results on fluorocarbons.
(1012) (a) M. G. Hutchings, J. D. Andose, and K. Mislow, *J. Am. Chem. Soc.*, **97**, 4553, 4562 (1975); (b) J. G. Nourse and K. Mislow, *ibid.*, **97**, 4571 (1975).
(1013) M. E. Jason and J. A. McGinnety, *Inorg. Chem.*, **14**, 3025 (1975).
(1014) H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975).
(1015) J. B. Collins, J. D. Dill, E. D. Jemmis, Y. Apeloig, P. v. R. Schleyer, R. Seeger, and J. A. Pople, *J. Am. Chem. Soc.*, in press.
(1016) C. F. Wilcox, Jr., and G. D. Graham, *J. Org. Chem.*, **40**, 1974 (1975).