

CHAPTER 8

Cyclopropyl homoconjugation —Experimental facts and interpretations

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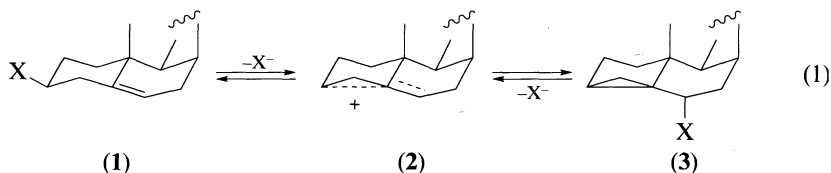
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I. INTRODUCTION

Homoconjugation has a long and important history in organic chemistry. Its importance goes well beyond the specific phenomenon itself as the concept has led to a large amount of work directed towards understanding conjugation and its role in determining the properties of an organic molecule.

The initial suggestion that a remote double bond could be involved in a displacement reaction was made by Shoppee in 1946 in order to account for the stereochemical results of the transformations of 3-cholesteryl derivatives¹. Building on the considerable work then underway on neighbouring group participation in ionization reactions^{2,3}, Shoppee suggested that the double bond in the cholesteryl system, **1**, could function in a similar manner to Lewis base containing groups such as acetate or alkoxy, etc.

Further studies on the cholesteryl/*i*-cholesteryl system were reported by Dodson and Reigel⁴ and particularly by Winstein and his coworkers^{5,6}. This early work showed that the interconversion of the two cholesteryl derivatives, one of which has an open or 'homoallyl' form **1** and the other a 'cyclopropylcarbinyl' form **3**, could be understood in terms of the intermediate **2** (equation 1). Electron delocalization in **2** was suggested to occur across the intervening carbon atom rather than between adjacent carbon atoms as in normal conjugated systems.



In 1950 both Winstein, Walborsky and Schreiber⁷ and Roberts, Bennett and Armstrong⁸ independently broadened the concept from the cholesteryl system starting point to a range of other examples including the norbornenyl cations. Winstein and colleagues used the terms homoallyl and homoconjugation to describe the phenomenon, terms which have become widely adopted. On the other hand, Roberts and coworkers suggested the phenomenon be called hyperconjugation. The importance of the correct geometry for homoconjugation was recognized at this early stage of development. Simonetta and Winstein made early use of theory in the form of Hückel calculations to explore the phenomenon⁹.

The expansion of the concept to encompass cyclic electron delocalization or homoaromaticity occurred in the late 1950s. In 1956 Applequist and Roberts pointed out that the cyclobutenyl cation resembles the cyclopropenium cation¹⁰. Doering and colleagues suggested that the cycloheptatriene carboxylic acids could be regarded as planar pseudoaromatic type structures with a homoconjugative interaction between C(1) and C(6)¹¹. Based on the results of solvolytic studies on the bicyclo[3.1.0]hexyl system, Winstein set out the general concept of homoaromaticity in 1959^{12,13}.

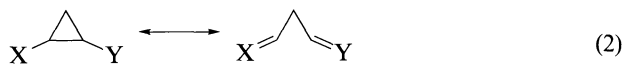
Since the original development of the concepts of homoconjugation and homoaromaticity there has been a very large amount of work carried out to probe, test and find other examples of molecules or ions whose properties can be understood in this context. Several reviews of this work have appeared^{14–22}.

The concept of homoconjugation is now over 45 years old. Like many models in organic chemistry, while not without some original sceptics²³, it was initially embraced with enthusiasm and used to account for the properties of a wide range of systems. Subsequent to the original spate of claims there has been some detailed questioning of the notion. Some claims have been shown to be unjustified. Indeed, this questioning has continued to the extent that in the case of homoaromaticity, it has been suggested that there are only a limited number of medium ring cations where the phenomenon is important²⁴.

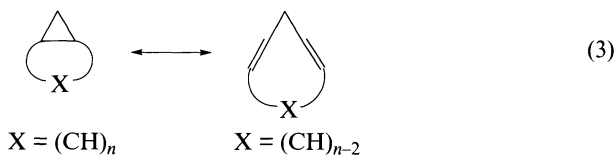
A. Requirements and Criteria for Homoconjugation and Homoaromaticity

In terms of homoconjugation, there are two basic starting points for a particular system. These are well illustrated in equation 1 for the cholesterol/*i*-cholesterol system. It is possible to start with an open form, **1**, and consider through-space interactions, or one can start from a closed form, in this case a cyclopropyl system, **3**, and consider its conjugation. Homoconjugation does not require that the closed form consists of a cyclopropyl ring. However, in practice most, if not all, known examples formally involve a cyclopropane or three-membered ring form as the ring-closed valence tautomer. It is this that has led the editor to include a discussion of homoconjugation in a volume on the chemistry of the cyclopropyl group. However, in many systems to be discussed in this chapter the starting point is an 'open' structure and linkage to the closed, or cyclopropane, form can at times seem tenuous.

In this review we are concerned particularly with cyclopropyl homoconjugation and not simply the conjugation of a cyclopropyl group to an unsaturated centre. The distinction is important. The focus of our attention is on conjugation and delocalization of electrons through space or through a cyclopropane bond (equation 2). Cyclopropyl conjugation, on the other hand, does not necessarily embrace this 'transmission' aspect of homoconjugation and its main focus is normally on the effect of a cyclopropane as a substituent.



Homoconjugation can be a linear phenomenon. That is, one can be concerned with conjugation and electron delocalization through space between two unsaturated fragments. The special and most important case is where the unsaturated fragment or fragments are combined in a cyclic system such that a through-space interaction potentially leads to a cyclically delocalized system (equation 3), which can be stabilized by homoaromaticity. In short, cyclopropyl homoconjugation is a special case of homoconjugation; homoconjugation is particularly important when manifested in terms of homoaromaticity (or homoantiaromaticity) in (bi)cyclic systems. As a result, any discussion of cyclopropyl homoconjugation implies also a discussion of homoconjugation and homoaromaticity. These latter terms are of course embedded in the broader concepts of conjugation and aromaticity.



An advanced description of homoconjugation and homoaromaticity has been given by Cremer and coworkers²⁵⁻²⁸ who distinguish between *bond* and *no-bond homoconjugation*, the former covering cyclopropyl homoconjugation and the latter all the various possibilities of through-space homoconjugation. Cremer and coworkers base their classification on a clear definition of covalent bonding²⁹ and a careful determination of molecular properties with the aid of high-level *ab initio* theory. Based on the distinction between bond and no-bond homoconjugation, they derived a detailed definition and set of requirements for homoaromaticity which can be summarized as follows²⁵⁻²⁸:

- (1) the system in question should possess one or more homoconjugative interactions (either through bond or through space) closing cyclic conjugation;
- (2) the bond or interaction indices of the homoconjugative interactions should be significantly greater than zero, thus indicating either a partial bond (cyclopropyl homoconjugation) or substantial through-space interactions (no-bond homoconjugation);
- (3) electron delocalization in the closed cyclic system should be characterized by:
 - (a) effective overlap between the π -orbitals of the cyclic system,
 - (b) bond orders and π -character indices that are approaching those of an aromatic π -system,
 - (c) delocalization of positive or negative charge throughout the cyclic system in case of charged molecules,
 - (d) a relatively large degree of bond equalization with bond lengths differing from those of normal single or double bonds;
- (4) for either cyclopropyl or no-bond homoaromatic systems the number of π -electrons participating in cyclic electron delocalization should be close to $4q + 2$;
- (5) homoaromaticity should lead to a stabilizing resonance energy $> 2 \text{ kcal mol}^{-1}$;
- (6) no-bond homoaromatic systems should possess exceptional magnetic properties^{25,27,28} that should lead to:
 - (a) significant equalization of ^{13}C chemical shifts in the cyclic system,
 - (b) the magnetic susceptibility, χ , adopting a maximum value for an unconstrained homoaromatic system, i.e. the exaltation of the magnetic susceptibility indicates homoaromatic electron delocalization,
 - (c) a large chemical shift difference between the *endo*- and *exo*-oriented protons when the system in question possesses a CH_2 group properly located above the ring.

In the case of bond (cyclopropyl) homoconjugation, Cremer and coworkers found that potentially homoantiaromatic $4q$ electron systems prefer to delocalize along the periphery of the bicyclic system, thus increasing the number of electrons involved in cyclic delocalization from $4q$ to $4q + 2$ ^{26,30}. Hence, in line with orbital descriptions suggested by Hehre³¹, homoantiaromaticity seems to result from an antiaromatic Möbius $4q + 2$ electron system³² rather than an antiaromatic Hückel $4q$ electron system²⁵⁻²⁸. In any case, homoantiaromaticity is reflected by a destabilizing resonance energy²⁵⁻²⁸.

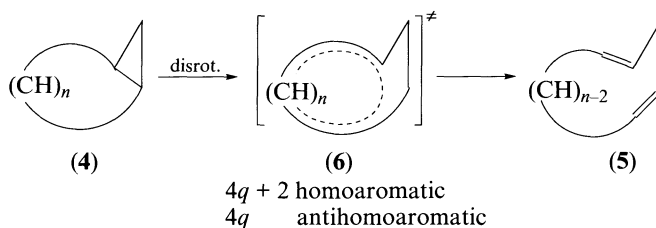
Setting out the requirements for homoaromaticity and homoantiaromaticity in the manner above, in principle, makes it easy to identify a system as homoaromatic. Clearly, an appropriate geometry or structure of the species in question is required. This pertains not only to the appropriate placement of the AOs at the homoconjugative centres, but also to the structural changes associated with the cyclic delocalization of $(4q + 2)$ π -electrons. The cyclic delocalization should also be reflected in the stability of a system and its spectro-

scopic properties, including particularly its NMR spectrum. The use of high-level theory in conjugation with experimental observations to examine electron delocalization, bonding, structure, stability and magnetic properties is also important.

B. Role of Homoconjugation and Homoaromaticity in Organic Chemistry

The initial formulation of the concept of homoaromaticity provided a major stimulus to the probing of the boundaries of electron delocalization in organic molecules and ions as is clearly demonstrated by the extensive amount of work reported in this area¹³⁻²². Some of the basic questions which have arisen in this work are those which test the limits of this type of delocalization. These include, for example, the important issue of just how far a chemical bond can be distorted for it still to be considered a bond and of importance in the description and understanding of the properties of a molecule. Related to this fundamental question is that of the degree to which a cyclopropyl group can conjugate. In most instances the homoconjugative or homoaromatic 'bond' has a bond order less than one and the work performed in this area has led to a much better understanding of the role and importance of these 'fractional' bonds in organic chemistry.

While the initial formulation of homoaromaticity pre-dated the introduction of orbital symmetry by some eight years³³, the two concepts are inextricably linked³⁴. This is most evident when pericyclic reactions are considered from the perspective of aromatic or antiaromatic transition states³⁵ and the Hückel/Möbius concept³¹. The inter-relationship can be demonstrated by the electrocyclic reaction shown in Scheme 1³⁶.

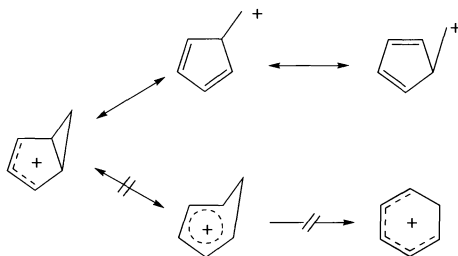


SCHEME 1. Relationship of an electrocyclic reaction to homoaromaticity

The closed and open forms, **4** and **5**, respectively, represent the formal starting and end points of an electrocyclic reaction. In terms of this pericyclic reaction, the transition state **6** can be analysed with respect to its configurational and electronic properties as either a stabilized or destabilized Hückel or Möbius transition state. Where **4** and **5** are linked by a thermally allowed disrotatory process, then **6** will have a Hückel-type configuration. Where the process involves $(4q + 2)$ electrons, the electrocyclic reaction is thermally allowed and **6** can be considered to be homoaromatic. In those instances where the **4/5** interconversion is a $4q$ process, then **6** is formally an homoantiaromatic molecule or ion.

A key question in terms of homoaromaticity is the profile of the potential energy surface linking **4** and **5** and, in particular, where the energy minima occur on this surface.

In the $4q$ case, **6** is not an important contributor to the ground state description of the properties of either **4** or **5**. However, with **4** there are alternative modes of homoconjugation possible that involve the external cyclopropane bonds^{30,32,37,38}. This is shown in Scheme 2 for the bicyclo[3.1.0]hexenyl cation. This alternative mode of conjugation of a cyclopropane in a $4q$ situation, an option not available to the parent $4q$ antiaromatic unsaturated ring systems³⁹, leads to a fundamentally different set of properties and reactions of these systems as compared to the potentially homoaromatic $4q + 2$ cases.



SCHEME 2. Delocalization in the bicyclo[3.1.0]hexenyl cation

C. Organization of the Chapter

The remainder of this chapter is organized into a series of sections which examine the currently available results on a variety of homoconjugative systems. The review is selective in terms of its coverage with examples being chosen that illustrate the issues at hand. Readers are referred to other reviews cited earlier for more comprehensive but, in most cases, less detailed accounts¹⁴⁻²².

We start with an examination of some examples of acyclic systems in which there is evidence or the possibility of cyclopropyl homoconjugation. We then move on to a broader examination of homoaromatic systems, treating cationic, neutral and anionic systems in separate sections. The results of experimental work and theoretical examinations are integrated so as to provide a cohesive overview of each system. In order to limit the size of the chapter, we refrain from reviewing in detail systems such as the bridged annulenes and radical species. The chapter concludes with a reflective section that seeks to draw together theory with experiment and point out new directions for future work.

II. HOMOCONJUGATION IN ACYCLIC SYSTEMS

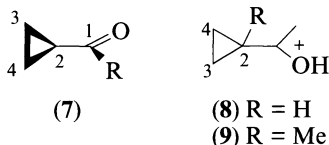
As was shown in the initial work involving the cholesteryl/*i*-cholesteryl system **1-3**, it is, in principle, possible to approach a homoconjugated or homoaromatic system from two directions. These formally involve either starting from a closed cyclopropane or equivalent ring and allowing this to conjugate with an appropriate π -system or, alternatively, starting with an open-chain π -system, or systems, and allowing a through-space interaction to occur between the end of the system(s).

The conjugative properties of a cyclopropane have been examined extensively. Early work in this area has been reviewed by Charton⁴⁰, Story and Clark¹⁷, de Meijere⁴¹ and an extensive overview of more recent work has been prepared by Tidwell⁴². Recent updates on this topic have been provided by Cremer and colleagues^{26,43,44}.

Studies on the ability of a cyclopropane to conjugate have involved a wide variety of approaches including spectroscopic, thermochemical, structural and theoretical examinations⁴². Two overall thrusts are apparent in the reported work. One approach has been to investigate the impact of a cyclopropyl substituent on the properties of an attached functional group or molecule. Typically, techniques used include measurement of the substituent parameters of a cyclopropyl group, determination of the acidity or basicity of functional groups attached to a cyclopropane, or measurement of the impact of a cyclopropyl substituent on the absorption spectrum of an attached chromophore⁴².

The second approach has been to focus attention on the properties of the cyclopropane itself. Thermochemical measurements and particularly structural studies involving both experiment and theory are the principal methods used. It is this second approach to studying cyclopropyl homoconjugation which is discussed in this chapter.

Allen has examined in detail the effect of conjugation on the structure of a cyclopropane⁴⁵⁻⁴⁷. The analysis, which was based on the available X-ray structures of cyclopropyl derivatives, showed that there were systematic changes in the geometry of the cyclopropane ring associated with π -electron acceptor groups such as the carbonyl group⁴⁵. Conjugation of cyclopropyl with an acceptor group leads to a lengthening of the two vicinal and a shortening of the distal cyclopropane bonds. As summarized for **7** in Table 1, the contraction of the distal bond was found to be approximately twice as large as the lengthening of the vicinal bonds as compared to an average cyclopropane C—C bond distance (1.504 Å).



The structural studies on cyclopropane derivatives have shown that there is a strong conformational preference observed in the structures of the cyclopropyl materials with the plane of the cyclopropane being aligned with that of the π -system of the acceptor group^{45,48}. Similar conclusions have also been reached on the basis of UV studies^{42,49} and theoretical calculations^{50-52,44} (see also the discussion in Chapter 2).

Allen estimated that conjugation of a cyclopropane with an attached substituent was about 70% as effective as conjugation with a double bond⁴⁵. This estimate is consistent with the 60% figure derived by Pete on the basis of an analysis of the UV spectra of cyclopropyl-containing systems⁵³.

The geometric changes resulting from conjugation of a cyclopropane with a conventional π -acceptor are greatly magnified when the acceptor group becomes positively charged. The cyclopropylcarbinyl cation, the formal archetype of these systems, has been studied extensively. Several reviews of this work exist⁵⁴, including one in this volume. In the parent cation the delocalized cyclopropylcarbinyl structure has been shown to be almost of the same energy as a bicyclobutonium ion⁵⁵ with a strong cross-ring interaction⁵⁶⁻⁵⁸. Both of these ions are significantly more stable than the corresponding homoallyl structure. The barrier to the interconversion of the bicyclobutonium and cyclopropylcarbinyl ions is small and substituents on the cation can profoundly alter the relative energies of the cyclopropylcarbinyl/bicyclobutonium/homoallyl forms of the parent cation.

The crystal structures of several different cyclopropylcarbinyl cations, each with a hydroxy function on the carbinyl carbon, have been reported⁵⁹⁻⁶¹. Of these structures some five represent relatively simple systems and in each of these cases a bisected or close to

TABLE 1. Internuclear distances (Å) of some cyclopropyl compounds and cations

Bond	7 ^a	8 ^b	9 ^b	10 ^c
C(1)—O	—	1.256(8)	1.268(8)	
C(1)—C(2)	—	1.405(10)	1.461(9)	1.343
C(2)—C(3)	1.517	1.516(8)	1.529(9)	2.159
C(2)—C(4)	—	1.516(8)	1.545(8)	1.543
C(3)—C(4)	1.478	1.418(12)	1.448(9)	1.453

^aReferences 43-45.

^bReferences 59-61.

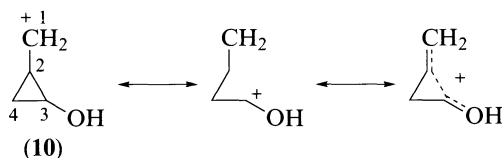
^cReference 56.

bisected conformation is observed. As can be seen from the data for the methyl-substituted systems **8** and **9**, summarized in Table 1, large bond-distance distortions of the three-membered rings are observed. In the case of **8**, the distal bond distance is remarkably short, being almost the same as is found for the C—C bond length in benzene.

While it is clear that a cyclopropyl group can effectively conjugate with an adjacent π -acceptor, particularly where this acceptor is a positively charged group, and the structure of the cyclopropane ring can be substantially modified, the question of importance in terms of homoconjugation and homoaromaticity in general is whether conjugation can be transmitted through a cyclopropane ring.

Early work based on the solvolysis of substituted cyclopropylcarbinyl systems^{62,63}, spectroscopic studies⁶⁴, calculations⁶⁵ and the structural work analysed by Allen^{45,46} all point to the cyclopropane ring being poor at the transmission of conjugation. For example, Pews and Ojha estimated that the cyclopropyl ring is about 27% as effective as a vinyl group in its ability to transmit conjugation⁶⁶. Wilcox, Loew and Hoffman have discussed the conjugative properties of a cyclopropane in terms of molecular orbital theory and suggested that the LUMO of the parent cation has relatively small coefficients at all of the cyclopropyl carbons, resulting in comparatively small π -interactions by substituents⁶⁷.

In cations the situation would appear to be somewhat different. Wiberg and colleagues have examined the effect of substituents on the cyclobutenium/cyclopropylcarbinyl/homoallyl cation energy surface using *ab initio* calculations at the MP2/6-31G(d) level⁵⁶. In general, π -donor substituents at the 3-position were found to favour a cyclopropylcarbinyl form of the ion with significant homoallyl character (Scheme 3). The optimized geometry of the *trans*-hydroxy substituted system, **10**, is summarized in Table 1. It is clear that there can be large structural changes associated with substitution of a π -electron donor on the cyclopropyl ring of one of these ions. It can be seen that the C(2)—C(3) bond in **10**, is extremely long with a calculated distance of 2.159 Å. The cation has a very asymmetric 'three-membered ring'.



SCHEME 3. The 3-hydroxycyclopropylcarbinyl cation

Overall it is clear that, while in neutral systems a cyclopropane ring is not particularly effective at transmitting conjugation, this situation can change when very strong π -acceptor groups such as carbenium ions are present or when the cyclopropane is part of a cyclic situation⁶⁸.

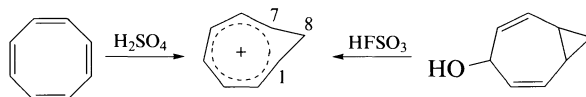
III. MONOHOMOAROMATIC AND HOMOANTIAROMATIC CATIONS

A. Homotropenylium Ions

In many respects the homotropenylium ion can be considered to be the archetype or 'benzene' of homoaromatic systems. It is not only one of the earliest examples of a homoaromatic system to be described, but well more than forty substituted derivatives of the homotropenylium cation have now been reported⁶⁹. These substituted ions have been examined by a broad range of experimental techniques and theoretical methods. It is interesting to note that unlike the trishomocyclopropenium cation, the initial homoaromatic system to be studied, characterization of the homotropenylium ion did not rely on a

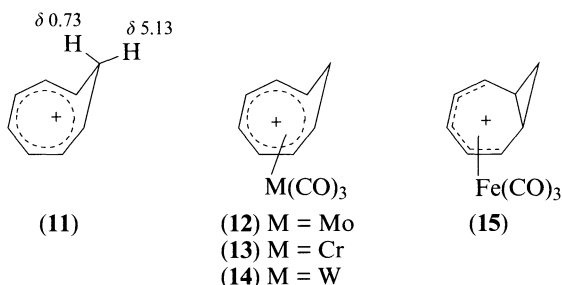
solvolytic approach. Rather from the outset, the characterization methods employed were the then relatively new stable ion techniques and, particularly, direct characterization of the ion by NMR spectroscopy.

Access to homotropenylium ions can be achieved by two general routes. The first involves the addition of an electrophile to a cyclooctatetraene or cyclooctatetraene derivative, an approach which can be considered to correspond to a homoallyl route (Scheme 4). In this route the electrophile is generally attached stereoselectively to the *endo* position on C(8)^{18,70-74}. The second approach involves the ionization of a bicyclo[5.1.0]octadienyl derivative. This is the cyclopropylcarbinyl approach (Scheme 4). This route has the potential of generating a wide range of differently substituted cations; however, the starting materials can be difficult to access⁷⁵⁻⁷⁸.



SCHEME 4. Routes to the homotropenylium ion

The original report of the preparation of the homotropenylium ion was by Pettit and coworkers in 1962. They showed that treatment of cyclooctatetraene with strong acids led to the formation of a stable $C_8H_9^+$ cation that exhibited remarkable properties⁷⁹. Apart from its stability, which allowed for the isolation of its salts as solids, the key feature noted was its unusual ¹H NMR spectrum in which the resonances attributable to the two protons of a methylene group were non-equivalent and separated by 5.86 ppm⁸⁰. In fact, one of the proton resonances was found at higher field than tetramethylsilane (TMS) at -0.73 ppm, a remarkable position for any hydrocarbon let alone a cation. Pettit and colleagues suggested that the structure of the cation corresponded to bicyclo[5.1.0]octadienyl cation with extensive delocalization of the internal cyclopropane bond. The unusual chemical shifts found for the methylene proton resonances were attributed to an induced ring current in **11**^{81,82} although Deno expressed a contrary view²³.



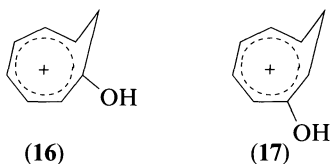
Since Pettit's original report, the homotropenylium ion has been studied extensively. The resulting large body of work has previously been reviewed¹⁴⁻²². The account given here highlights the different lines of evidence for the electronic nature of the cation.

1. NMR and magnetic properties of homotropenylium ions

Subsequent to the initial work outlined above, high field ¹H and ¹³C NMR studies of **11** and model compounds supported the original suggestion for its structure^{80,83}. In terms of model compounds one of the key approaches taken was to use the metal carbonyl complexes of the homotropenylium ion system. Thus the molybdenum, **12**, chromium, **13**, and

tungsten tricarbonyl, **14**, derivatives were all considered to be homoaromatic while the corresponding iron complex, **15**, in which only four electrons are donated from the π -system to the metal, was suggested to have a localized structure⁸⁴.

A distinctive feature of the ¹H NMR spectra of homotropenylium ion derivatives is that the magnitude of the chemical shift difference ($\Delta\delta$) between the 8-*exo* and 8-*endo* proton resonances is found to be dependent on the nature and position of substituents on the 'seven-membered' ring^{72,78,85,86}. In all cases, a donor substituent on one of the basal ring carbons attenuates the chemical shift difference. For example, the 1- and 2-hydroxy substituted homotropenylium ions, **16** and **17**, have $\Delta\delta$ values only some 50–55% of that found for the parent cation^{77,85}. Systematic variation in the donor properties of the oxygen substituent using the Lewis acid scale developed by Childs and colleagues⁸⁷ led to a linear change in $\Delta\delta$ ⁶⁹.



It has been suggested that this attenuation of $\Delta\delta$ with substitution is attributable to a reduction in cyclic electron delocalization in the homoaromatic ring and a consequent attenuation in the induced ring current⁸⁶. However, as will be shown later, substitution also results in some fairly major changes in the structure of the homotropenylium ion and the impact of these structural changes on the relative position of the C(8) protons and/or ring current have not been disentangled.

The key underlying assumption of all the NMR studies of the homotropenylium systems is that there is an induced ring current when the ions are in a magnetic field and that this effects the two C(8) protons in a different manner. Dauben, Wilson and Laity measured the diamagnetic susceptibility of **11** and showed that it has a susceptibility exaltation which is similar in magnitude to that of the tropylium ion⁸⁸.

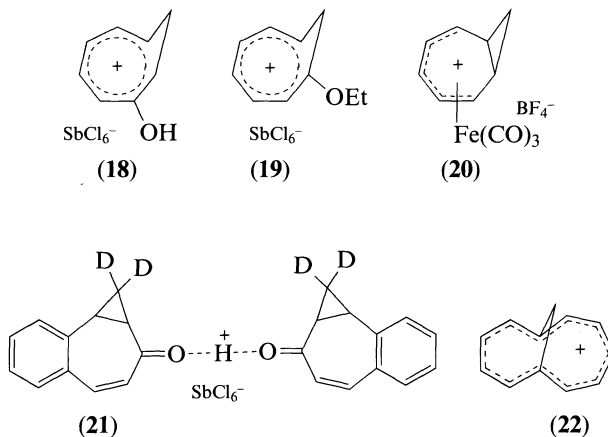
Winstein and colleagues carried out a ring current calculation for **11** using the Johnson–Bovey⁸⁹ approach and by assuming that atoms C(1)–C(7) adopted a planar configuration¹⁴. This planar configuration was subsequently shown to be incorrect and a further ring current calculation was undertaken by Childs, McGlinchey and Varadarajan in 1984⁹⁰. This second calculation used as a starting point the known geometry of the 2-hydroxyhomotropenylium ion⁹¹. It also took into account local anisotropic contributions. Using this approach it was possible to account for the large chemical shift difference of the C(8) protons. However, there were two surprising results of this more recent work. First, both the 8-*exo* and 8-*endo* protons were found to be shielded, albeit the shielding of the former resonance was found to be small compared to the latter. Second, the local anisotropic contribution to the chemical shifts of the C(8) protons was very significant and accounted for more than 40% of the total calculated chemical shift difference. The intrinsic chemical shift of the two protons in the absence of an induced ring current was estimated to be 5.5 ppm, indicating that C(8) cannot be considered to be a cyclopropyl like carbon.

2. Absorption spectra

Winstein and coworkers measured the UV spectrum of the homotropenylium ion and showed that its long-wavelength absorption band (λ_{\max} 313 nm) was intermediate between that of the tropylium (λ_{\max} 273.5 nm) and heptatrienyl (λ_{\max} 470 nm) cations⁷⁰. Using a Hückel molecular orbital approach the C(1)–C(7) bond order was estimated to be 0.56.

3. Structural studies

The structures of five different homotropenylium or closely related systems determined using X-ray crystallographic techniques have been reported. These ions are **18**⁹¹, **19**⁹², **20**¹⁹, **21**⁹³ and **22**⁹⁴.



Up to this time there has been no report of the experimental determination of the structure of the parent homotropenylium ion. The three simplest systems that have been studied are **18**, **19** and the iron complex **20**. Cations **18** and **19** each have an oxygen-containing electron-donor substituent and, as such, appear to have smaller induced ring currents than the parent ion. In fact **18** and **19** have almost identical chemical shift differences ($\Delta\delta = 3.10$ ppm) between the two C(8) protons. In the case of **20**, $\Delta\delta$ is very small and it was considered to be a non-cyclically delocalized model for the bicyclo[5.1.0]heptadienyl cation⁶⁹.

Each of the cations **18**, **19** and **20** were found to adopt similar shallow boat-type conformations with C(8) being positioned over the 'seven-membered' ring. Despite their similarity in conformation, the cations were found to be substantially different in terms of their internuclear distances, particularly the C(1)–C(7) distance (Table 2).

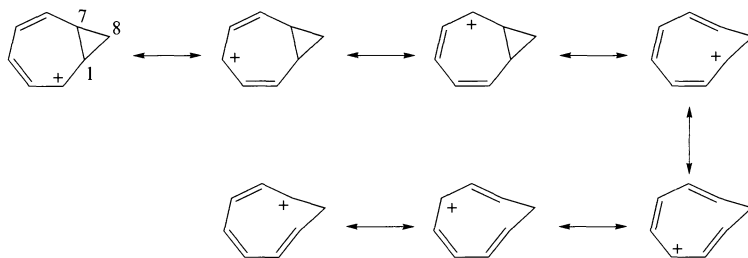
TABLE 2. Selected bond distances (Å) of homotropenylium and related ions

Bond	19	18	20	21	22	11
C(1)–C(7)	2.284(5)	1.626(8)	1.474(11)	1.544(8)	2.293(3)	1.906
C(1)–C(8)	1.480(5)	1.488(7)	1.498(11)	1.515(9)	1.487(3)	1.478
C(7)–C(8)	1.506(6)	1.488(7)	1.497(12)	1.471(9)	1.487(3)	1.478
C(1)–C(2)	1.407(5)	1.422(12)	1.488(10)	1.439(10)	1.373(5)	1.397
C(2)–C(3)	1.359(5)	1.37(2)	1.395(10)	1.425(10)	1.416(6)	1.396
C(3)–C(4)	1.420(5)	1.378(13)	1.402(10)	1.341(8)	1.375(5)	1.404
C(4)–C(5)	1.364(6)	1.378(13)	1.400(10)	1.446(7)	1.375(5)	1.404
C(5)–C(6)	1.429(7)	1.37(2)	1.393(11)	1.413(7)	1.416(6)	1.396
C(6)–C(7)	1.337(5)	1.422(12)	1.495(11)	1.484(7)	1.373(5)	1.397
$\Delta\delta^a$ (ppm)	3.10	3.10	0.18	—	—	5.86
References	92	91	69/19	93	94	27

^a $\Delta\delta$ is the chemical shift difference between the two resonances of the bridging (C₈) methylene protons.

As can be seen from the data in Table 2, the C(1)–C(7) distance in **18** is 1.626(8) Å while in **19** the same internuclear distance is 2.284(5) Å. In both instances, the bond distance is substantially longer than that normally found for a cyclopropane, 1.504 Å⁴⁵ (see also Chapter 2 of this volume)⁴⁴, or in the iron complex **20** (Table 2).

It has been suggested that the difference in the C(1)–C(7) distance in the two cations can be understood in terms of the effect of the strongly electron-donating oxygen donating substituents on the relative importance of the various resonance structures in the two cations (cf Scheme 5)^{92,93}. A 2-hydroxy group favours those resonance structures which have a closed cyclopropane bond, as in these structures charge can be stabilized by the hydroxy group. Conversely, hydroxy or alkoxy substituents at C(1) will favour resonance structures with an open cyclopropyl bond.



SCHEME 5. Resonance structures of the homotropenyl cation

The long C(1)–C(7) distance in **18** and **19** are consistent with a homoaromatic formulation of each of these cations. However, as was pointed out in the introduction to this review, homoaromaticity requires more than just the presence of a long homoconjugate bond and there should be structural changes throughout the molecule that are consistent with cyclic delocalization. The conformations of **18** and **19** are such that there can be effective overlap of the cyclic π -systems^{95,96}.

In the case of **18**, the various C–C bond distances in the basal ‘seven-membered’ ring are consistent with there being a significant degree of cyclic electron delocalization and the ion being classified as homoaromatic. The C(1),C(7) bond order of **18** was estimated to be 0.56 on the basis of the measured internuclear distance⁹¹. It is interesting to note that the bond distances found for **18** are substantially different from those reported for the protonated cyclopropyl ketones discussed above.

With **19**, Childs and colleagues pointed out that although its conformation is suitable for cyclic electron delocalization, the internuclear distances found for the basal ring carbons are not consistent with such a formulation of its structure⁹². Rather, the C–C bond distances around the ring indicate a progressive increase in bond alternation on proceeding from C(1)–C(2) to C(6)–C(7). Similar patterns of increasing bond length alternation have been observed with several other 1-substituted polyenyl cations^{97,98}. It was concluded that the structure of **19** was completely consistent with it being considered to be a 1-ethoxyheptatrienyl cation. As such, **19** would appear to fail the third criterion established at the outset and not be homoaromatic, despite it exhibiting a large chemical shift difference between the C(8) protons.

The concern that the solid state structures do not represent those in the solution phase in which the ¹H NMR data were obtained was addressed by comparing the NMR spectra in both phases. Thus it was demonstrated for **17** and **18** through the use of solid state CPMAS and solution ¹³C NMR spectroscopy that there were no fundamental differences in the structure or charge distribution of the cation in solution or the solid state^{91,92}.

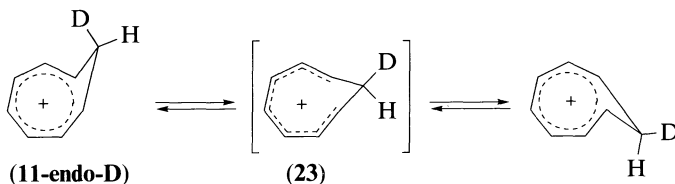
The structure of **20** was suggested to be fully consistent with a $5C/4\pi$ bonding of the iron atom to the cation and the presence of a fully formed cyclopropane ring as proposed on the basis of its NMR spectrum^{69,92}.

Analysis of the structure of the unusual dimeric cation **21** led Childs and coworkers to conclude that this system could best be regarded as exhibiting cyclopropylcarbinyllike delocalization⁹³. The bridged ion **22** again exhibits a large homoconjugative internuclear distance (Table 2)⁹⁴, and the question arises as to whether there is a significant C(1)—C(7) overlap or whether it can best be regarded as a perturbed annulene.

4. Thermochemical measurements

A variety of approaches have been used to assess the importance of homoaromatic delocalization on the thermodynamic stability of homotropanylium ions. The earliest of these involved measurement of the barrier to ring inversion of stereoselectively labelled homotropanylium ions.

Winstein and colleagues reported that the *8-endo-D* cation, **11-endo-D**, underwent a slow exchange reaction with the corresponding *exo* derivative (Scheme 6)⁷⁰. The barrier to this process was found to be $22.3 \text{ kcal mol}^{-1}$. Winstein's postulate that the process involved a ring inversion process and the planar cyclooctatrienyl cation **23** was later confirmed by Berson and Jenkins⁹⁹. The barrier to the inversion process can then be regarded as indicative of the difference in energy between **11** and **23** and, as such, a measure of the extra stability of the homotropanylium ion over the planar, linearly conjugated **23**. However, it would be wrong to attribute all of this energy difference to homoaromatic stabilization. There are major differences in strain energy between **11** and **23** and these also have to be taken into account.

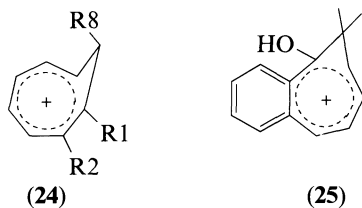


SCHEME 6. Inversion of the homotropanylium ring

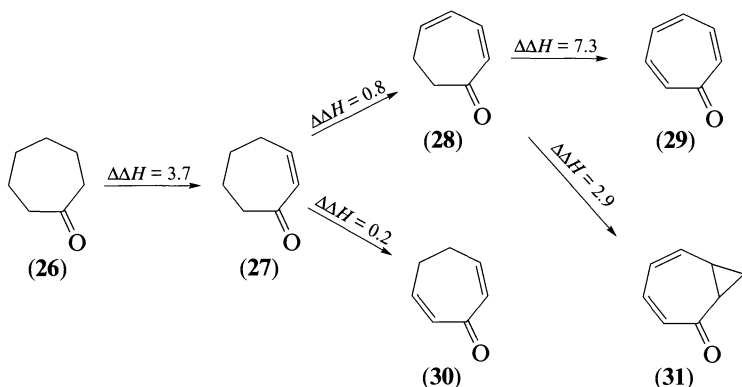
The reported barriers to the inversion of C(8) of substituted homotropanylium ions vary over a wide range of energies (Table 3)^{72,77,100,101}. The highest barrier reported is for **24e**⁷⁷ and the smallest for **25**¹⁰⁰. The differences in these barriers can be understood in terms of the effect of basal ring substituents on the C(1)—C(7) internuclear distance as described above.

TABLE 3. Barriers to inversion of homotropanylium cations

Cation	Barrier to inversion (kcal mol^{-1})	Reference
24a : R8 = D, R1 = R2 = H	22.3	70
24b : R8 = Cl, R1 = R2 = H	22.6	72
24c : R8 = D; R1 = OMe, R2 = H	19.6	101
24d : R8 = Me, R1 = OH, R2 = H	17.1	77
24e : R8 = R1 = H, R2 = OH	>27.0	77
25	9.5	100



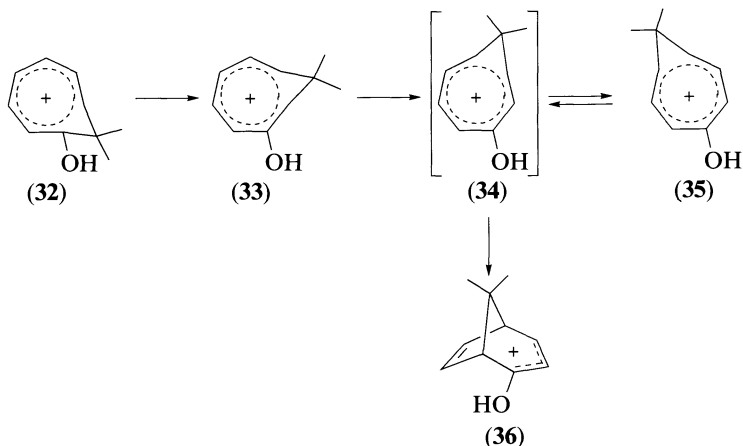
A more direct approach to measurement of homoaromatic stabilization was taken by Childs and colleagues in which the heats of protonation of the series of ketones **26–31** in FSO_3H were measured¹⁰². Of particular interest are the differences in heats of protonation for the various ketones and these data are summarized in Scheme 7.



SCHEME 7. Differences in heats of protonation (kcal mol^{-1})

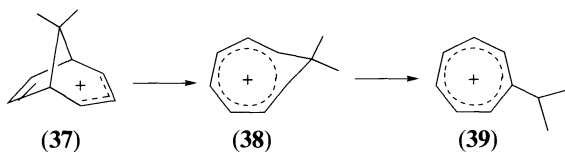
As can be seen, the introduction of a conjugated double bond into the seven-membered ring of **26** increases the heat of protonation by $3.7 \text{ kcal mol}^{-1}$. As expected, the effect of introducing a second double bond is much smaller (**27** \rightarrow **28** or **27** \rightarrow **30**). There is, however, a major effect on introduction of the third double bond, **28** \rightarrow **29**, where a very large incremental jump in the heat of protonation is observed. This large discontinuity is associated with the well established aromaticity of the hydroxytropylium ion³⁹. The effect of the introduction of a cyclopropane, **31**, is smaller (40%) than that of the third double bond, but there is still a substantial discontinuity. It was concluded by Childs and colleagues¹⁰² that the 2-hydroxyhomotropylium ion, **17**, is homoaromatic and that homoaromatic delocalization is an important factor in determining the overall stability of this cation. The evidence for homoaromatic stabilization of the 1-hydroxyhomotropylium ion was less clear-cut. This has been confirmed by *ab initio* calculations carried out by Cremer and Colleagues¹⁰³.

A further, less direct way in which homoaromatic stabilization of substituted homotropylium ions has been assessed is by measurement of their rates of interconversion and equilibrium positions between isomeric homotropylium and other ions. This has been achieved with the 8,8-dimethyl-substituted systems which have been shown to undergo a series of circumambulatory rearrangements, as demonstrated in Scheme 8⁷⁷. It was reported that the order of stability of the isomeric ions was **34** $<$ **32** $<$ **33** $<$ **35** $<$ **36**, with the free-energy differences between the various hydroxyhomotropylium ions being relatively small (total spread being *ca* 2 kcal mol^{-1}), while **36** was found to be $15.5 \text{ kcal mol}^{-1}$ more stable than **33**^{77,69}. The surprising feature of this series of rearrangements was the finding

SCHEME 8. Isomerization of **32**

that **36**, formally a bishomoantiaromatic ion, was more stable than any of the isomeric homotropanylium ions.

The position of the equilibrium between the 8,8-dimethylhomotropanylium ions and the bicyclo[3.2.1]octadienyl system was shown to be very dependent on the nature of any additional substituents^{77,104}. Thus the parent system **37** was shown to rearrange to **39** via **38** at low temperatures (Scheme 9). In the case of the ring methylated cations, an equilibrium was found to exist between the bicyclo[3.2.1]octadienyl and homotropanylium ions.

SCHEME 9. Isomerization of **37**

On the basis of the measurement of the heats of protonation and isomerization and estimates of the heats of formation of the starting ketones, it has been shown that the additional delocalization energy in **33** as compared to **36** is $2.8 \text{ kcal mol}^{-1}$ ⁶⁹.

Scott and colleagues have suggested that there is a qualitative relationship between the magnitude the chemical shift difference of the methylene proton resonances of the bridging carbon $\Delta\delta$ for a series of isomeric hydroxy-substituted systems and their relative thermodynamic stability⁸⁶.

5. Theoretical calculations

A number of different groups have undertaken theoretical examinations of the structure and properties of the homotropanylium ion. These include Hehre^{31,105}, Goldstein and Hoffmann³⁴, Jorgensen³⁸, Haddon¹⁰⁶⁻¹⁰⁸, Cremer, Bader and coworkers⁸⁰, Barzaghi and Gatti¹⁰⁹, Schleyer, Cremer and coworkers^{110,111} and Cremer and coworkers (see Section IV. B of Chapter 7^{25,27,103}).

The underlying reason for the large number of studies is that the calculated ground state structure of the homotropanylium ion is dependent on the level of theory used. In partic-

ular, the calculated C(1)–C(7) internuclear distance, and the shape of the potential energy surface as this distance is varied, have been found to be very sensitive to the choice of the theoretical method.

The highest level of calculations have been reported by Haddon¹⁰⁶ in 1988 (HF and MP2 single-point calculations) and Cremer and coworkers^{25,27} in 1991 [HF and MP2 geometry optimizations, MP3 and MP4(SDQ) single-point calculations]. In each of these studies it was concluded, in contrast to earlier work, that there is a single energy minimum on the homotropanylium potential energy surface (PES) as the C(1)–C(7) distance is altered. The PES was found to be relatively flat as a function of change in the C(1)–C(7) distance. The minimum energy form had a C(1)–C(7) distance close to 2 Å (Haddon 1.91 and Cremer 2.03 Å).

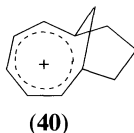
Cremer and colleagues also calculated the ¹H and ¹³C NMR chemical shifts as a function of the C(1)–C(7) distance^{25,27}. Comparison of these calculated and observed shift values of the homotropanylium ion confirmed a C(1)–C(7) distance of 2 Å. At this distance the chemical shift difference between the *exo* and *endo* C(8) protons became a maximum. In addition the calculated magnetic susceptibility adopted a maximum value, i.e., a distinct susceptibility exaltation was found for the C(1)–C(7) equilibrium distance of 2 Å^{25,27}.

Analysis of the MP2 electron density distribution of the homotropanylium ion in its equilibrium geometry indicated, according to the Cremer–Kraka criterion of covalent bonding, that atoms C(1) and C(7) are connected by strong through-space interactions (interaction index 0.35) rather than a covalent bond^{25,27}. However, Cremer pointed out that the lack of a bond does not exclude electron delocalization in the seven-membered ring closed by the C(1)–C(7) interactions. On the contrary, the 2 Å distance found for the 1,7 distance seems to be sufficient for effective electron delocalization. This was confirmed by: (a) the similarity in the calculated CC bond distances which are all close to 1.4 Å, indicating almost perfect bond equalization, (b) calculated CC bond orders of 1.5, typical of an aromatic system, (c) the π -character of all CC bonds in the ‘seven-membered’ ring and (d) the high degree of equalization of the positive charge in the ‘seven-membered’ ring. As a consequence of this equalization of the charge, the ¹³C chemical shifts were found to be very similar.

In the context of the criteria for homoaromaticity given in Section I. A above, the calculated and measured properties of the homotropanylium cation suggest that it is the prototype of a no-bond homoaromatic molecule^{25,27}. However, this conclusion seems to be at odds with the estimates of the homoaromatic resonance energy^{27,106}. Using a bicyclic form of the homotropanylium ion with a fixed C(1)–C(7) distance of 1.5 Å as an internal reference, Cremer and colleagues calculated a stabilization energy of just 4 kcal mol⁻¹ [MP4(SDQ)/DZ + P] for the homotropanylium ion²⁷. However, this value reflects the extra stabilization caused by no-bond homoconjugation compared to normal cyclopropyl homoconjugation. Despite this problem with a reference state, both Cremer²⁷ and Haddon¹⁰⁶ point out that homoaromaticity is just a matter of a few kcal mol⁻¹. This is consistent with the experimental thermochemical results outlined above and the calculated resonance energies of neutral homoaromatic compounds (Section III. G in Reference 25).

The potential energy surface of the homotropanylium ion is rather flat in the 1,7 direction. This means that external effects, such as any ‘seven-membered’ ring substituents, will have a profound effect on the C(1)–C(7) distance. Experimentally, this has been found to be the case, as shown for **18** and **19** above. In addition, Cremer and colleagues have confirmed this C(1)–C(7) distance dependence on substitution by high-level *ab initio* calculations on hydroxy-substituted homotropanylium ions¹⁰³.

Scott and Hashemi have examined the effect of constraining the C(1)–C(7) distance in the homotropanylium ring by linking these two atoms by a three carbon bridge (termed a ‘molecular caliper’), **40**¹¹². While the structure of **40** has not been determined, the C(1)–C(7)



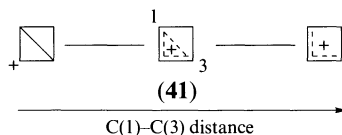
distance is expected to be small and in the range of 1.5–1.7 Å, and not possibly in the 2 Å range of the parent ion. The chemical shift difference of the methylene protons of **40** was found to be 5.08 ppm, some 87% of that found for the parent system.

In summary, the four major lines of approach to understanding the properties of the homotropanylium ion all lead to the same conclusion, namely that this ion is a cyclically delocalized, homoaromatic system. It should be stressed that this conclusion has been reached by using a combination of a battery of magnetic, spectroscopic, thermochemical, structural and theoretical techniques and these all give a consistent picture of the nature of the electron delocalization in the cation.

B. Homocyclopropenium Ions and Related 2π-Electron Systems

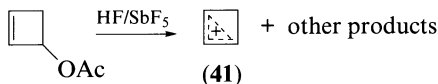
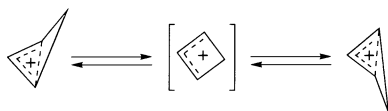
Roberts and coworkers, investigating the ionization reactions of cyclobutene derivatives, found that the resulting cyclobutenyl ions were unusually stable^{10,113}. They suggested that rather than regarding these ions as simple allyl cations, their properties were consistent with a C(1),C(3) interaction and cyclic delocalization of the π-electrons. As such, these 2π-electron systems were considered to be the homoaromatic counterparts of the well established, aromatic cyclopropenium ions³⁹.

Since this original work, a large number of studies of the cyclobutenyl/homocyclopropenium ion, **41**, and its derivatives have been reported. The nature of their electronic structure has been probed using a variety of experimental techniques and theoretical methods¹⁴⁻²¹. The approaches employed parallel those used with the homotropanylium system and include an early examination of the UV spectra of the ions¹¹⁴. However, in contrast to its 6π-electron counterpart, fewer thermochemical measurements have been reported for **41** and its derivatives. As for theoretical treatments, the publication of Schleyer, Otto, Cremer and colleagues gives a good summary of previous work¹¹¹. As these latter authors point out, the key question comes down to the nature of the potential energy surface as a function of the C(1)–C(3) internuclear distance (Scheme 10) and, in particular, what are the relative energies of the bicyclobutyl, homocyclopropenium and cyclobutenyl models for the structure of this cation.



SCHEME 10. Cations on the $C_4H_5^+$ potential energy surface

Olah and collaborators have reported the synthesis and characterization of the parent ion **41** as a stable species (Scheme 11)¹¹⁵. The 1H and ^{13}C NMR spectra of **41** indicated that it exists in a non-planar, envelope-type conformation. Variable-temperature studies demonstrated that **41** undergoes an isomerization that interconverts the *exo* and *endo* protons. It was assumed that this process involved a ring inversion (Scheme 12), rather than a more deep-seated rearrangement such as a circumambulation. Subsequent studies have shown that circumambulation of C(4) around the basal 'three-membered' ring in homocyclopropenium ions is a high-energy process¹¹⁶.

SCHEME 11. Formation of **41**SCHEME 12. Ring inversion of **41**

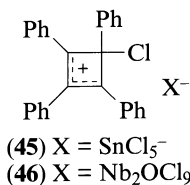
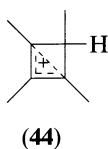
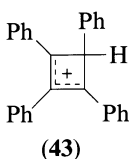
The barrier to the isomerization in **41** (Scheme 12) was found to be 8.4 kcal mol⁻¹, a value substantially lower than that reported for the homotropenyl cation⁷⁰. Olah suggested that the energy barrier for inversion of **41** was a measure of its homoaromatic stabilization¹¹⁵. However, other factors than homoaromatic delocalization contribute to this energy difference.

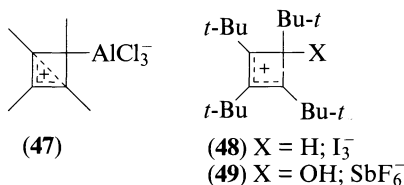
The finding that **41** has a non-planar conformation does not necessarily mean that there is a significant C(1)–C(3) π -interaction and that the system can be classified as homoaromatic¹¹⁵. Olah and colleagues addressed this issue by carefully examining the NMR chemical shifts of the allylic carbons of **41** and related derivatives and comparing these with comparable open-chain allyl cations. The key and important feature to emerge from these comparisons was that there is a fundamental difference in the charge distribution in **41** as compared to a conventional allyl cation such as **42**. In **42**, the ¹³C resonances of C(1)/C(3) occur at lower field than that of C(2) ($\Delta\delta_{C(1)-C(2)} = +89.0$ ppm). In **41**, the reverse is the case and the C(2) resonance is significantly further downfield as compared to the resonances of C(1)/C(3). ($\Delta\delta_{C(1)-C(2)} = -54.1$ ppm). The NMR spectra of **41** and its charge distribution are entirely consistent with a significant C(1)–C(3) bonding interaction.



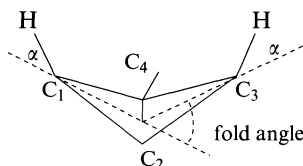
Olah and coworkers showed that substitution on the unsaturated basal ring carbons of the homocyclopropenium ion has a considerable effect on the magnitude of the chemical shift difference between the ¹³C NMR chemical shifts of C(1)/C(3) and C(2) of the homocyclopropenium cations¹¹⁵. With 1,3-diphenyl substituents the system was shown to behave like a typical allyl cation with the C(1)/C(3) resonances being downfield that of C(2) (e.g. $\Delta\delta = +38.6$ ppm for **43**)¹¹⁷. With methyl substituents e.g. in **44**, the chemical shifts C(1), C(2) and C(3) are the same ($\Delta\delta = 0$ ppm).

Direct evidence as to the impact of substituents on the structure of the cyclobutenyl/homocyclopropenium ion system comes from X-ray crystal structures of five different





salts: **45**¹¹⁸, **46**¹¹⁹, **47**¹²⁰, **48** and **49**¹²¹. Key information on each of these cations is summarized in Table 4. The terms used in this Table are defined in Scheme 13.



SCHEME 13. Definition of structural parameters used in Table 4

In the phenyl-substituted salts **45** and **46**, the four-membered ring is found to be nearly planar with a relatively large distance between C(1) and C(3). The conformations of the phenyl groups on C(1) and C(3) are such that they can effectively conjugate with the allylic system.

In contrast to the planar structures of **45** and **46**, the four-membered rings in each of the cations **47–49** are non-planar. As shown in Scheme 13, the conformation of the rings can be described in terms of the angle between planes defined by C(1),C(2),C(3) and C(1),C(3),C(4). As can be seen from Table 4, the angles between these planes are large and, as a result, C(1) and C(3) are brought much closer together than is found in the planar conformations of **45** and **46**. Maier and colleagues¹²¹ pointed out that not only are p-orbitals C(1) and C(3) angled towards each other as a result of the bending of the four-membered rings of **47–49**, but p-orbital overlap is enhanced by a distortion of the substituents on these atoms away from their trigonal planes (α in Scheme 13). This type of distortion is consistent with the suggestion of Haddon concerning the importance of the π -orbital axis vector in non-planar systems^{107,122}.

The structures of ions **47–49** are fully consistent with them being classified as homocyclopropenium or homoaromatic ions. On the other hand, **45** and **46** are clearly cyclobutenyl in character. The observations of Olah and colleagues on the chemical shift

TABLE 4. Selected structural data for cyclopropenium ions and related compounds

Ion or compound	Reference	Method used	C(1)–C(3) distance (Å)	Fold angle (°)	α (°)	δ (ppm)
41 (bent)	111	MP2/6-31G(d)	1.735	35.5	18.2	
41 (planar)	111	MP2/6-31G(d)	1.972	0	0	
46	119	X-ray	2.032(10)	4.4	3.1/2.5	38.6
47	120	X-ray	1.775(4)	31.5	13.8	2.3
48	121	X-ray	1.806(6)	37.3	11.4	–40.0
49	121	X-ray	1.833(4)	36.4	10.1/16.6	–23.4
52	128	X-ray	1.915(4)	31.2	na ^a	
54	131	X-ray	1.792(15)	32.9	na ^a	

^aNot available.

differences and, hence, charge distribution of the allylic carbons as a function of substituent are fully compatible with the more recent structural information.

Further information on the electron delocalization in **41** was provided by Katz and Gold. These workers pointed out that the UV spectra of alkyl-substituted derivatives of **41** were intermediary in position (λ_{\max} ca 250 nm) between that of corresponding allyl or cyclopropenium cations (λ_{\max} ca 300 and 185 nm, respectively)¹²³.

A large number of theoretical treatments of **41** have been reported^{31,38,107,124–126}. Most of these earlier calculations did not yield a non-planar structure for **41** that is in accord with the experimental observations.

The most extensive study of the structure of **41** was reported recently by Schleyer, Otto, Cremer and coworkers¹¹¹. As has been described for the homotropylium cation, their approach involved high-level calculations [MP4(SDQ)/6-31G(d) and IGLO]. These authors concluded that **41** is homoaromatic with a bent structure, relatively short C(1)–C(3) distance (1.737 Å), a considerable 1–3 interaction index and nearly equal charges on C(1), C(2) and C(3), the basal ring carbons. The calculated chemical shifts and barrier of inversion of **41** agreed well with those observed by Olah and colleagues¹¹⁵. Various estimates of the stabilization energy of **41** were made.

It is clear from the consistent results of the various approaches used to probe the structure of **41** that this cation can be properly regarded as a homoaromatic system that meets the requirements set out in Section I.A above (see also Chapter 7²⁵). Substitution of the cation has also been demonstrated to lead to large changes in the structure and by no means can all the derivatives of **41** be classified as homoaromatic¹²⁷. This sensitivity of homoaromatic delocalization to substitution parallels that demonstrated with the homotropylium cations.

1. Boron analogues of the homocyclopropenium ions

As was mentioned in the introduction, cyclopropyl homoconjugation and homoaromaticity need not be restricted to simple carbocyclic systems. In the case of the homocyclopropenium ions, two ring substituted boron analogues have been reported. In order for the systems to retain 2π -electrons they must, in the case of **50**, with a single boron replacement, be neutral or, in the case of **51**, with two boron atoms, be negatively charged. While these systems can rightly be regarded as potentially neutral or anionic examples of homoaromaticity, their isolobal relationship to the homocyclopropenium cations makes their inclusion in this section a logical choice.



(41)



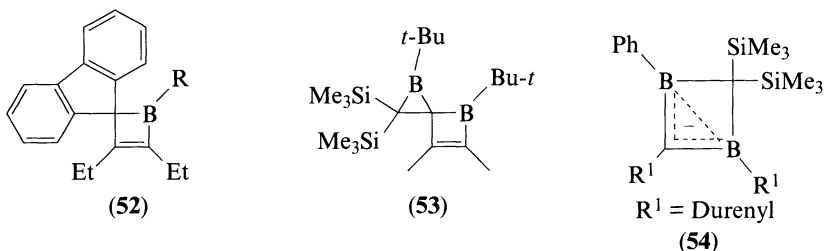
(50)



(51)

Berndt and colleagues have reported the preparation and characterization of **52**¹²⁸ and **53**¹²⁹. The latter ion was characterized by NMR methods and these indicated the existence of a strong 1,3 interaction. Calculations reported by Cremer and colleagues on the parent system, **50**, indicated that this too would have a folded conformation with a substantial 1,3 interaction¹³⁰. More recent *ab initio* calculations on **51** again indicated the adoption of a folded conformation (fold angle 23°)¹³¹. A significant B(1)–B(3) interaction was found with a 1,3 interaction index of 0.24. The calculated barrier of inversion in **54** was 4.3 kcal mol⁻¹.

The anion **54** has recently been reported by Berndt and coworkers¹³¹. Again, this species adopts a folded conformation (Table 4), which brings the two boron atoms into close



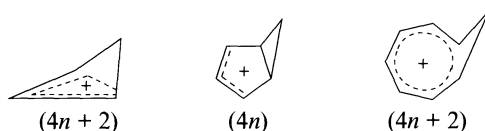
proximity [B–B distance 1.729(15) Å]. Ring inversion was found to occur with a barrier of 7.9 kcal mol⁻¹, a barrier essentially the same as that reported by Olah for **41**. Analysis of the ¹³C NMR chemical shifts of **54** as compared to model systems indicated that they were consistent with a cyclic homoaromatic 2π-electron delocalization.

Ab initio calculations for the parent anion **51** were also reported¹³¹. A similar conformation and structure was calculated for **51** as was determined for **54** (fold angle 34°, B–B distance 1.859 Å). The barrier to inversion in **52** was estimated to be 7.4 kcal mol⁻¹.

The structures and electron delocalization in these boron-substituted derivatives of the cyclobutenyl/homocyclopropenium cations are fully consistent with their designation as homoaromatic systems.

C. Bicyclo[3.1.0]hexenyl and Cyclohexadienyl Cations

Just as the unusual stability and reactivity of benzene are placed into their proper context by comparison with cyclobutadiene and cyclooctatetraene³⁹, the 4*n*-electron homologues of benzene, it is instructive to compare the formally homoantiaromatic bicyclo[3.1.0]hexenyl/cyclohexadienyl cation systems with the homocyclopropenium and homotropylium ions (Scheme 14). Such a comparison not only puts in context the properties of the latter two homoaromatic cations, but also reveals a different mode of cyclopropyl conjugation that occurs in the 4*n*-electron systems.

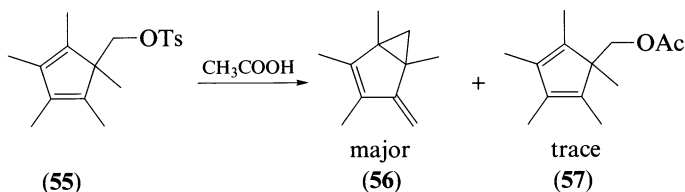


SCHEME 14. The monohomo- and homoantiaromatic cation series

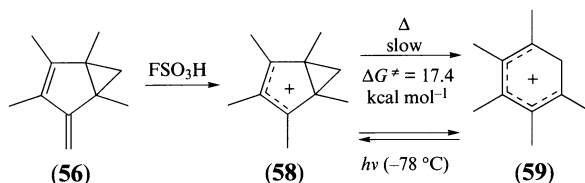
While considerable work has been reported on the bicyclo[3.1.0]hexenyl cation and its derivatives, the results of these studies have not been reviewed as extensively as those of the corresponding homoaromatic systems. The most detailed accounts of these systems are those of Koptyug¹³² and Barkhash¹³³. Numerous reviews on the cyclohexadienyl cations have appeared^{132,134}.

The initial work on the bicyclo[3.1.0]hexenyl system was reported by de Vries¹³⁵ and Winstein and Battiste in 1960¹³⁶. It was shown that acetolysis of the tosylate **55** occurred with a 10¹⁰-fold acceleration over neopentyl tosylate. The ionization of **55** was found to be anchimerically assisted with the predominant kinetic product of the reaction being the homofulvene **56**. Small amounts of the acetate **57** were also present. Pentamethylbenzene, the anticipated product, was notably absent under kinetic control conditions.

Further insight into this system was provided by the stable ion studies reported by Childs, Sakai and Winstein in 1968¹³⁷. These workers generated the cation **58** from **56** in



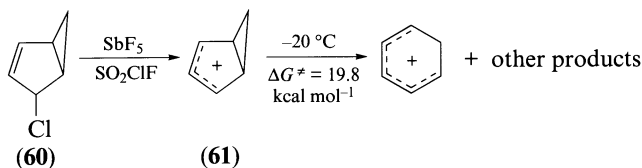
super-acid solution and showed that while its conversion to **59** occurred cleanly, the rearrangement was a relatively slow process involving a substantial activation barrier (Scheme 15). Subsequent work showed unequivocally that this isomerization involved a formally symmetry-forbidden electrocyclic ring-opening reaction and not a more deep-seated rearrangement process¹³⁸. It was suggested that charge delocalization in **58** involved the two external cyclopropane bonds rather than the internal one.



SCHEME 15. Interconversion of the bicyclo[3.1.0]hexenyl and cyclohexadienyl cations

Childs and Winstein also showed that irradiation of **59** led to a clean photoisomerization and the formation of a photostationary state consisting of **58** and **59**¹³⁹⁻¹⁴¹. Thus, in contrast to the homotropylium or homocyclopropenium ion systems, the 'open' and 'closed' forms of these $4n$ systems are interconverted in the first excited rather than ground state.

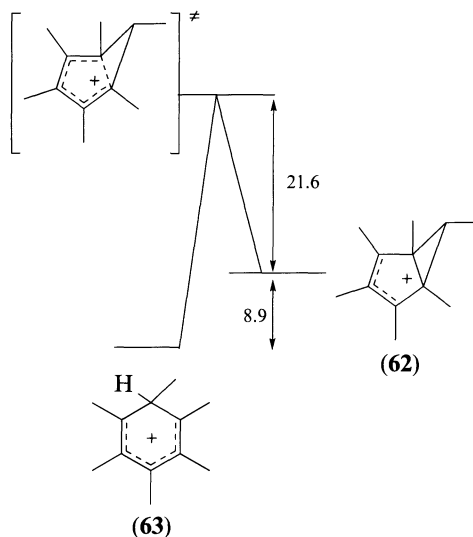
Berson and colleagues studied the parent cation **61** as a long-lived species in SO_2ClF as well as a transient species under solvolytic conditions¹⁴². It was again found that ring opening to the benzenium ion involved a substantial activation energy (Scheme 16). Consistent with this finding was the observation that solvolysis of **60** led to the formation of bicyclo[3.1.0]hexenyl derivatives and not benzene¹⁴³.



SCHEME 16. Formation of **61**

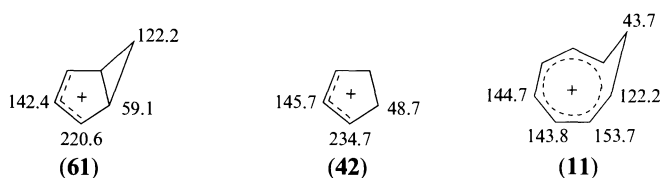
These early studies on the bicyclo[3.1.0]hexenyl/cyclohexadienyl cation system have been amply reinforced by many additional studies^{144,145}. Taken together, these results clearly show that the potential energy surface linking the bicyclo[3.1.0]hexenyl and cyclohexadienyl cations has energy minima corresponding to each of these two structures and that the cyclically delocalized homoconjugate structure is a transition state for their interconversion. This is illustrated in Scheme 17 for the hexamethyl-substituted bicyclohexenyl and cyclohexadienyl cations where a detailed thermochemical investigation has been under-

taken¹⁴⁶. There is a fundamental difference in the nature of the potential energy surface linking cations such as **62** and **63** to that found in the homocyclopropenium and homotropenylium ions. In the latter case, the cation occupies a single minimum on the potential energy surface, whereas ions **62** and **63** correspond to two local minima connected by an intermediate transition state. This transition state is located at about the same interaction distance as the no-bond homoaromatic homotropenylium and homocyclopropenium ions. The consequences of these differences are discussed in Section II. D of the accompanying review²⁵.



SCHEME 17. Isomerization of **62** (energies in kcal mol⁻¹)

Information on electron delocalization in the bicyclo[3.1.0]hexenyl cations is available from their reported NMR spectra¹³⁷⁻¹⁴⁵. Data obtained with a variety of systems point to a completely different charge delocalization pattern to that found with the homotropenylium ions. For example, Olah and colleagues have obtained the ¹³C NMR spectrum of the parent ion¹¹⁴, **61**, and compared this with those of **42** and **11**. As can be seen from the data summarized in Scheme 18, the chemical shifts of the five-membered ring carbons of **61** resemble those of the cyclopentenyl cation. There is a considerable difference in chemical shifts, and hence charge distribution, at C(2), C(4) and C(3) of **61**. There is no evidence for the fairly even charge distribution as is found for the homotropenylium and homocyclopropenium ions (see previous Sections III. A and III. B). It was also noted by Olah that the chemical shift of C(6) is consistent with large delocalization to this position, i.e. to conjugation of the allyl system of **61** with the external cyclopropyl bonds.

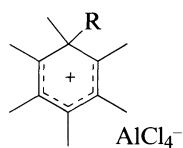


SCHEME 18. ¹³C NMR shifts (ppm)

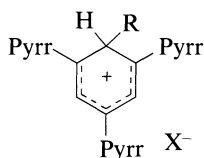
There have been a large number of studies of the NMR spectra of cyclohexadienyl cations^{147,132,133}. These systems behave as open-chain hexadienyl cations and no C(1)–C(5) homoconjugative interaction is evident or needed to account for their spectroscopic properties.

1. Structures of the cations

The structures of the bicyclo[3.1.0]hexenyl and cyclohexadienyl cations have been examined using X-ray crystallography as well as theory. Crystal structures of cyclohexadienyl cations such as **62**¹⁴⁸, **63**¹⁴⁹ and **64**¹⁵⁰ have been reported. Unfortunately, the errors associated with these determinations are relatively large and, as a result, no significance can be placed on variations in individual C–C bond distances in the unsaturated fragments. However, it is clear in the cases where the C(6) substituents are the same that the cations adopt a planar or near-planar conformation. Where the C(6) substituents are dissimilar, the cations adopt a shallow envelope-type conformation with C(6) being out of the plane of the pentadienyl unit. However, there is no suggestion in any of these structures for any significant C(1)–C(5) through-space interaction.

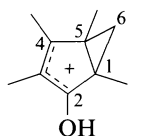


(**62**) R = Me
(**63**) R = Ph

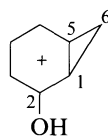


(**64**) R = H; X = ClO₄⁻
Pyrr = *N*-Pyrrolyl

In terms of the bicyclo[3.1.0]hexenyl ions, the structure of the protonated ketone **65** was determined by Childs, Lock and colleagues⁶⁰. The bond distances associated with the protonated carbonyl group and unsaturated portion of **65** were completely consistent with those expected for a protonated enone (Table 5). However, comparison of the cyclopropyl portion of structure **65** with that of the 2-hydroxyhomotropenylium ion (*vide supra*) and



(**65**)



(**66**)

TABLE 5. Selected bond distances (Å) for **65**, **66**^a and **61**

Compound	C1—C2	C2—C3	C3—C4	C4—C5	C5—C6	C1—C6	C1—C5
65 ^b	1.474	1.410	1.351	1.510	1.501	1.547	1.511
66 ^c	1.403			1.502	1.433	1.534	1.559
61 ^d	1.492	1.392	1.392	1.492	1.535	1.535	1.501

^aNumbering scheme for **66** is non-standard as shown on the structure.

^bAverage σ is 0.008 Å.

^cAverage σ is 0.011 Å.

^dCalculated structure STO-3G³⁰.

other protonated cyclopropyl ketones, e.g. **66**⁶¹, revealed several unusual features. In the first instance, the homoconjugate bond, C(1)—C(5), distance is the same as that of a normal cyclopropyl ring. It is much shorter than encountered with that found for the comparable internuclear distance in the homotropenylium ion or that expected for a comparable bond in a non-cyclically conjugated protonated cyclopropyl ketone. Secondly, it was suggested that the C(1)—C(2) and C(4)—C(5) bond distances were in each case significantly longer than those expected for comparable bonds between a protonated carbonyl carbon atom or vinyl carbon atom and a cyclopropyl carbon, respectively. The authors tentatively suggested that the cation adopts a structure which minimized interaction of the internal cyclopropane bond with the allyl portion of the system. The relatively long C(1)—C(6) bond was taken to be suggestive of conjugative involvement of this external cyclopropane bond.

No other experimental structure determinations of bicyclo[3.1.0]hexenyl cations have been reported. Theoretical calculations have been undertaken by Hehre^{105,151} and Cremer and colleagues³⁰. While in each of these instances the calculations were at a low level, the results are consistent with the presence of a short C(1)—C(5) and long C(1)—C(6)/C(5)—C(6) internuclear distances for the parent cation.

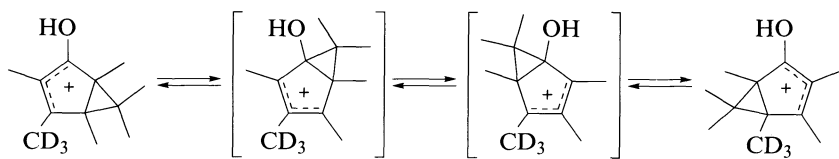
While more work is required in order to complete our understanding of the structure of **65**, the picture that emerges from these studies is that of a cation in which conjugation involves the allyl portion of the five-membered ring with the two external cyclopropane bonds. Hehre pointed out^{105,151} that such a conjugated system is formally Möbius system with 6π electrons and thus formally antiaromatic (see the discussion in Section III. C of the preceding chapter²⁵). Cremer and coworkers^{26,30} concluded on the basis of an electron density analysis of **65** that close to six electrons are involved in electron delocalization along the periphery of the bicyclic system in a similar mode as was found for bicyclo[2.1.0]pent-2-ene (see the discussion in Section V. A. and the preceding chapter²⁵). Applying the definitions given in Section I. A above, the latter system is clearly homoantiaromatic in view of its energetic and structural properties. Similarly, it is likely that the bicyclo[3.1.0]hexenyl cation falls into the same category. However, a detailed analysis of its relative stability has to confirm this characterization.

2. Rearrangements of bicyclo[3.1.0]hexenyl cations

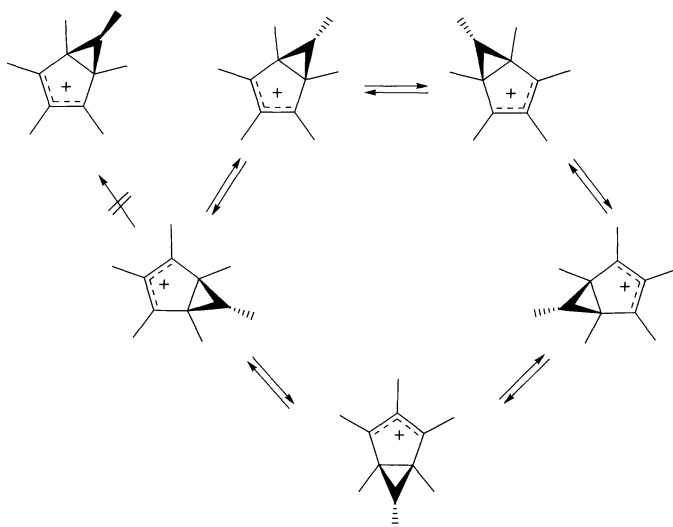
The basic differences in electron delocalization between the homoaromatic homotropenylium and homocyclopropenylium ions and the bicyclo[3.1.0]hexenyl cations result in fundamentally different reactions of these cations. As was noted earlier, the homotropenylium and homocyclopropenylium ions undergo a characteristic ring-inversion process which interconverts the *exo* and *endo* substituents on the methylene bridge. With **61** and its derivatives no such reaction occurs. Rather, two different types of thermal isomerization occur. The first of these is the irreversible rearrangement to the cyclohexadienyl ions mentioned above. The second thermal isomerization involves a circumambulation of the methylene group around the periphery of the five-membered ring^{137-143,145,152}.

Typical examples of circumambulatory rearrangements of bicyclo[3.1.0]hexenyl cations are shown in Schemes 19 and 20. Swatton and Hart reported the isomerization shown in Scheme 19 in 1967 and proposed that the observed deuterium scrambling could be accounted for on the basis of a cyclopropyl walk reaction¹⁵³. This circumambulation is comparable to that proposed by Zimmerman and Schuster as part of the sequence of reactions involved in the type A photorearrangement of 2,5-cyclohexadienes¹⁵⁴.

Childs and Winstein observed the rapid, five-fold degenerate circumambulation of the hepta- and hexamethylbicyclo[3.1.0]hexenyl cations in 1968¹³⁹ (Scheme 20) and subse-

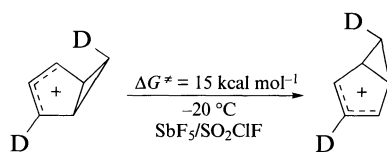


SCHEME 19. Circumambulatory rearrangement of a protonated bicyclohexenone

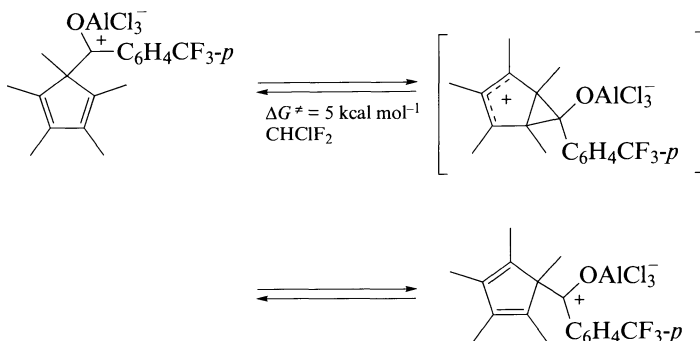


SCHEME 20. Degenerate circumambulatory rearrangement of a hexamethylbicyclo[3.1.0]hexenyl cation

quently went on to show the remarkably high stereoselectivity associated with these reactions¹⁴⁰. Rearrangements of the parent ion have been examined by Berson and colleagues¹⁴² (Scheme 21).

SCHEME 21. Circumambulation of **61D**

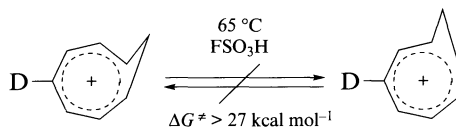
Overall, these rearrangements are facile, low activation energy processes which occur with very high stereoselectivity. The energy barriers to the isomerizations are lowered by electron-donating substituents placed on C(6). In fact, Childs and Zeya have shown that with the appropriate choice of substituents it is possible to invert the energies of the ground and transition states for these circumambulations¹⁵⁵. For example, as is shown in Scheme 22, the Lewis acid complexes of the 5-acylpentamethylcyclopentadienes undergo facile circumambulatory rearrangements in which the corresponding bicyclo[3.1.0]hexenyl cations are now transition states for these degenerate isomerizations.



SCHEME 22. Circumambulation of a cyclopentadienylcarbinylium cation

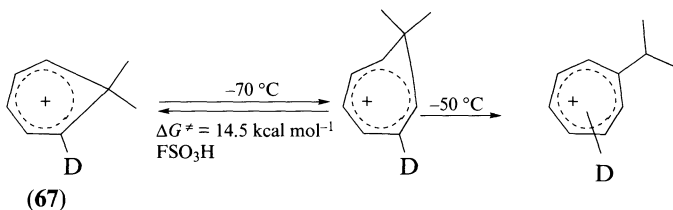
It is interesting to note that the bicyclo[3.1.0]hex-3-en-2-yl radical corresponding to the cation **61** also undergoes a degenerate circumambulatory rearrangement. The barrier to this rearrangement is lower than the ring-opening reaction to give the cyclohexadienyl radical¹⁵⁶.

Berson and Jenkins have looked for a comparable circumambulation in the parent homotropenylium ion **11** using the 4-deuterium labelled ion (Scheme 23)¹⁵⁷. They were unable to detect the occurrence of any circumambulation prior to decomposition of the ion and, as a result, it was only possible to obtain a lower limit of 27 kcal mol⁻¹ for the barrier for circumambulation. Hehre calculated (HF/STO-3G) the barrier to thermally induced circumambulation in **11** as being 43 kcal mol⁻¹^{105,151}. Once more it is clear that there is a fundamental difference in the properties of the bicyclo[3.1.0]hexenyl cations and the homotropenylium ions which can be attributed to the difference in electron delocalization of the two systems.

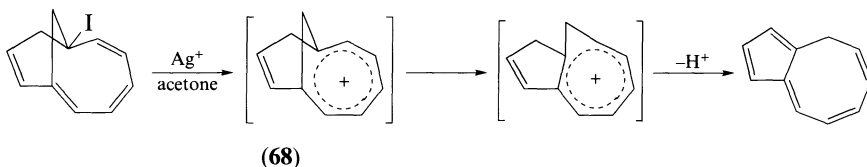
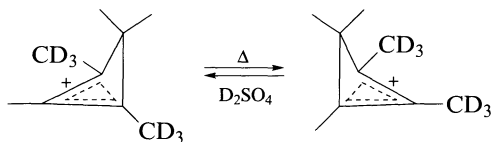
SCHEME 23. Examination of circumambulation in **11D**

It is possible to detect thermally induced circumambulations in certain substituted homotropenylium ions. Hehre in his theoretical study (HF/STO-3G) of **11** suggested that the placement of methyl substituent at C(8) of the homotropenylium ions should reduce the barrier to the thermally induced circumambulation^{105,151}. The correctness of this prediction was confirmed by Childs and Varadarajan who reported the generation of the deuterium labelled cation **67** and the measurement of the rate of deuterium scrambling associated with circumambulation of C(8) around the 'seven-membered' ring (Scheme 24)¹⁵⁸. The barrier for this circumambulation was found to be 14.5 kcal mol⁻¹. Scott and Brunsvold have also reported the occurrence of a circumambulation in a bridged homotropenylium ion, **68** (Scheme 25)¹⁵⁹.

Circumambulation of the bridging methylene carbon of the homocyclopropenylium ion has not been observed experimentally. Devaquet and Hehre, in examining this reaction using theory (HF/STO-3G), have suggested that circumambulation is a relatively high-energy process that will take place preferentially by the formally symmetry-forbidden pathway¹⁶⁰. Koptuyg and colleagues have reported that a circumambulation of the bridg-



SCHEME 24. Rearrangement of 8,8-dimethylhomotropenylium ion

SCHEME 25. Rearrangement involving the bridged homotropenylium ion **68**

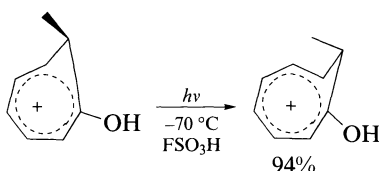
SCHEME 26. Degenerate rearrangement of a homocyclopropenylium ion

ing $C(CH_3)_2$ group can be detected with the labelled pentamethyl cation (Scheme 26)¹⁶¹. Specific deuterium-labelling experiments ruled out the alternative 1,2-methyl shift process¹⁶².

The different electronic properties of the bicyclo[3.1.0]hexenyl, homotropenylium and homocyclopropenylium ions is reflected in the nature of the transition state for the two circumambulatory rearrangements. For example, in the case of **61**, migration of C(6) involves inversion at C(6) leading to an overall retention of stereochemistry. This least motion allowed process occurs with the conservation of orbital symmetry¹⁶³. In the case of **11**, the symmetry-allowed rearrangement formally involves migration with retention of configuration at C(8) which would lead to a net interconversion of the *exo* and *endo* substituents. Such a rearrangement places severe geometry constraints on the transition state for migration.

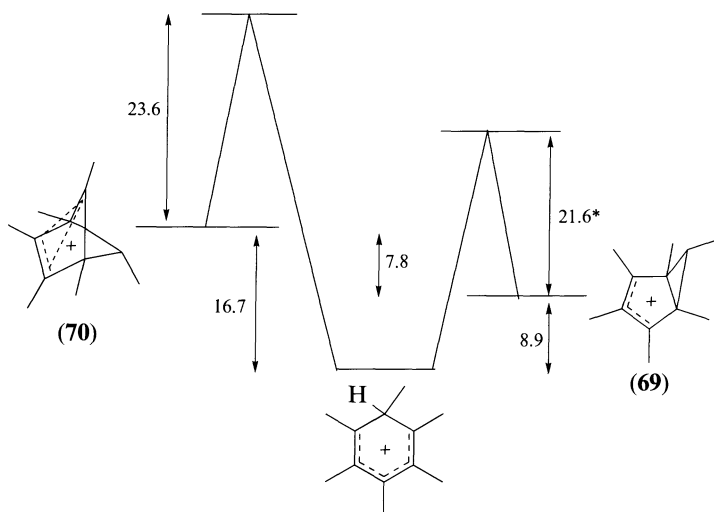
The geometric limitation for migration with retention of configuration should be lifted in the first excited state of the homotropenylium ions. Childs and Rogerson showed that this was indeed the case and reported a number of examples where photochemically induced circumambulations take place. An example is given in Scheme 27¹⁶⁴.

In concluding this section on the homoaromatic and homoantiaromatic cations, it should be pointed out that in the case of both the homotropenylium and bicyclo[3.1.0]



SCHEME 27. Photochemical rearrangement of a homotropenylium ion

hexenyl cations there are other isomeric ions which can be produced by different types of rearrangement of the bridging methylene group. This has already been pointed out for the homotropenylium ions in Scheme 8 where their interconversion with the bicyclo[3.2.1]octadienyl ions was presented. As was pointed out earlier, the bicyclooctadienyl cation is formally a bishomoantiaromatic system. In contrast, in the case of **69**, the isomeric bicyclo[2.1.0]hexenyl ions, **70**, can be obtained by a 1,2 sigmatropic shift of C(6), (Scheme 28). The bicyclo[2.1.0]hexenyl ions are formally bishomoaromatic systems and thus might be considered to be more stable than **69**. In fact with the hexamethyl-substituted ions such as **70**, which have been extensively studied by Hogeveen and Volger¹⁶⁵ and Paquette, Olah and colleagues¹⁶⁶, this has been shown not to be the case. Thermochemical measurements by Childs, Mulholland and Nixen⁸⁷ have shown that the bicyclo[2.1.1] ions are less stable ($\Delta H = 7.8 \text{ kcal mol}^{-1}$) than the bicyclo[3.1.0]systems (Scheme 28).

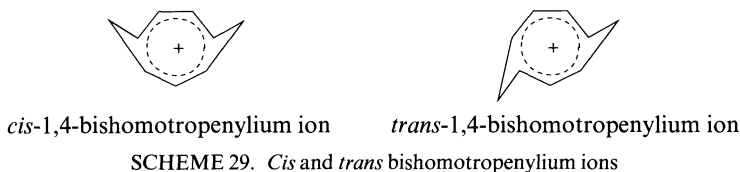


SCHEME 28. Thermochemical relationship between bicyclohexenyl cations (all values are enthalpies except for a ΔG^\ddagger value marked with* and are in kcal mol^{-1})

In summary, the bicyclo[3.1.0]hexenyl cations clearly show that homoconjugation is an important factor in determining the chemistry and properties of these cationic systems. The properties of the bicyclo[3.1.0]hexenyl cations are sharply different from those of the homotropenylium and cyclopropenylium ions, reinforcing the designation of the latter two cations as being examples of homoaromatic systems.

IV. HIGHER HOMOAROMATIC CATIONS

As was mentioned in the introductory sections of this chapter, in principle it is possible to insert more than one homoconjugative interaction in an aromatic system. For example, two homoconjugative linkages would give a potentially bishomoaromatic molecule. In addition to the number and relative positions around the base ring of the bridging groups associated with the homoconjugative linkages, it is also possible for these bridges to adopt a *cis* or *trans* orientation with respect to each other. This possibility is illustrated in Scheme 29 for the 1,4-bishomotropenylium ion.

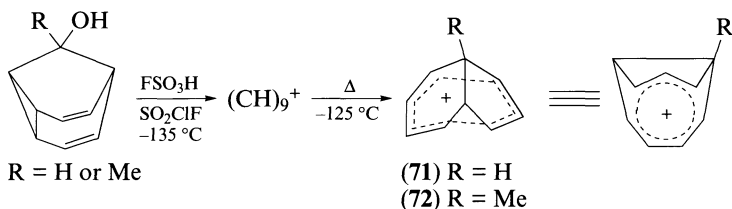


A further general point needs to be made before specific systems are examined. In the introduction, we laid out the two general approaches to homoconjugative systems. These involved the 'bond' and 'no-bond' starting points. We also pointed out that, in terms of the context of this chapter on cyclopropyl-homoconjugation, the formal starting point is the 'bond' or closed cyclopropane ring. Depending on the relative placement of the homoconjugative linkages, it may not be possible in a given system to have as a formal starting point a resonance structure with all of the linkages being in the closed or cyclopropane form.

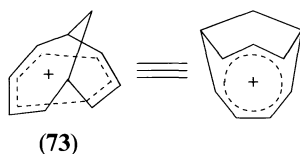
A. Bishomotropanylium Ions

Early work on the bishomotropanylium ions has been reviewed by Paquette¹⁸ and a more recent account given by Williams and Kurtz²¹. In this section, we will pick up the highlights and particularly emphasize recent work on these cations that helps to define the nature of their electron delocalization and structure.

In 1970 Ahlberg, Harris and Winstein reported the preparation of **71** and **72**, the first examples of bishomotropanylium ions¹⁶⁷. These 1,4-bishomoaromatic cations were prepared by ionization of the corresponding barbaralyl systems as shown in Scheme 30. The formation of **71** and **72** proceeds by way of an initial barbaralyl cation, the structure and nature of which has been the subject of a considerable amount of work¹⁶⁸⁻¹⁷⁰. The initially formed unsubstituted barbaralyl cation rearranges to **71** at -125°C .



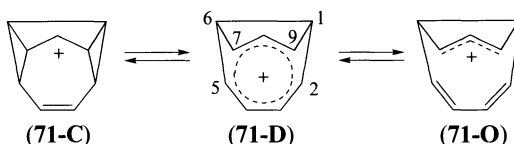
Since these original reports, a variety of different routes have been used to prepare these ions¹⁷¹⁻¹⁷⁴. A related 1,4-bishomotropanylium ion, **73**, was prepared independently by Roberts, Hamberger and Winstein¹⁷⁵ and Schröder and colleagues¹⁷⁶.



The ease of formation of **71**, **72** and **73** and their relative stability belies the difficulties which have been encountered in defining their structures and mode of charge delocaliza-

tion. Most of the recent work has been conducted on **71** and it is on this system that most attention will be focussed.

The key issue in adequately understanding the structure and properties of **71** again lies in defining the shape of the potential energy surface linking the open, closed and delocalized structures, **71-O**, **71-C** and **71-D**, respectively (Scheme 31). Is **71-D** a transition state linking the two other species or is it the overall energy minimum (see Section I of preceding chapter²⁵)?



SCHEME 31. Bishomotropanylium ion potential energy surface

The closed form **71-C** has not been considered to be the energy minimum on the potential energy surface. Not only are the properties of the observed cation inconsistent with the presence of two cyclopropane rings, but this ion is expected to be highly strained. Distinction between **71-D** and **71-O** has proved to be more difficult.

Examination of the ^1H NMR spectrum of **71** provided comparatively little definitive information on its structure and electron delocalization¹⁷¹. In particular, the absence of *exo* and *endo* protons on the bridging carbons meant that the difference in their chemical shifts, the traditional but overly simplistic indicator of homoaromatic delocalization, could not be used. Detailed analyses of the ^1H NMR spectra of the cations suggested that their structures could be understood in terms of a bishomotropanylium formulation rather than the non-cyclically delocalized cation **71-O**. Further evidence on the nature of the charge delocalization was provided by the ^{13}C NMR spectra of **71** and, in particular, their ^{13}C – ^{13}C coupling constants¹⁷⁷. All of the NMR evidence is consistent with the delocalized structure **71-D** and a fairly even distribution of charge over the basal ring carbons. However, examination of these systems solvolytically provided less than convincing evidence for the importance of a bishomotropanylium formulation of the structure of **71**^{171–178}.

More recent work on these cations has focussed on the theoretical examination of their structure and stability. Initial theoretical approaches using semi-empirical methods led to no firm conclusions¹⁷⁹. The most recent calculations of the potential energy surface linking the two ions were reported by Cremer, Ahlberg and colleagues in 1993²⁸. These high level calculations [MP2, MP3, MP4(SDQ) employing DZ+P basis set, IGLO calculations and MP2 electron density analysis] showed, in contrast to earlier Hartree–Fock results¹⁸⁰, that **71-D** rather than **71-O** is the energy minimum. However, the homoaromatic stabilization of **71** was found to be small and only of the order of 3 kcal mol⁻¹.

The key features of the calculated structure of **71** were homoconjugative interaction distances close to 2.0 Å and equalization of both the various C—C bond distances and the atomic charges (Table 6). Cremer and colleagues matched the calculated ^{13}C NMR chemical shifts with those observed for **71** as a function of the homoconjugative distance and found a good fit for **71** (mean deviation 8.5 ppm) with a fold angle of 93° and a distance of 2.1 Å (Table 7). As can be seen from the data in Table 7, structure **71-O** gave a very poor fit of the NMR chemical shifts (mean deviation 19 ppm). The authors note that the chemical shifts of the C(7)/C(9) resonances are particularly sensitive to changes in the C(5)/C(7) [C(2)/C(9)] interaction distance and that an exact fit of the observed chemical shift of 155.5 ppm can be obtained with a small reduction in this interaction distance.

TABLE 6. Calculated structures of **71**^{28,169,180}.

Bond	71-D ^a	71-D ^b	71-O ^c
C(2)—C(3)/C(4)—C(5)	1.380 Å	1.348 (Å)	1.357 (Å)
C(3)—C(4)	1.411	1.427	1.442
C(7)—C(8)/C(8)—C(9)	1.393	1.378	1.390
C(2)—C(9)/C(5)—C(7)	2.147	2.075	2.356
Fold angle (deg)	100.0	93.2	113.8

^aGeometry at calculated [MP4(SDQ)-MP2/6-31G(d)] energy minimum.

^bGeometry calculated [MP2/6-31G(d)] for fold angle of 93° obtained from best fit of IGLO calculated chemical shifts.

^cMP2/6-31G(d) calculated geometry.

TABLE 7. Calculated (IGLO) and observed ¹³C chemical shifts (ppm) of **71**^{28,169,180}

Carbon	71-D	71-O	Experiment
C(1)/C(6)	45.9	46.4	52.6
C(2)/C(5)	121.5	121.2	117.2
C(3)/C(4)	145.4	141.9	140.2
C(7)/C(9)	176.9	227.4	155.5
C(8)	145.4	148.3	144.0

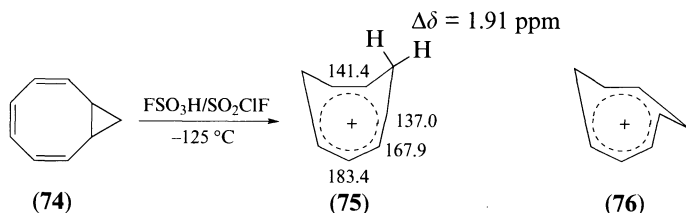
It should be noted here that it was the exploration of the **71** potential energy surface which led to the establishment of the criteria for homoaromaticity set out at the start of this chapter and the accompanying review²⁵.

Overall, it is clear that **71** can rightly be considered to be a bishomoaromatic system. However, it was pointed out by Cremer, Ahlberg and colleagues that the relatively small stabilization energy associated with **71** means that substitution could have a major effect on the relative energies of **71-D** and **71-O**. The classification of **71** as bishomoaromatic does not mean that derivatives of **71** will also have a comparable electron delocalization pattern and structure.

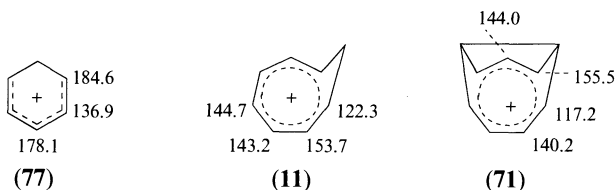
Cation **71** has a bridge which links the 'cyclopropyl' carbons and thus maintains an appropriate orientation for homoconjugation. While such a linkage is not formally required for homoaromatic delocalization, it is an open question as to whether examples of bishomotropenylium ions exist which lack such a framework.

Protonation of **74** in FSO₃H at low temperatures was shown by Warner and Winstein to give a cation which was suggested to be the *cis*-1,3-bishomotropenylium cation, **75**¹⁸¹. The main evidence for the structure of **75** was its ¹H and ¹³C NMR spectra^{18,182}. However, the ¹H NMR spectrum showed only a small difference in chemical shifts between the *exo* and *endo* bridge protons ($\Delta\delta = 1.91$ ppm). The authors suggested that the pattern of the shifts of the resonances of the vinyl protons and the unsaturated carbons was indicative of a somewhat more even distribution of charge than is found in a pentadienyl cation. They concluded that **75** should be considered as being homoaromatic.

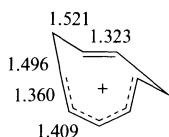
However, comparison of the ¹³C NMR spectrum of **75** with the model compounds raises in our minds serious questions as to the validity of these claims. Apart from the ¹³C chemical shifts of the C(1)/C(5) carbon resonances (137.0 ppm) the rest of the resonances are in positions typical of a dienyl cation and an isolated double bond [C(6) and C(7)]. The large spread in the ¹³C chemical shifts reported for **75** indicated a very uneven charge distribution in the ion.



Recent *ab initio* calculations by Cremer and coworkers carried out for the *cis* isomer **75** and the corresponding *trans* isomer **76** provide convincing evidence that both isomers preferentially exist in 'classical' valence tautomeric forms rather than delocalized homoaromatic systems¹⁸³. The *cis* isomer **75** was shown to prefer the closed form by about 7 kcal mol⁻¹ while **76** prefers the open form by 4 kcal mol⁻¹.



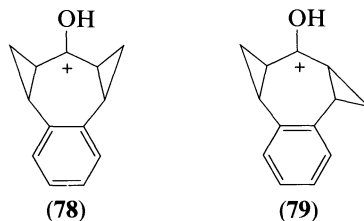
The *trans* isomer **76** was found to be more stable than the *cis* form **75** by 6 kcal mol⁻¹. Since the experimental ¹³C NMR shift values exclude the possibility of a closed form, it would appear that Warner and Winstein prepared **76** rather than **75**. Cremer and coworkers also pointed out that agreement between the calculated and experimental ¹³C NMR spectrum can only be obtained by re-assigning the shifts assigned to C(1) and C(2)¹⁸³. When this is done, the chemical shifts resemble those of **77** rather than the homoaromatic models **11** or **71**. This conclusion is supported by the calculated geometry of **76** which suggests the existence of an almost isolated double bond that does not interact with the pentadienyl system (Scheme 32)¹⁸³.



SCHEME 32. Calculated bond distances of **76**

Cremer and colleagues concluded the **76** is non- or only very weakly, bishomoaromatic¹⁸³. However, the transition state for the valence tautomeric interconversions of **75** and **76** was found to possess all the characteristics of homoaromatic electron delocalization.

Other attempts to prepare non-bridged *cis* and *trans* bishomotropenylium ions have also not been successful. Childs and Corver prepared 1,4-bridged cations **78** and **79** by protonation of the corresponding ketones¹⁸⁴. It was concluded on the basis of ¹H NMR studies that neither cation could be regarded as being homoaromatic. It would appear that in the *cis*-isomer, steric interactions between the two methylene groups prevent the cation from attaining an appropriate geometry for cyclic homoconjugation of the two cyclopropane rings. In the case of the *trans*-isomer, the steric problem associated with the two methylene groups is absent. However, it is not possible for the cation to adopt a boat-type conformation, as has been found for the parent homotropenylium ion, that allows both cyclopropanes to be situated for effective homoconjugation. The results with **78** and **79**, both potentially 1,4-bishomotropenylium ions, are consistent with the findings of Cremer and



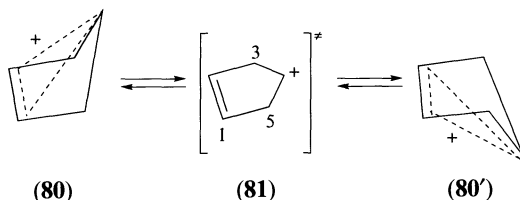
colleagues, discussed above, of the very small homoaromatic stabilization energy associated with the 1,4-bishomotrophenylium ions.

There have been several attempts to prepare trishomotrophenylium ions. However, these have all been unsuccessful¹⁸⁵.

B. Bishomocyclopropenium Ions

A large amount of work has been reported on potentially bis- or trishomocyclopropenium ions. Many reviews exist including those by Winstein^{14,16}, Story and Clark¹⁷, Williams and Kurtz²¹, Koptug¹³², Hogeveen and Kwant¹⁸⁶, Lenoir and Siehl¹⁸⁷ and a particularly full account by Barkhash¹³³. The topic also overlaps that of the pyramidal cations and related boranes¹⁸⁸. In this present section we will again not give an exhaustive account but concentrate on a few key systems where there has been some recent definitive work reported.

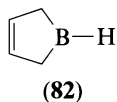
In terms of systems lacking a bridging framework to hold the homoconjugative linkages in an appropriate geometry, the cyclopentenyl cation **80** is the important example. In order for homoconjugative stabilization to be effective in **80**, the cation must exist in a non-planar configuration such that the double bond and C(3), the cationic centre, are placed in a suitable geometry (Scheme 33). In the planar conformation, no homoconjugative stabilization is possible but rather an inductive destabilization of the charge at C(4) by the double bond is expected. Calculations by Schleyer and colleagues at the MP2(FC)/6-31G(d)//6-31G(d) level indicate that the non-planar form **80** is about 19 kcal mol⁻¹ lower in energy than the planar form, **81**¹⁸⁹. More recent high-level calculations of Szabo, Kraka and Cremer revealed that MP2 seriously exaggerates the energy difference¹⁹⁰. At MP4/DZ+P using MP2 geometries, the non-planar form **80** is 6 kcal mol⁻¹ more stable than **81**. The envelope form of **80** is strongly folded (fold angle *ca* 90°), thus reducing the distance between the two interacting atoms C(3) and C(5) from 2.33 Å in **81** to 1.76 Å in **80**. Cremer and colleagues pointed out that both hyperconjugative interactions and strain effects favour the planar form **81**¹⁹⁰. This means that the energy difference of 6 kcal mol⁻¹ provides only a lower limit to the true homoaromatic resonance energy of **80**.



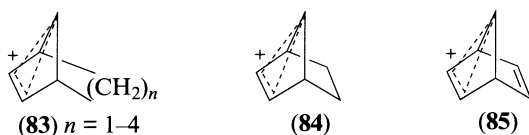
SCHEME 33. Ring inversion of **80**

Despite the seeming stability of **80**, all attempts to prepare the cation as a stable species in super-acid media have been unsuccessful^{191,192}. The retention of configuration at C(4) in solvolysis of cyclopentene derivatives suggests that there is some involvement of the

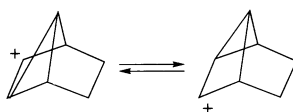
double bond in charge delocalization; however, this participation is not clearly reflected in the rates of ionization of these systems^{22,193}. It is interesting that the calculations on the borolene **82** corresponding to **80** indicate that the potential energy surface is almost flat with only very shallow minima for the bent forms²².



There have been a larger number of reports on the preparation of bridged bishomocyclopropenium ions in which the homoconjugative bridges are linked together by an appropriate carbon framework. Most of these systems have the general structure **83** and the special case **85** where the bridge is a —CH=CH— unit. The reviews cited above cover much of the work reported on these systems. The focus here will be on recent results with the 7-norbornenyl, **84**, and the 7-norbornadienyl cations, **85**.

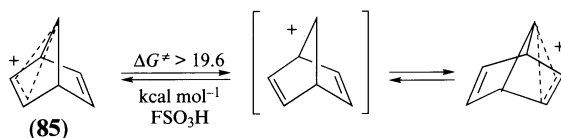


The initial report on the formation of **84** was by Winstein and colleagues in 1955¹⁹⁴. These workers noted the remarkable anchimeric acceleration and high regioselectivity of product formation associated with the ionization of *anti*-7-norbornenyl derivatives. The 7-norbornadienyl derivatives were found to show even larger rate accelerations¹⁹⁵. These unusually large rate accelerations were attributed to neighbouring group participation or homoconjugation. Later these ions were called bishomocyclopropenium ions¹⁹⁶. Brown and Bell offered a contrary view and suggested that **84** could be considered to be a rapidly equilibrating pair of cyclopropylcarbanyl cations (Scheme 34)¹⁹⁷.



SCHEME 34. Equilibrating cyclopropylcarbanyl cations

Both **84** and **85** have been prepared as stable ions in super-acid media and their NMR properties studied¹⁹⁸⁻²⁰¹. The conclusions reached from the extensive amount of work done with the parent and a variety of substituted systems is that both ions can be considered to be bishomoaromatic. In the case of **85** it should be noted that the C(7) bridge was found to lean towards and interact with one of the double bonds. Cation **85** was found to undergo an inversion process in which there is an interchange of the participating double bond (Scheme 35). Winstein and coworkers were able to place a lower limit of 19.6 kcal mol⁻¹ on



SCHEME 35. Interconversion of 7-norbornadienyl cations

TABLE 8. Structures of 7-norbornenyl cations and related compounds^a

Cation	Method	C(2)—C(3)	C(2)—C(7)	Reference
86	X-ray	1.38(1)	1.86(1)	202
84	6-31G(d)	1.380	1.938	203
85	6-31G(d)	1.380	1.719	203
85	MP2(FU)/6-31G(d)	1.400	1.701	203
87	MP2(FU)/6-31G(d)	1.396	1.775	204
87	MP2(FU)/6-31G(d)	1.392	1.759	204
89	X-ray	1.375	1.864	205
90	X-ray		1.814	205

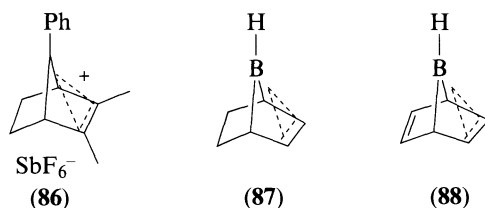
^aAll distances given in Å.

the barrier to this process¹⁹⁸. The value of this barrier can be thought of as an estimate of the stabilization achieved by homoconjugative participation of the double bond with C(7). Substitution at C(7) was found to lower the barrier to inversion.

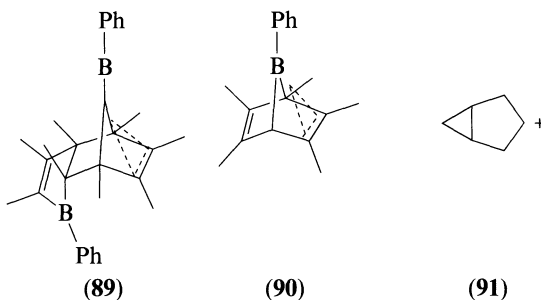
Structural information on these systems was recently provided by two groups. Laube reported the X-ray structure determination of the norbornenyl cation **86**²⁰² while Schleyer and colleagues published the results of high-level calculations on **84** and **85**²⁰³.

While **86** has a phenyl substituent at C(7) and, as has been noted above for the dienyl system, this substitution could substantially reduce the need for interaction of C(7) with the double bond, the structure found by Laube is fully consistent with a bishomoaromatic formulation (Table 8). The C(7) bridge was found to lean towards the double bond bearing the two methyl groups giving C(2)—C(7)/C(3)—C(7) distance of 1.86(1) Å. This distance is well within the range encountered for the homoconjugative distance in homoaromatic systems. The C(2)—C(3) distance of 1.38(1) Å is intermediate in length between that of C, C single and double bonds.

The calculations of Schleyer and colleagues at the MP2(FU)/6-31G(d) level gave very similar results for **85** and an even more distorted structure for **84**. The calculated ¹³C NMR spectra of these ions were comparable to those observed experimentally; however, no systematic structural changes have yet been reported which optimize the fit of the calculated chemical shifts.



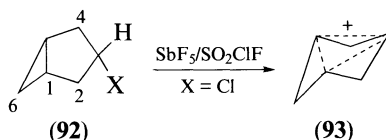
Recently, work has been reported on the 7-boranorbornene (**89**) and 7-boranorbornadiene (**90**) systems related to **84** and **85**. Schleyer and colleagues have examined the parent molecules **87** and **88** theoretically [MP2(FU)/6-31G(d)] and concluded that they have very similar structures and electron delocalizations to the related cations (Table 8)^{203,204}. X-ray structures of substituted derivatives of **89** and **90** have been determined and these have very similar distorted conformations to those of **84**, **85** and **86**²⁰⁵. Calculated (IGLO) NMR chemical shifts of **87** and **88** correspond well with those observed experimentally.



C. Trishomocyclopropenium Ions

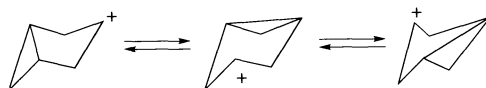
The trishomocyclopropenium species **91** has been an important cation in terms of the development of the concept of homoaromaticity. It also provides an example of a different mode of cyclopropyl homoconjugation to that encountered in the systems discussed thus far. In **91**, the cyclopropane is formally interacting with the remote positive charge in an edge-on manner. All of the previous examples discussed have involved a cyclopropyl carbonyl-type interaction with the conjugating group being joined to the cyclopropane.

Winstein, Sonnenberg and de Vries first proposed the intermediacy of **91** in order to account for the solvolytic properties and products of derivatives of **92**²⁰⁶. A major advance in understanding the properties and structure of **91** came from the laboratories of Masamune and colleagues, who reported the preparation of the cation as a stable species in super-acid media²⁰⁷, a preparation later repeated by Olah and colleagues^{192,208} and Kelly and coworkers (Scheme 36)²⁰⁹.



SCHEME 36. Formation of trishomocyclopropenium ion

The key feature of the NMR spectra of **91** is its simplicity. Thus the ¹³C NMR spectrum consists of only two resonances at 4.9 and 17.6 ppm, indicating either a symmetrical trishomocyclopropenium cation, **93**, or rapid equilibration between three equivalent structures (Scheme 37). The positions of the ¹³C NMR resonances of the cation strongly suggested the formulation of its structure as the trishomocyclopropenium ion, **93**²¹⁰. This conclusion was reinforced by the preparation of the deuterated cation and examination of the isotopic perturbation of its ¹³C chemical shifts^{208,211}, and measurement of the ¹³C-¹H coupling constants²⁰⁹.



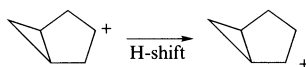
SCHEME 37. Equilibration between classical bicyclohexyl cations

Szabo, Kraka and Cremer have recently carried out an extensive *ab initio* investigation of **93** using MP2, MP3 and MP4 in conjugation with DZ+P basis, calculating chemical shifts and magnetic susceptibility and analyzing orbitals and electron density distribu-

tions¹⁹⁰. In addition, they studied the mechanisms of formation and decomposition of **93** and several hetero analogues. According to MP2 optimizations, **93** possesses a 1,3 interaction distance of 1.824 Å resulting from a folding of the formal five-membered ring by 87°, similar to that found for ion **80**¹⁹⁰. The authors concluded on the basis of the calculated energetic, structural, electronic and magnetic properties that **93** fulfils the criteria for homoaromaticity given above in Section I. A and in the preceding chapter²⁵. As such **93** is clearly the prototype of a trishomoaromatic cation.

Cremer and colleagues pointed out that an exact determination of the homoaromatic resonance energy of **93** is not possible because of strong hyperconjugative, strain and inductive effects present in the cation¹⁹⁰. However, they suggested a value of 17.4 kcal mol⁻¹ as a lower limit to the true resonance energy. This indicates that homoconjugative electron delocalization is much more developed in **93** than in any other homoaromatic system studied thus far. The high-field shift of the ¹³C NMR signals by about 350 ppm and the magnetic susceptibility exaltation found by Cremer and coworkers confirm this description.

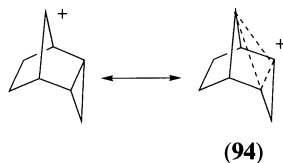
Cremer and colleagues found that **93** can undergo an inversion (with a barrier of 26 kcal mol⁻¹) to an envelope conformation that is 17 kcal mol⁻¹ less stable than **93**. This envelope conformation provides a reasonable reference for estimating the homoaromatic resonance energy of **93**. The envelope form was found to rearrange readily to the slightly more stable (3 kcal mol⁻¹) bicyclo[3.1.0]hex-2-yl cation by a shift of the *trans* hydrogen atom at C(2) (energy barrier 1 kcal mol⁻¹) (Scheme 38)¹⁹⁰.



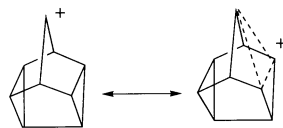
SCHEME 38. Isomerization of the envelope form of **93**

Replacement of C(6) of **93** by various heteroatoms was found by Cremer and coworkers to decrease the homoaromatic resonance energy with increase in the electronegativity of the heteroatom (24 kcal mol⁻¹ when X = BH to 4 kcal mol⁻¹ when X = O)¹⁹⁰. Silicon atoms in positions 1,3 and 5 were found to give homoaromatic analogues of **93**; however, it was found difficult to segregate homoaromatic stabilization and Si—C⁺ hyperconjugation effects.

A variety of other more highly bridged ions would appear to provide further examples of trishomocyclopropenium ions. These include the 7-norbornene and norbornadiene homologues **94**^{212,207} and **95**²¹³. In general these more complex systems have been studied in less detail than some of the simpler systems reviewed here. The chemistry of these systems is covered in the existing reviews.

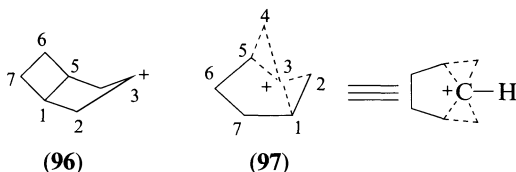


(94)

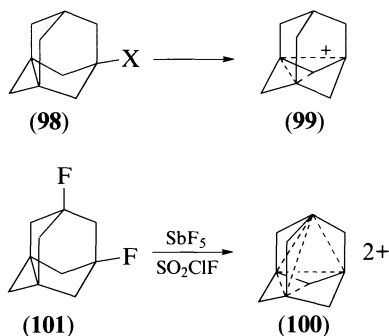


(95)

Szabo and Cremer have also investigated the possibility of cyclobutyl homoconjugation in **96** by determining its structure, conformation and energetics²¹⁴. They found no evidence for a non-classical structure. The only stable form was the classical envelope form of the ion. Upon forced ring inversion (barrier 9 kcalmol⁻¹), **97** rather than a trishomoaromatic species was formed. Ion **97** contains a centre-protonated spirocyclopentane unit with intriguing structural and electronic properties. The authors point out that **97** is the 'missing link' between the bicyclo[3.2.0]hept-3-yl and the 7-norbornyl cations on the C₇H₁₁⁺ potential energy surface. Cation **97** was found at a local energy minimum surrounded by relatively high barriers which provide kinetic stability for the ion.



An interesting and somewhat different system worth noting here is one based on the adamantyl framework. Scott and Pincock provided evidence for cyclopropyl participation in the ionization of **98** and suggested that the trishomocyclopropenium ion **99** was formed²¹⁵. Recently Bremer, Schleyer and colleagues have produced and characterized the stable dication **100** from the difluoride **101**²¹⁶. The ¹³C NMR spectrum of **100** and calculations were suggested to be fully consistent with the formation of the caged pyramidal cation. MP2/6-31G(d) interaction distances were found to be 2.084 Å, somewhat longer than for the trishomocyclopropenium ion discussed above (1.824 Å). Dication **100** is an example of a three-dimensional homoaromatic molecule (homoradial aromaticity²⁵) with six homoconjugative linkages, built up from the linkage of four trishomocyclopropenium ions.

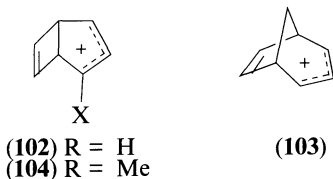


D. Bishomoantiaromatic Cations

This section will be quite short in that we are unaware of any examples of cations which display bishomoantiaromatic character. There are several potential candidates including derivatives of **102** and **103** in which a bishomocyclopentadienyl-type delocalization could occur. Examples of these cations are known; however, there is no evidence for any significant degree of cyclic delocalization²¹⁷⁻²²².

The clearest example is that of **104** described by Winstein and colleagues²¹⁷. This cation, which rearranges to the isomeric 1- and 5-methyl-7-norbornadienyl ions at -125°C,

exhibits a ^1H NMR spectrum which is typical of a cyclopentenyl cation and an isolated cyclobutene.



In concluding this section on the polyhomoaromatic cations, several points stand out:

First, there is only a limited number of examples of systems which can be classified as being cyclically delocalized systems and, thus, termed homoaromatic. These include a number of bridged bishomotropenylium ions and a somewhat larger series of bridged or caged bis- and trishomocyclopropenium ions.

Second, the only non-bridged or non-caged example which has a strong weight of evidence pointing to its homoaromatic delocalization is the parent trishomocyclopropenium ion.

Third, no examples of bishomoaromatic systems with a *trans* orientation of the rings are known.

Fourth, the extra stability associated with homoaromatic delocalization in the bishomotropenylium ions is small and insufficient to overcome any strain associated with conformational changes required for a system to achieve a geometry suitable for homoconjugation. This means that there will likely be few other related 6π -cations described which will be found to be homoaromatic.

Lastly, no examples of bishomoantiaromatic cations are known.

V. NEUTRAL HOMOAROMATIC SYSTEMS

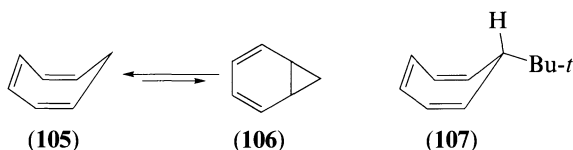
There has been considerable controversy over whether there are any existing examples of neutral homoaromatic systems²²³. Perhaps as a result of the difficulties in this area, a large amount of work has been reported^{224,14-22}.

We assert in this review that, at this point in time, there are several examples of neutral molecules which have been shown to display either bond or no-bond homoaromaticity. These include, in addition to the boranes mentioned above in Section III. B, cycloheptatriene, norcaradiene, bridged cycloheptatrienes and norcaradienes, semibullvalenes, barbaralanes, bridged annulenes, etc. Confirmation of the homoaromatic character of these systems comes from thermochemical and spectroscopic studies, and force field and *ab initio* calculations. In particular, the work of Roth and coworkers must be mentioned in this connection in that they were the first to provide reliable resonance energies of a large number of these neutral molecules^{225,226}. These authors have also demonstrated that systems such as bicyclo[2.1.0]pentene are homoantiaromatic.

The major confusion as to the existence of neutral homoaromatic systems results from the fact that homoaromatic resonance energies, contrary to aromatic resonance energies, are normally less than 10 kcal mol⁻¹^{225,226}. In general it is difficult to separate homoaromatic resonance energies from energies that are due to steric strain, hyperconjugative or inductive effects. These difficulties and the possible ways they are overcome are discussed extensively in the preceding chapter²⁵. We concentrate here on the results of this analysis of these systems coupled with related experimental work. The focus in this section will be on cycloheptatriene, norcaradiene, semibullvalene and a limited number of other potentially homoaromatic systems.

A. Monohomoaromatic Systems

Cycloheptatriene, **105**, and its valence tautomer norcaradiene, **106**, have been studied extensively²²⁷. The seven-membered ring of **105** adopts a boat-type conformation with C(7) forming the 'prow' of the boat²²⁸. The barrier to interconversion of the two boat forms, a process that exchanges the *exo* and *endo* C(7)-protons, is relatively low (6 kcal mol^{-1})²²⁹. Cycloheptatriene is related to **106** by a thermally allowed disrotatory process^{33,36} involving an aromatic transition state³¹. The bicyclic valence tautomer **106**, an important species in terms of the chemistry of the system, is considerably less stable than **105**. Substitution at C(7) can dramatically alter the relative stability of the two valence tautomers and, in certain instances, make **106** the preferred valence tautomer^{230–232}. Attempts have been made by Dunitz and coworkers to map the course of the ring closure of bridged derivatives of **105** to **106**²³³. In principle, such an approach could reveal intermediary structures, as has been attempted with semibullvalene; however, the nature of the bridges makes segregation of the properties of the **105/106** component difficult.



While **105** and **106** cannot be viewed as resonance structures of a common delocalized species, the question at issue is whether **105** and **106** can individually be regarded as homoaromatic systems? In terms of thermochemical evidence, it has been recently pointed out that the available experimental data are among the most precise data available in the thermochemical literature²³⁴. The issue comes down to the interpretation of these data and the proper consideration of contributing factors such as strain, etc.

Liebman and coworkers conclude from three different approaches that **105** is homoaromatically stabilized to the extent of about 6 kcal mol^{-1} ²³⁴. This result is consistent with the results of Roth and his coworkers, who have given a value of $4.5 \text{ kcal mol}^{-1}$ as the homoaromatic resonance energy of **105**^{225,226}. This latter value is based on the experimental heats of formation coupled with molecular mechanics calculations, as outlined in Section II. G of the preceding chapter²⁵. This approach largely separates steric and conjugative effects and can be considered to give a reliable value.

Further evidence supportive of cyclic delocalization in **105** comes from its magnetic properties. Dauben and colleagues measured the diamagnetic susceptibility exaltation, Λ , of **105** and found a value of $-8.5 (10^6 \text{ cm}^3 \text{ mol}^{-1})$ ²³⁵. Childs and Pikulik extended these measurements to a series of 7-substituted-cycloheptatrienes and found that the magnitude of Λ increased with the steric size of the substituent²³⁶. The largest exaltation found was for 7-*t*-butylcycloheptatriene, **107**, $\Lambda = -14.8$, a value which, surprisingly, is larger than that found for benzene itself (-13.7)^a. It was suggested that variation in Λ with substitution at C(7) was related to changes in the conformation of the seven-membered ring and, in particular, to changes in the relative orientation and positions of C(1) and C(6).

The diamagnetic susceptibility measurements are consistent with the NMR properties of cycloheptatrienes. Pikulik and Childs compared the ¹H NMR chemical shifts of the C(7) proton of 7-substituted cycloheptatrienes and the corresponding 1,4-cycloheptadienes and showed that there was a considerable upfield shift of the resonance of the former protons

^a Comparison of the magnitude of diamagnetic susceptibility exaltations of different systems must take into account the area of the unsaturated cyclic system. In the case of benzene and cycloheptatrienes (homobenzene) the areas of the cyclic π -systems are similar.

when in the pseudo-axial position²³⁷. The chemical shifts of the methylene protons of **105** and related bridged cycloheptatrienes can be accounted for on the basis of an induced ring current.

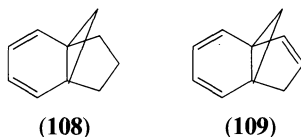
The conclusions reached on the basis of magnetic and thermochemical results for **105** are supported by structure investigations²²⁸ and recent high-level *ab initio* calculations [MP2 and CCSD(T)]²³⁸. This recent theoretical work qualifies and corrects older or less reliable *ab initio* or semi-empirical calculations^{239–243}.

The boat conformation of **105** is appropriate for a C(1)–C(6) interaction. Cremer, Dick and Christen²³⁹ have pointed out that the existing experimentally based structural data (ED and MW) are rather imprecise in terms of the exact measurement of conformation and the 1–6 distance. Kraka and Cremer²³⁸ have found the boat form of **105** to be rather flat in its stern (MP2 fold angle 152°, just 28° from a planar ring form), but strongly folded in its bow (MP2 fold angle 123°, i.e. 57° from a planar form). As a result the π orbitals at C(1) and C(6) can orient in a way that small but significant overlap is possible despite a C(1)–C(6) distance (MP2) of 2.39 Å²³⁸.

Comparison of the calculated C–C bond distances (MP2) of **105** [C(1)=C(2) 1.357, C(2)–C(3) 1.439, C(3)=C(4) 1.371, C(1)–C(7) 1.497 Å] with *trans*-butadiene [C(1)=C(2) 1.341, C(2)–C(3) 1.461 Å]²⁴⁴ shows that a considerable degree of bond equalization is present in **105**. Cremer and Kraka suggest that this is the consequence of homoconjugative electron delocalization²³⁸. This conclusion was confirmed by these authors from the values of the calculated bond orders and π -character indices. These results are contrary to predictions obtained at lower, less reliable levels of theory^{239–243}.

In conclusion, the energy, geometry and magnetic properties of **105** are fully consistent with it being classified as a neutral homoaromatic molecule with a small, but significant, resonance energy of 4.5 kcal mol⁻¹.

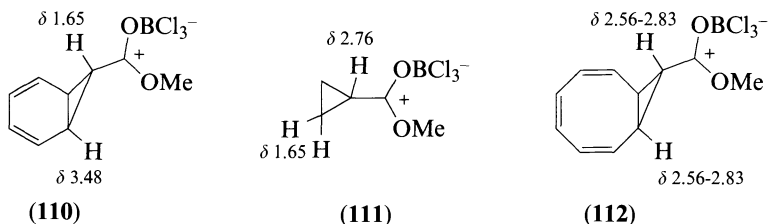
A similar conclusion can be reached in terms of norcaradiene, **106**. Roth and colleagues^{225,226} estimated a resonance energy of 5.6 kcal mol⁻¹ for **106** based on an assumed heat of formation ΔH_f° of 49.6 kcal mol⁻¹ derived from *ab initio* calculations of Cremer and Dick²⁴⁰ and Schulman, Disch and Sabio²⁴¹. Experimental estimates of the enthalpy difference between **105** and **106** range from 4 to 4.5 kcal mol⁻¹²⁴⁵. However, these estimates are too low in view of the recent CCSD(T)/DZ+P calculations (at MP2/DZ+P geometries including MP2 ZPE corrections) of Kraka and Cremer which predict an enthalpy difference of 5.5 kcal mol⁻¹ and a heat of formation of 50.1 kcal mol⁻¹²³⁸. The latter value is in good agreement with Roth's estimate given above. However, Kraka and Cremer's resonance energy of **106** is just 3.8 kcal mol⁻¹ (see preceding chapter, Section II. G²⁵). The bridged system **108** and **109**, in which the norcaradiene forms are more stable than the open cycloheptatriene forms, were reported to have homoaromatic resonance energies of 3.5 and >5.7 kcal mol⁻¹^{225,226}, values which are comparable to that calculated by Kraka and Cremer²³⁸.



Calculations of the geometry of **106** have been reported by a number of groups^{238–243}. The most accurate data are those from the calculations of Kraka and Cremer based on MP2/DZ+P and CCSD(T)/DZ+P calculations²³⁸. The C(1)–C(6) distance in the latter work was found to be 1.572 Å, which is clearly longer than the value found for cyclopropane. The C(1)–C(6) bond order is significantly smaller than 1, indicating a partial bond between these atoms. π -Electron delocalization, as reflected by the ratio of calculated bond lengths [C(1)–C(2) 1.461, C(2)–C(3) 1.357, C(3)–C(4) 1.446 Å], appeared to be

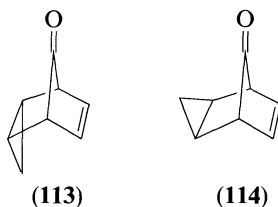
comparable or slightly weaker than that in **105**. However, it should be noted that the six-membered ring in **106** is formed by a partial bond with considerable π -character.

There is limited experimental magnetic information on norcaradienes and most of the currently available information comes from theory. Pikulik and Childs examined the ^1H NMR spectra of the type **110** and pointed out that the chemical shifts of the C(7) and C(1)/C(6) proton resonances were anomalous as compared to complexes of related cyclopropyl compounds such as **111** and **112**²⁴⁶. They argued that the chemical shifts of **110** could be accounted for on the basis of an induced ring current.



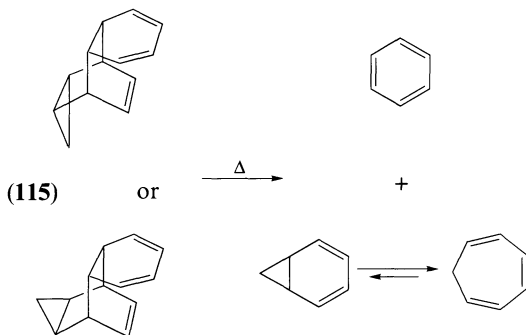
Kraka and Cremer have calculated the ^1H and ^{13}C NMR chemical shifts and magnetic susceptibility as a function of interaction distance of both the cycloheptatriene and norcaradiene systems²³⁸. They point out that both the magnetic susceptibility and the shift difference between the *endo* and *exo* protons at C(7) are at a maximum at the transition state for the valence tautomeric rearrangement between the two systems. The transition state is characterized by a C(1)–C(6) distance of 1.864 Å and an almost complete equalization of C–C bond lengths, bond orders, atomic charges and ^{13}C shifts of C(2)–C(5). Although a resonance energy could not be calculated for the transition state, Kraka and Cremer showed that it could be considered to exhibit no-bond homoaromaticity with a homoconjugative electron delocalization which probably exceeds that of **105** and **106**²³⁸.

Kinetic studies on the decarbonylation of **113** and **114** are of interest in terms of the homoaromatic character of **105/106**. It has been reported that the rate of decarbonylation of **113** was 1×10^5 times greater than that of **114**²⁴⁷. It was suggested that this reactivity difference was due to partial opening of the cyclopropane in the transition state and overlap between the Walsh orbitals of the cyclopropane and the rehybridizing s-orbitals of the breaking bonds. Homoaromatic electron delocalization in a norcaradiene/cycloheptatriene-like transition state is only possible with the *anti*-isomer **113**.



The kinetic measurements carried out by Grimme, Warner and coworkers for the cycloreversion reaction shown in Scheme 39 are consistent with the effects seen with **113** and **114**²⁴⁸. The ratio $k(\mathbf{115}\text{-endo})/k(\mathbf{115}\text{-exo})$ was found to be 8.9×10^3 at 164.5 °C which corresponds to a $\Delta\Delta G^\ddagger = 7.9 \text{ kcal mol}^{-1}$ ²⁴⁸. These authors also attribute the high reactivity of the *anti*-isomer **115** to the possibility of 6π -electron delocalization in the developing norcaradiene component of the transition state.

In the case of **116** the work of Roth and coworkers suggests that cyclopropyl homoconjugation leads to destabilization of 10 kcal mol^{-1} ^{225,226}. This result has been confirmed by

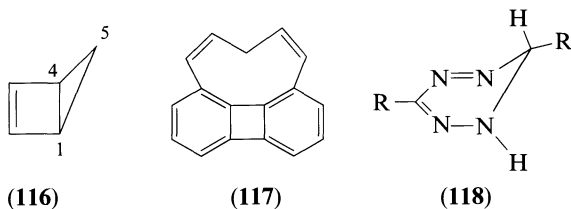


SCHEME 39. Cycloreversion reactions

ab initio calculations as described in the preceding chapter²⁵. The magnitude of the difference between the resonance energies of **106** and **116** is startling. Jörgensen noted the unique properties of **116** on the basis of a MO theory analysis of the molecule²⁴⁹.

The structure of **116** has been calculated by Karka and Cremer²⁶ at the HF/6-31G(d) level of theory and by Skancke and coworkers at a lower level²⁵⁰. The intriguing feature of the calculated structure is the relatively long C(1)–C(5) and C(4)–C(5) distances as compared to the C(1)–C(4) distance and the corresponding distances in **106**. Kraka and Cremer²⁶ have reported calculated bond orders of 0.88 for the external cyclopropane bonds of **116**. This magnitude of these bond orders suggests a peripheral delocalization of electrons²⁵.

Bicyclo[2.1.0]pentene, **116**, can be considered to be the prototype of a neutral homoantiaromatic molecule. The types of structural and bonding effects found for this molecule parallel in many respects those found for the bicyclo[3.1.0]hexenyl cation reported above. Further studies on both of these $4q$ systems will likely be rewarding in terms of fully understanding the nature of cyclopropyl homoconjugation and homoantiaromaticity.

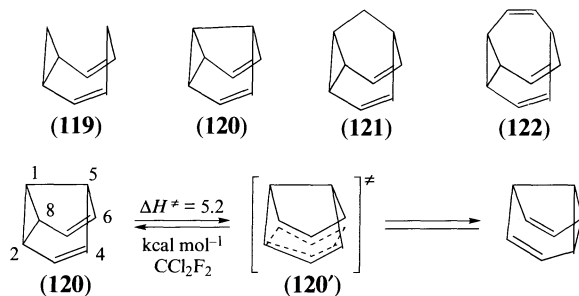


Neutral homoantiaromaticity has also been invoked for **117** by Wilcox and coworkers²⁵¹. A shift difference of 2.25 ppm was found for the methylene protons of **117** which was interpreted as arising from a paratropic ring current and local anisotropies. Support for the importance of the homoantiaromaticity in describing **117** was also suggested from a consideration of its UV and PE spectra. However, we note our earlier caution about the use of PE as a criterion for homoaromaticity.

The dihydrotetrazines **118** were suggested by Van der Plas and colleagues to be homoaromatic molecules on the basis of their NMR spectra, particularly the anomalous chemical shifts of the C(6) protons²⁵². The more recent work of Mackay and colleagues using acyl derivatives nicely reinforces the induced ring current model for the anomalous chemical shifts²⁵³. On the other hand, the structures of dihydrotetrazines provide a less compelling case for cyclic delocalization with large N(1)–N(5) internuclear distances.

B. Bis- and Higher Homoaromatic Systems

Homotropylidene (**119**), semibullvalene (**120**) and the related barbaralane (**121**) and bullvalene (**122**) systems undergo degenerate Cope-type rearrangements. The transition states for these rearrangements have been considered to be examples of bishomoaromatic 6-electron systems. The barriers to these degenerate rearrangements are the smallest in semibullvalene (Scheme 40). As such, this system has been studied intensively as it has been considered to be the most likely platform for bishomoaromatic delocalization in a neutral system²⁵⁴. Following the suggestion of Doering and colleagues of diradical character in the transition states of analogous acyclic systems, there has been debate about the nature of the transition state in these degenerate Cope rearrangements²⁵⁵. With semibullvalene it would appear that a homoaromatic transition state is of lower energy than one possessing diradical character²⁵⁶.

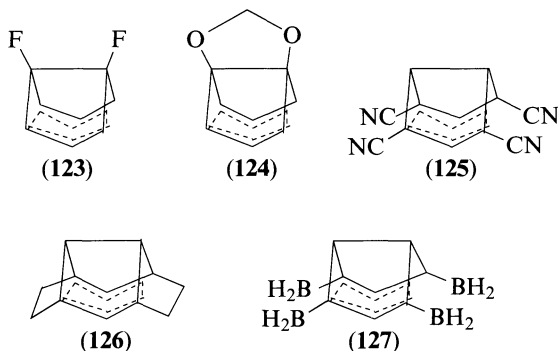


SCHEME 40. Degenerate rearrangement of semibullvalene

As is shown in Scheme 40, the activation enthalpy of the degenerate valence isomerization in **120** is only $5.2 \text{ kcal mol}^{-1}$ ²⁵⁷. Recent *ab initio* calculations by Szabo and Cremer give values of $4.0 \text{ (MP2/DZ+P+ZPE)}$ and $6.5 \text{ kcal mol}^{-1} \text{ (MP4/DZ+P+ZPE)}$ for this barrier²⁵⁸. Calculated geometrical, electron density and magnetic properties of the transition state clearly indicate it as being bishomoaromatic with a C(2)–C(8) distance of 2.03 \AA (MP2). These results confirm the earlier expectations based on MO theory and semi-empirical calculations.

Hoffmann and Stohrer²³¹, using MO theory, and Dewar and Lo, using MINDO/2²⁵⁶, predicted that appropriately placed substituents could alter the relative energies of **120** and **120'** and possibly make the intermediary structure lower in energy than **120**. While a wide range of substituted semibullvalenes have been made and systems with remarkably low barriers to degenerate valence tautomerism found, the experimental quest for a symmetrical semibullvalene system has not been fruitful. However, recent semi-empirical calculations by Williams and Kurtz suggest that ethano-bridging in positions 2 and 8 as well as 4 and 6 in **126** (Scheme 41), will lead to the stable homoaromatic form **120'** as being the energy minimum on the potential energy surface^{242,259}. If this could indeed be demonstrated experimentally, then **126** could be regarded as a frozen transition state^{231,256,260,261}.

Convincing evidence for the existence of homoaromatic semibullvalenes corresponding to **120'** has recently been provided by Szabo and Cremer on the basis of high-level *ab initio* calculations (MP2 and MP4)²⁵⁸. These authors investigated a series of substituted systems. The results of this study did not support the previous claims based on semi-empirical calculations that 1,5-dimethylsemibullvalene and 3,7-diazasemibullvalene should exist in the 'frozen transition state form' **120'**²⁶². However, the *ab initio* investigation revealed that **123–127** (Scheme 41) increasingly in the order given, prefer to exist as (homoaromatic) 'frozen transition state' structures. For **123** and **124**, the classical and non-classical forms



SCHEME 41. Semibullvalenes calculated to possess symmetrical ground state structures

differ by 1 kcal mol⁻¹ or less. **125** was shown to prefer the homoaromatic structure by 2 kcal mol⁻¹. In support of the results of Williams, Kurtz and Farely^{242,259}, **126** was found to be more stable than the classical forms by 6 kcal mol⁻¹. In the case of **127** the energy difference was found to be 8 kcal mol⁻¹. The calculated homo-interaction distances were found to range from 2 to 2.2 Å. Electron density and magnetic properties were indicative of homoaromaticity, meeting the criteria set out in this and the preceding chapter²⁵.

In view of the clear homoaromatic character of **120'** as demonstrated by the recent work on **123–127**, the question arises as to whether cyclic homoconjugation is important for the ground state of semibullvalene, **120**.

The structures of semibullvalene derivatives have been determined. It was initially suggested that there was a systematic variation in the C(2)–C(8) and C(4)–C(6) distances as the barrier to interconversion of the two valence tautomers varied. Such a variation would be good evidence for cyclic delocalization. However, recent work of Jackman, Quast and coworkers using CP-MAS ¹³C NMR has shown that the earlier work did not take into account the presence of two valence tautomers²⁶³.

The C(2)–C(8) distances of substituted semibullvalenes are typically found to be *ca* 1.58 Å²⁶⁴, a distance which is longer than that of a typical cyclopropane bond^{45–47}. While AM1 calculations reported by Dewar and Jie²⁶⁰ do not replicate this long internal cyclopropane bond, the recent calculations of Szabo and Cremer discussed above give a value of 1.58 Å²⁵⁸. These latter authors also find evidence of significant π -character in the cyclopropane bond of **120** indicative of electron delocalization and some degree of homoconjugation in the parent molecule.

Baxter, Cowley and coworkers have reported a solid state investigation of the structure of a 9-phosphabarbaralane and suggested this has a symmetrical structure corresponding to a 'frozen transition state'²⁶⁵. In solution the molecule exists as a classical structure.

Several systems have been examined in the context of potential tris- and higher homoaromatic systems²¹. These include *cis,cis,cis*-1,4,7-cyclononatriene (**128**), triquinacene (**129**), hexaquinacene and the cyclic polyacetylenes such as **130**. The conformations of some of these systems are such that they could be considered to be examples of 'in plane' homoaromatic systems²⁶⁶.

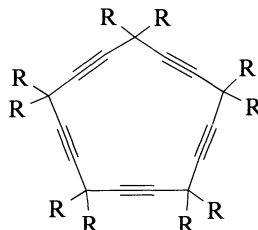
In general, there is no strong evidence to support homoaromatic formulations of the structures of any of these systems. There are indications from PE spectroscopy of some degree of interaction between the unsaturated fragments of these molecules. However, as we have pointed out, PE spectroscopy as a technique has limited value in probing homoaromaticity. Magnetic evidence has either not been examined in detail in most systems or, where chemical shifts have been examined, is not definitive. Thermochemical



(128)



(129)



(130)

approaches have been used. For example, Roth and colleagues have found a small destabilization for **128**, a result in line with other evidence for this system^{225,226}.

Considerable attention has been paid to the thermochemical results obtained by Paquette and coworkers for **129** in which homoaromatic stabilization was suggested²⁶⁷ and later supported by Rogers and colleagues²³⁴. However, more recent work has shown that this is not the case²⁶⁸. Similarly, Scott and coworkers have shown that any resonance stabilization in **130**, R = Me, if present, is small and cannot be quantified given the accuracy of the thermochemical methods available with these large molecules²⁶⁹.

In summing up this section on neutral homoaromatic compounds we point out that a considerable number of neutral molecules have been identified as benefiting from homoconjugative electron delocalization. These include cycloheptatriene as well as several bridged derivatives of these molecules. We anticipate that further work on these systems and the related homoantiaromatic bicyclo[2.1.0]pentene will prove rewarding.

The bishomoaromatic neutral systems are of particular interest. Evidence for the importance of neutral homoaromatic delocalization appears to exist solely with certain substituted semibullvalenes. In terms of the latter systems the best candidates for experimental work appear to be **126** and **127**.

There are no neutral molecules with trishomoaromatic character. This is not surprising, given the small size of the resonance energies associated with neutral homoaromatic molecules and the magnitude of the strain effects associated with a potential trishomoaromatic system.

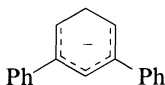
VI. HOMOAROMATIC ANIONS

Anionic systems represent a problematical area with respect to homoaromaticity. Williams and Kurtz in their review summarize the position as there being no anions which are currently recognized as being homoaromatic²¹. In our view, the situation is not as simple as this and there well may be examples of homoaromatic anions. Certainly, this is an area of considerable scrutiny at present and the issues are far from being fully settled.

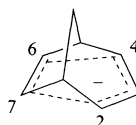
With cations it was the monohomo systems which showed the clearest evidence for homoaromaticity, *vide supra*. However, with the corresponding anion **131** and its derivatives, there is no experimental or theoretical evidence to suggest that homoconjugation is important²⁷⁰. The deliberate attempt of Tolbert and Rajca to bias the system by placing phenyl substituents at C(2)/C(5) (cf **132**), did not provide a sufficient driving force to make homoconjugation a significant factor²⁷¹.



(131)



(132)

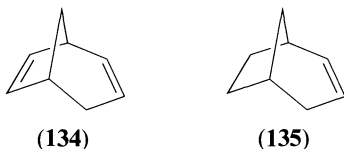


(133)

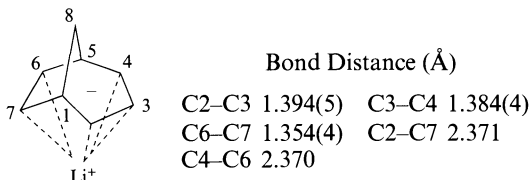
The bridged bicyclic system **133** represents the earliest example of an anion that was claimed to be homoaromatic²⁷². Studies of this system actively continue and the importance of homoconjugation in accounting for the properties of the anion has been a matter of some controversy and debate.

Homoaromatic delocalization in **133** was initially invoked in order to account for its enhanced stability and NMR properties²⁷³. However, this explanation was challenged in 1981 by two different groups. On the basis of calculations Grutzner and Jorgensen²⁴ (MINDO/3) as well as Mayr, Schleyer and colleagues²⁷³ (MNDO and STO-3G) concluded independently that the properties of **133** could be accounted without resort to homoaromatic delocalization. Moreover, they also stated more generally that homoaromatic stabilization was not expected to be an important phenomenon in anions.

Matters were not allowed to rest with these conclusions. Brown and colleagues criticized the work of both groups and suggested on the basis of HF/STO-3G calculations that homoconjugation was in fact important in **133** and that the negative charge was delocalized to the C(6)—C(7) ethylene fragment²⁷⁴. Christl and coworkers provided further NMR evidence to support the claim for homoaromatic stabilization of **133** and its phenyl-substituted derivatives²⁷⁵. NMR evidence supporting some degree of charge delocalization was presented by Köhler and Hertkorn²⁷⁶ while Trimitsis and Zimmermann cautioned against the use of chemical shifts to probe for homoconjugative interactions in **133** and its derivatives²⁷⁷. More direct approaches to understanding the nature of **133** were provided by acidity measurements on the two hydrocarbons **134** and **135**. Solution-phase acidities of **134** were reported by Washburn²⁷⁸ and measurements in the gas phase were undertaken by Lee and Squires²⁷⁹. These latter results showed that **134** possesses a very high gas-phase acidity that is nearly 10 kcalmol⁻¹ greater than that of **135**.



Structural information on **133** was provided by Köhler and coworkers who, in 1986, reported the isolation of its lithium salt and the determination of its crystal structure²⁸⁰. This structure showed the lithium cation to be situated on the *endo* surface of the anion and coordinated with both the allyl portion and the C(6)—C(7) double bond. Key internuclear distances of the anionic portion of the salt are summarized in Scheme 42.

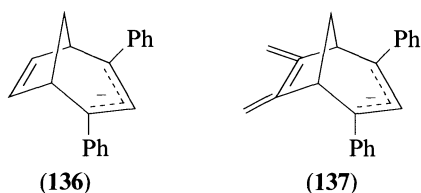


SCHEME 42. Structure of the lithium salt of **133**

In 1986 two groups, each using theoretical calculations, again questioned the evidence for significant homoaromatic delocalization in **133**. Schleyer and colleagues, using MNDO, argued that the properties of **133** could be accounted for on the basis of hyperconjugation and gegenion interactions²⁸¹. Lindh and colleagues, on the basis of CASSCF with minimal and split basis sets, suggested that in addition to the gegenion stabilization

an electrostatic factor, in which the quadrupole moment in the C(6)—C(7) bridge stabilizes the charge in the allyl portion of the ion, was important²⁸².

This second major challenge to the need for homoaromatic delocalization to account for the properties of **133** has led to a further series of reports on its properties. These include work of Trimitsis and his group examining the rates of deuterium exchange, which led them to conclude that there was no special stability of derivatives of **133**²⁸³. A counter-view was expressed by Tuncay and colleagues, also based on exchange experiments²⁸⁴. Christl and Müller have continued to examine the NMR spectra of aryl-substituted derivatives of **133** and the impact of counter-ion on the properties of these salts²⁸⁵. Hertkorn and Köhler²⁸⁶ have also addressed the question of cation/anion interactions and reached the same conclusion as Christl, that the properties of **133** cannot be accounted for on the basis of specific ion-pairing. Christl and colleagues have also prepared the anion **136** and, in comparing its properties with those of **137**, reached the conclusion that **136** should be considered to be homoaromatic²⁸⁷.



Squires, in a recent review²⁸⁸, examines and dismisses the explanations put forward by Schleyer and colleagues²⁸¹ and Lindh and coworkers²⁸² as being unable to account for the large difference in acidities of **134** and **135**. He reaches the conclusion that **133** does exhibit homoaromatic delocalization.

In our view the question remains open as to the importance of homoaromatic delocalization in determining the properties of **133**. There is a wealth of experimental evidence available, much of which points to such a delocalization. However, we are troubled by the absence of high-level theoretical calculations of the structure of **133** and its magnetic properties to back up this claim.

There are other anions for which the claim of homoaromatic delocalization has been made. Work on these systems is relatively old and has been reviewed extensively¹⁴⁻²¹. Overall, it is not clear there are any good examples of anions which are homoaromatic. Perhaps, with further work, **133** will be demonstrated to be an example; however, it is clear that homoaromatic delocalization is not generally going to be an important phenomenon in carbanions.

VII. CONCLUDING REMARKS

At the outset of this chapter we presented a series of criteria for homoaromaticity (Section I. A). The criteria were developed as a result of the detailed theoretical consideration of homoaromaticity given in the previous chapter²⁵. The criteria seek to go further than a simple topological definition of homoaromaticity which, coupled with an electron count and NMR spectrum, have frequently been the sole basis for the classification of a system as homoaromatic. In the subsequent sections of this chapter we have presented a detailed consideration of a selected range of potentially homoaromatic molecules and ions in the light of these criteria. It is clear from these analyses that there are a range of systems, including charged and neutral molecules, which can be classified as being homoaromatic.

We would stress that it is important in the consideration of a molecule or ion as a homoaromatic system to use as wide a range of the various criteria we have suggested as is

possible. It is clear from the work we have described that it is essential to couple high-level calculations with experimental observations in order to fully understand these systems. In particular, we point to the very important recent advance that uses a geometry optimization technique based on the comparison of calculated ^{13}C NMR chemical shifts with those observed experimentally. This powerful combination of theory and experiment is one which should routinely be used with all potentially homoaromatic or homoantiaromatic systems.

A further key point to make is the desirability of examining related $4q$ as well as $4q + 2$ systems. We believe that the results we have outlined in Sections III and V well demonstrate the additional information that comes in placing a potentially homoantiaromatic system in juxtaposition with its homoaromatic counterparts. Further work with the $4q$ systems is required in many series of systems.

Most of the work reported in this area is limited to carbocyclic systems. The recent developments with the boron analogues of the cyclobutenyl/homocyclopropenium and norbornenyl/norbornadienyl cations point to the potential importance of cyclopropyl homoconjugation and homoaromaticity in a much wider sphere of organic systems. This will likely be an area where there will be considerable further work.

The concepts of cyclopropyl homoconjugation and homoaromaticity have a long history in organic chemistry. Work in this field has passed through various phases. At this point we have largely left the stage where lots of new candidates are being proposed as homoaromatic systems. The last few years have seen a re-emphasis on a detailed examination of the core of basic homoaromatic and homoantiaromatic molecules. As we hope this chapter will show, the results of this 'mature' phase of the investigation of homoaromaticity have and, indeed, are still leading to a deeper understanding of the role and importance of the concept in organic chemistry.

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IX. REFERENCES

1. C. W. Shoppee, *J. Chem. Soc.*, 1147 (1946).
2. C. K. Ingold, in *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, New York, 1953.
3. S. Winstein and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2780 (1942); S. Winstein and E. Grunwald, *J. Am. Chem. Soc.*, **70**, 828 (1948).
4. R. M. Dodson and B. Riegel, *J. Org. Chem.*, **13**, 424 (1948).
5. S. Winstein and R. Adams, *J. Am. Chem. Soc.*, **70**, 838 (1948).
6. S. Winstein and A. H. Schlesinger, *J. Am. Chem. Soc.*, **70**, 3528 (1948).
7. S. Winstein, H. M. Walborsky and K. Schreiber, *J. Am. Chem. Soc.*, **72**, 5795 (1950).
8. J. D. Roberts, W. Bennett and R. Armstrong, *J. Am. Chem. Soc.*, **72**, 3329 (1950).
9. M. Simonetta and S. Winstein, *J. Am. Chem. Soc.*, **76**, 18 (1954).

10. D. E. Applequist and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 4012 (1956).
11. W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *J. Am. Chem. Soc.*, **78**, 5448 (1956).
12. S. Winstein, J. Sonnenberg and L. deVries, *J. Am. Chem. Soc.*, **81**, 6523 (1959).
13. S. Winstein, *J. Am. Chem. Soc.*, **81**, 6524 (1959).
14. S. Winstein, *Spec. Publ. Chem. Soc.*, **21**, 5 (1967); *Quart. Rev. Chem. Soc.*, **23**, 141 (1969).
15. P. M. Warner, *Top. Nonbenzenoid Aromat. Chem.*, **2** (1976).
16. S. Winstein, in *Carbonium Ions*, Vol. III (Ed. G. A. Olah and P. v. R. Schleyer), Wiley, New York, 1972, pp 965–1005.
17. P. R. Story and B. C. Clark, Jr., in *Carbonium Ions*, Vol. III (Ed. G. A. Olah and P. v. R. Schleyer), Wiley, New York, 1972, pp. 1007–1098.
18. L. A. Paquette, *Angew. Chem., Int. Ed. Engl.*, **17**, 106 (1978).
19. R. F. Childs, *Acc. Chem. Res.*, **17**, 347 (1984).
20. A. T. Balaban, M. Banciu and V. Ciorba, in *Annulenes, Benzo-, Hetero-, Homo-derivatives and their Valence Isomers*, Vol. III. Chap. 9, CRC Press Inc., Boca Raton, Florida, 1987, pp. 144–163.
21. R. V. Williams and H. A. Kurtz, *Adv. Phys. Org. Chem.*, **29**, 273 (1994).
22. R. F. Childs, M. Mahendran, S. D. Zweep, G. S. Shaw, S. K. Chadda, N. A. D. Burke, B. E. George, R. Faggiani and C. J. L. Lock, *Pure Appl. Chem.*, **58**, 111 (1986).
23. N. C. Deno, *Prog. Phys. Org. Chem.*, **2**, 129 (1964).
24. J. B. Grutzner and W. L. Jorgensen, *J. Am. Chem. Soc.*, **103**, 1372 (1981); E. Kaufmann, H. Mayr, J. Chandrasekhar and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 1375 (1981).
25. D. Cremer, R. F. Childs and E. Kraka, see the preceding chapter (Chapter 7) in this volume and references cited therein.
26. E. Kraka and D. Cremer, in *Theoretical Models of Chemical Bonding, The Concept of the Chemical Bond* (Ed. Z. B. Maksić), Springer-Verlag, Berlin, 1990, p. 453; D. Cremer, *Tetrahedron*, **44**, 7427 (1988).
27. D. Cremer, F. Reichel and E. Kraka, *J. Am. Chem. Soc.*, **113**, 9459 (1991); D. Cremer, L. Olsson, F. Reichel and E. Kraka, *Israel J. Chem.*, **33**, 369 (1993).
28. D. Cremer, P. Svensson, E. Kraka, Z. Konkoli and P. Ahlberg, *J. Am. Chem. Soc.*, **115**, 7457 (1993); P. Svensson, F. Reichel, P. Ahlberg and D. Cremer, *J. Chem. Soc., Perkin Trans. 2*, 1463 (1991).
29. D. Cremer and E. Kraka, *Angew. Chem., Int. Ed. Engl.*, **23**, 627 (1984); *Croat. Chem. Acta*, **57**, 1259 (1984); D. Cremer, in *Modelling of Structure and Properties of Molecules* (Ed. Z. B. Maksić), Ellis Horwood, Chichester, 1988, p. 125.
30. D. Cremer, E. Kraka, T. S. Lee, R. F. W. Bader, C. D. H. Lau and T. T. Nguyen-Dang, *J. Am. Chem. Soc.*, **105**, 5069 (1983).
31. W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 5207 (1974).
32. H. E. Zimmerman, *J. Am. Chem. Soc.*, **88**, 1564, 1566 (1966); *Acc. Chem. Res.*, **4**, 272 (1971); E. Heilbronner, *Tetrahedron Lett.*, 1923 (1964).
33. R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395, 2046, 2511 (1965); R. B. Woodward, *Spec. Publ. Chem. Soc.*, **21**, 217 (1967); R. B. Woodward and R. Hoffmann, in *The Conservation of Orbital Symmetry*, Verlag Chemie, GmbH, Weinheim, 1970.
34. M. J. Goldstein and R. Hoffmann, *J. Am. Chem. Soc.*, **93**, 6193 (1971).
35. M. J. S. Dewar, in *The Molecular Orbital Theory of Organic Chemistry*, McGraw-Hill, New York, 1969; *Tetrahedron Suppl.*, **8**, 75 (1966).
36. For reviews on pericyclic reactions see: T. L. Gilchrist and R. C. Storr, in *Organic Reactions and Orbital Symmetry*, Cambridge University Press, Cambridge, 1972; G. B. Gill and M. R. Willis, in *Pericyclic Reactions*, Chapman-Hall, London, 1974; I. Fleming, in *Frontier Orbitals and Organic Chemical Reactions*, Wiley, London, 1976; A. P. Marchand and R. E. Lehr (Eds), *Pericyclic Reactions*, Vols. 1 and 2, Academic Press, New York, 1977.
37. W. J. Hehre and A. J. P. Devaquet, *J. Am. Chem. Soc.*, **98**, 4370 (1976).
38. W. L. Jorgensen, *J. Am. Chem. Soc.*, **98**, 6784 (1976); **97**, 3082 (1975).
39. P. J. Garratt, in *Aromaticity*, Wiley, New York, 1986; D. Lewis and D. Peters, in *Facts and Theories of Aromaticity*, McMillan, London, 1975.
40. M. Charton, in *The Chemistry of Alkenes*, Vol. 2 (Ed. J. Zabicky), Interscience-Wiley, London, 1970, pp 511–610.
41. A. de Meijere, *Angew. Chem., Int. Ed. Engl.*, **18**, 809 (1979).

42. T. T. Tidwell, in *The Chemistry of the Cyclopropyl Group* (Ed. Z. Rappoport), Wiley, London, 1987, pp.565–632.
43. E. Kraka and D. Cremer, in *Molecular Structure and Energetics, Structure and Reactivity*, Vol. 7 (Eds. J. F. Liebman and A. Greenberg), VCH Publishers, New York, 1988, p. 65; D. Cremer and J. Gauss, *J. Am. Chem. Soc.*, **108**, 7467 (1986).
44. D. Cremer, E. Kraka and K. J. Szabo, in *The Chemistry of the Cyclopropyl Group* (Ed. Z. Rappoport), Chap. 2, Wiley, Chichester, 1995.
45. F. H. Allen, *Acta Crystallogr., Sect. B*, **B36**, 81 (1980).
46. F. H. Allen, *Acta Crystallogr., Sect. B*, **B37**, 890 (1981).
47. F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, **16**, 146 (1983).
48. R. E. Dumright, R. H. Mas, J. S. Merola and J. M. Tanko, *J. Org. Chem.*, **55**, 4098 (1990).
49. F. A. Van-Catledge, D. W. Boerth and J. Kao, *J. Org. Chem.*, **47**, 4096 (1982).
50. D. Cremer and E. Kraka, *J. Am. Chem. Soc.*, **107**, 3811 (1985).
51. K. B. Wiberg and K. E. Laidig, *J. Org. Chem.*, **57**, 5092 (1992).
52. T. Clark, G. W. Spitznagel, R. Close and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **106**, 4412 (1984).
53. J.-P. Pete, *Bull. Soc. Chim. France*, 357 (1967).
54. H. G. Richey, Jr., in *Carbonium Ions*, Vol. III (Eds. G. A. Olah and P. v. R. Schleyer), Wiley, New York, 1972, pp. 1201–1294; K. B. Wiberg and B. A. Hess Jr., in *Carbonium Ions*, Vol. III (Eds. G. A. Olah and P. v. R. Schleyer), Wiley, New York, 1972, pp. 1295–1345; E. C. Friedrich, in *The Chemistry of the Cyclopropyl Group* (Ed. Z. Rappoport), Wiley, Chichester, 1987, pp. 633–700; H. C. Brown (with comments by P. v. R. Schleyer), in *The Non-classical Ion Problem*, Chap. 5, Plenum, New York, 1977; G. A. Olah, V. Prakash-Reddy and G. K. Prakash, *Chem. Rev.*, **92**, 69 (1992).
55. R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 4390 (1959).
56. K. B. Wiberg, D. Shobe and G. L. Nelson, *J. Am. Chem. Soc.*, **115**, 10645 (1993).
57. M. Saunders, K. E. Laidig, K. B. Wiberg and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **110**, 7652 (1988); W. Koch, B. Liu and D. J. DeFrees, *J. Am. Chem. Soc.*, **110**, 7325 (1988).
58. P. C. Myhre, G. G. Webb and C. S. Yannoni, *J. Am. Chem. Soc.*, **112**, 8992 (1990); H. Vancik, V. Gabelica, D. E. Sunko, P. Buzek and P. v. R. Schleyer, *J. Phys. Org. Chem.*, **6**, 427 (1993).
59. R. F. Childs, R. Faggiani, C. J. L. Lock, M. Mahendran and S. D. Zweep, *J. Am. Chem. Soc.*, **108**, 1692 (1986).
60. S. K. Chadda, R. F. Childs, R. Faggiani and C. J. L. Lock, *J. Am. Chem. Soc.*, **108**, 1694 (1986).
61. R. F. Childs, M. D. Kostyk, C. J. L. Lock and M. Mahendran, *J. Am. Chem. Soc.*, **112**, 8912 (1990).
62. P. v. R. Schleyer and G. W. Van Dine, *J. Am. Chem. Soc.*, **88**, 2321 (1966).
63. D. F. Eaton and T. G. Traylor, *J. Am. Chem. Soc.*, **96**, 1226 (1974); J. M. Harris, J. R. Moffatt, M. G. Case, F. W. Clarke, J. S. Polley, T. K. Morgan, Jr., T. M. Ford and R. K. Murray, Jr., *J. Org. Chem.*, **47**, 2740 (1982); V. Buss, R. Gleiter and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 3927 (1971); J. M. Stewart and G. K. Pagenkopf, *J. Org. Chem.*, **34**, 7 (1969).
64. A. B. Turner, R. E. Lutz, N. S. McFarlane and D. W. Boykin, Jr., *J. Org. Chem.*, **36**, 1107 (1971); G. Montaudo and C. G. Overberger, *J. Org. Chem.*, **38**, 804 (1973); A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).
65. L. D. Kispert, C. Engelman, C. Dyas and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **93**, 6948 (1971); C. A. Deakyn, L. C. Allen and N. C. Craig, *J. Am. Chem. Soc.*, **99**, 3895 (1977); M. B. Formicheva and V. A. Zubkov, *J. Struct. Chem.*, **20**, 631 (1979).
66. R. G. Pews and N. D. Ojha, *J. Am. Chem. Soc.*, **91**, 5769 (1969).
67. C. F. Wilcox, L. M. Loew and R. Hoffmann, *J. Am. Chem. Soc.*, **95**, 8192 (1973).
68. R. S. Brown and T. G. Traylor, *J. Am. Chem. Soc.*, **95**, 8025 (1973).
69. A. Varadarajan, Ph.D. Thesis, McMaster University, Hamilton, Ontario, Canada, 1983.
70. S. Winstein, C. G. Kreiter and J. I. Brauman, *J. Am. Chem. Soc.*, **88**, 2047 (1966).
71. C. E. Keller and R. Pettit, *J. Am. Chem. Soc.*, **88**, 604 (1966).
72. G. Boche, W. Hecht, H. Huber and R. Huisgen, *J. Am. Chem. Soc.*, **89**, 3344 (1967); J. Gasteiger and R. Huisgen, *Tetrahedron Lett.*, 3665 (1972); R. Huisgen, G. Boche and H. Huber, *J. Am. Chem. Soc.*, **89**, 3345 (1967); R. Huisgen and J. Gasteiger, *Angew. Chem., Int. Ed. Engl.*, **11**, 1104 (1972); *Tetrahedron Lett.*, 3661 (1972).
73. L. A. Paquette, J. R. Malpass and T. J. Barton, *J. Am. Chem. Soc.*, **91**, 4714 (1969).

74. G. I. Fray and R. G. Saxton, in *The Chemistry of Cyclooctatetraene and its Derivatives*, Cambridge University Press, Cambridge, 1978.
75. J. D. Holmes and R. Pettit, *J. Am. Chem. Soc.*, **85**, 2531 (1963).
76. J. A. Berson and J. A. Jenkins, *J. Am. Chem. Soc.*, **94**, 8907 (1972).
77. R. F. Childs and C. V. Rogerson, *J. Am. Chem. Soc.*, **98**, 6391 (1976); **100**, 649 (1978); **102**, 4159 (1980).
78. O. L. Chapman and R. A. Fugiel, *J. Am. Chem. Soc.*, **91**, 215 (1969).
79. J. L. Rosenberg, Jr., J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **84**, 2842 (1962).
80. P. Warner, D. L. Harris, C. H. Bradley and S. Winstein, *Tetrahedron Lett.*, 4013 (1970).
81. S. Winstein, H. D. Kaesz, C. G. Kreiter and E. C. Friedrich, *J. Am. Chem. Soc.*, **87**, 3267 (1965).
82. C. E. Keller and R. Pettit, *J. Am. Chem. Soc.*, **88**, 606 (1966).
83. L. A. Paquette, M. J. Broadhurst, P. Warner, G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **95**, 3386 (1973); J. F. M. Oth, D. M. Smith, U. Prange and G. Schröder, *Angew. Chem., Int. Ed. Engl.*, **12**, 327 (1973).
84. H. D. Kaesz, S. Winstein and C. G. Kreiter, *J. Am. Chem. Soc.*, **88**, 1319 (1966); R. Aumann and S. Winstein, *Tetrahedron Lett.*, 903 (1970); G. N. Schrauzer, *J. Am. Chem. Soc.*, **83**, 2966 (1961); A. Davison, W. McFarlane, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 4821 (1962).
85. M. Brookhart, M. Ogliaruso and S. Winstein, *J. Am. Chem. Soc.*, **89**, 1965 (1967).
86. L. T. Scott, M. Oda and M. M. Hashemi, *Chem. Lett.*, 1759 (1986).
87. R. F. Childs, D. L. Mulholland and A. Nixon, *Can. J. Chem.*, **60**, 801, 809 (1982).
88. H. J. Dauben, J. D. Wilson and J. L. Laity, in *Nonbenzenoid Aromatics*, Vol. II (Ed. J. P. Snyder), Academic Press, New York, 1971, p. 167.
89. C. E. Johnson, Jr. and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).
90. R. F. Childs, M. J. McGlinchey and A. Varadarajan, *J. Am. Chem. Soc.*, **106**, 5974 (1984).
91. R. F. Childs, A. Varadarajan, C. J. L. Lock, R. Faggiani, C. A. Fyfe and R. E. Wasylshen, *J. Am. Chem. Soc.*, **104**, 2452 (1982).
92. R. F. Childs, R. Faggiani, C. J. L. Lock and M. Mahendran, *J. Am. Chem. Soc.*, **108**, 3613 (1986).
93. R. F. Childs, R. Faggiani, C. J. L. Lock and A. Varadarajan, *Acta Crystallogr., Sect. C*, **C40**, 1291 (1984).
94. R. Destro and M. Simonetta, *Acta Crystallogr., Sect. B*, **B35**, 1846 (1979).
95. R. Haddon, *J. Am. Chem. Soc.*, **109**, 1676 (1987).
96. R. C. Haddon and L. Scott, *Pure Appl. Chem.*, **58**, 137 (1986); R. C. Haddon, *J. Am. Chem. Soc.*, **108**, 2837 (1986); *J. Phys. Chem.*, **91**, 3719 (1987).
97. R. F. Childs, R. M. Orgias, C. J. L. Lock and M. Mahendran, *Can. J. Chem.*, **71**, 836 (1993).
98. B. D. Santarsiero, M. N. G. James, M. Mahendran and R. F. Childs, *J. Am. Chem. Soc.*, **112**, 9416 (1990).
99. J. A. Berson and J. A. Jenkins, *J. Am. Chem. Soc.*, **94**, 8907 (1972).
100. R. F. Childs, M. Mahendran, M. Sivapalan and P. Nguyen, *Chem. Commun.*, 27 (1989).
101. M. S. Brookhart and M. A. M. Atwater, *Tetrahedron Lett.*, 4399 (1972).
102. R. F. Childs, D. L. Mulholland, A. Varadarajan and S. Yeroushalmi, *J. Org. Chem.*, **48**, 1431 (1983).
103. D. Cremer, P. Svensson, F. Reichel and K. J. Szabo, to appear.
104. R. F. Childs and A. Varadarajan, *Can. J. Chem.*, **63**, 418 (1985).
105. W. J. Hehre, *J. Am. Chem. Soc.*, **95**, 5807 (1973).
106. R. C. Haddon, *J. Am. Chem. Soc.*, **110**, 1108 (1988).
107. R. C. Haddon, *J. Org. Chem.*, **44**, 3608 (1979).
108. R. C. Haddon, *Tetrahedron Lett.*, 2797 (1974); 863 (1975); *J. Am. Chem. Soc.*, **97**, 3608 (1975); *Aust. J. Chem.*, **30**, 1 (1977); *Croat. Chem. Acta*, **57**, 1165 (1984).
109. M. Barzaghi and C. Gatti, *J. Mol. Struct. (Theochem.)*, **43**, 431, 275 (1988); *J. Chim. Phys., Phys. Chim. Biol.*, **84**, 783 (1987).
110. P. Buzek, P. v. R. Schleyer and S. Sieber, *Chem. Unserer Zeit*, **26**, 116 (1992).
111. S. Sieber, P. v. R. Schleyer, A. H. Otto, J. Gauss, F. Reichel and D. Cremer, *J. Phys. Org. Chem.*, **6**, 445 (1993).
112. L. T. Scott and M. M. Hashemi, *Tetrahedron*, **42**, 1823 (1986).
113. E. J. Smutny, M. J. Caserio and J. D. Roberts, *J. Am. Chem. Soc.*, **82**, 1793 (1960); E. F. Kiefer and J. D. Roberts, *J. Am. Chem. Soc.*, **84**, 784 (1962); S. L. Manatt, M. Vogel, D. Knutson and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 2645 (1964).

114. T. J. Katz and E. H. Gold, *J. Am. Chem. Soc.*, **86**, 1600 (1964).
115. G. A. Olah, J. S. Staral, R. J. Spear and G. Liang, *J. Am. Chem. Soc.*, **97**, 5489 (1975); G. A. Olah, J. S. Staral and G. Liang, *J. Am. Chem. Soc.*, **96**, 6233 (1974).
116. R. F. Childs, *Tetrahedron*, **38**, 567 (1982).
117. A. E. Lodder, J. W. Hann, L. J. M. Ven and H. M. Buck, *Recl. Trav. Chim. Pays-Bas*, **92**, 1040 (1973).
118. R. F. Bryan, *J. Am. Chem. Soc.*, **86**, 733 (1964).
119. Von E. Hey, F. Weller and K. Dehnicke, *Z. Anorg. Allg. Chem.*, **502**, 45 (1983).
120. C. Krüger, P. J. Roberts, Y.-H. Tsay and J. B. Koster, *J. Organometal. Chem.*, **78**, 69 (1974).
121. G. Maier, R. Emrich, C.-D. Malsch, K.-A. Schneider, M. Nixdorf and H. Irngartinger, *Chem. Ber.*, **118**, 2798 (1985).
122. R. C. Haddon, *Acc. Chem. Res.*, **21**, 243 (1988).
123. E. H. Gold and T. J. Katz, *J. Org. Chem.*, **31**, 372 (1966).
124. A. J. P. Devaquet and W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 3644 (1974).
125. M. Schindler, *J. Am. Chem. Soc.*, **109**, 1020 (1987); D. R. Kelsey, *J. Chem. Res. (S)*, 44 (1986); P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, **16**, 217 (1972); *Theor. Chim. Acta*, **28**, 213 (1973); J. M. Bofill, J. Castells, S. Olivella and A. Sole, *J. Org. Chem.*, **53**, 5148 (1988); M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899, 4907 (1977); M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985); R. C. Bingham, M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, **97**, 1285, 1294, 1302 (1975); M. J. S. Dewar, D. H. Lo and C. A. Ramsden, *J. Am. Chem. Soc.*, **97**, 1307 (1975); J. J. P. Stewart, *J. Comput. Chem.*, **10**, 221 (1989).
126. R. C. Haddon and R. Raghavachari, *J. Am. Chem. Soc.*, **105**, 118 (1983).
127. G. A. Olah, G. Liang, L. A. Paquette and W. P. Melaga, *J. Am. Chem. Soc.*, **98**, 4327 (1976).
128. C. Pues, G. Baum, W. Massa and A. Berndt, *Z. Naturforsch.*, **B43**, 275 (1988).
129. R. Wehrmann, H. Klusik and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **23**, 369 (1984).
130. D. Cremer, J. Gauss, P. v. R. Schleyer and P. H. M. Budzelaar, *Angew. Chem., Int. Ed. Engl.*, **23**, 370 (1984).
131. P. Willerhausen, C. Kybart, N. Stamatis, W. Massa, M. Bühl, P. v. R. Schleyer and A. Berndt, *Angew. Chem., Int. Ed. Engl.*, **31**, 1238 (1992).
132. V. A. Koptug, *Top. Curr. Chem.*, **122**, 1-245 (1984).
133. V. A. Barkhash, *Top. Curr. Chem.*, **116/117**, 1-265 (1984).
134. D. M. Brouwer, E. L. Mackor and C. MacLean, in *Carbonium Ions*, Vol. II (Eds. G. A. Olah and P. v. R. Schleyer), Wiley, New York, 1970, pp. 837-897.
135. L. de Vries, *J. Am. Chem. Soc.*, **82**, 5242 (1960).
136. S. Winstein and M. Battiste, *J. Am. Chem. Soc.*, **82**, 5244 (1960).
137. R. F. Childs, M. Sakai and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7144 (1968).
138. R. F. Childs, M. Sakai, B. D. Parrington and S. Winstein, *J. Am. Chem. Soc.*, **96**, 6403 (1974).
139. R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7146 (1968).
140. R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, **96**, 6408 (1974).
141. R. F. Childs and B. D. Parrington, *J. Chem. Soc. (D)*, 1540 (1970).
142. P. Vogel, M. Saunders, N. M. Hasty, Jr. and J. A. Berson, *J. Am. Chem. Soc.*, **93**, 1551 (1971).
143. J. A. Berson and N. M. Hasty, Jr., *J. Am. Chem. Soc.*, **93**, 1549 (1971).
144. G. A. Olah, G. Liang and S. P. Jindal, *J. Org. Chem.*, **40**, 3259 (1975).
145. V. A. Koptug, L. I. Kuzubova, I. S. Isaev and V. I. Mamatyuk, *J. Chem. Soc. (D)*, 389 (1969); I. S. Isaev, V. I. Mamatyuk, T. G. Egorova, L. I. Kuzubova and V. A. Koptug, *Bull. Acad. Sci. USSR, Chem. Sci. Div.*, 1954 (1969); I. S. Isaev, V. I. Mamatyuk, L. I. Kuzubova, T. A. Gordymova and V. I. Koptug, *J. Org. Chem. USSR*, **6**, 2493 (1970); V. A. Koptug, L. I. Kuzubova, I. S. Isaev and V. I. Mamatyuk, *J. Org. Chem. USSR*, **6**, 1854 (1970); V. A. Koptug, V. I. Mamatyuk, L. I. Kuzubova and I. S. Isaev, *Bull. Acad. Sci. USSR, Chem. Sci. Div.*, 1524 (1969); V. I. Mamatyuk, A. I. Rezvukhin, I. S. Isaev, V. I. Buraev and V. A. Koptug, *J. Org. Chem. USSR*, **10**, 662 (1974).
146. R. F. Childs and D. L. Mulholland, *J. Am. Chem. Soc.*, **105**, 96 (1983).
147. G. A. Olah, R. H. Schlosberg, R. D. Porter, Y. K. Mo, D. P. Kelly and Gh. D. Mateescu, *J. Am. Chem. Soc.*, **94**, 2034 (1972); G. A. Olah, R. H. Schlosberg, D. P. Kelly and Gh. D. Mateescu, *J. Am. Chem. Soc.*, **92**, 2546 (1970).
148. G. I. Brodtkin, Sh. M. Nagi, I. Yu. Bagryanskaya and Yu. V. Gatilov, *J. Struct. Chem. USSR*, **25**, 440 (1984).

149. N. C. Baenziger and A. D. Nelson, *J. Am. Chem. Soc.*, **90**, 6602 (1968).
150. F. Effenberger, F. Reisinger, K. H. Schönwälder, P. Bäuerle, J. J. Stezowski, K. H. Jogun, K. Schöllkopf and W.-D. Stohrer, *J. Am. Chem. Soc.*, **109**, 882 (1987).
151. W. J. Hehre, *J. Am. Chem. Soc.*, **95**, 8908 (1973).
152. R. F. Childs, *Tetrahedron*, **38**, 567 (1982).
153. D. W. Swatton and H. Hart, *J. Am. Chem. Soc.*, **89**, 5075 (1967).
154. H. E. Zimmerman and D. I. Schuster, *J. Am. Chem. Soc.*, **84**, 4527 (1962); H. E. Zimmerman, *Pure Appl. Chem.*, **9**, 493 (1964).
155. R. F. Childs and M. Zeya, *J. Am. Chem. Soc.*, **96**, 6418 (1974).
156. S. Olivella and A. Solé, *J. Am. Chem. Soc.*, **113**, 8628 (1991); R. Sustmann and F. Lübbe, *J. Am. Chem. Soc.*, **98**, 6037 (1976); *Chem. Ber.*, **112**, 42 (1979).
157. J. A. Berson and J. A. Jenkins, *J. Am. Chem. Soc.*, **94**, 8907 (1972).
158. R. F. Childs and A. Varadarajan, *Can. J. Chem.*, **63**, 418 (1985).
159. L. T. Scott and W. R. Brunsvold, *J. Am. Chem. Soc.*, **100**, 6535 (1978).
160. A. J. P. Devaquet and W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 3644 (1974); W. J. Hehre and A. J. P. Devaquet *J. Am. Chem. Soc.*, **98**, 4370 (1976).
161. I. A. Shleider, I. S. Isaev and V. A. Koptuyug, *J. Org. Chem. USSR*, **8**, 1357 (1972).
162. P. B. J. Driessen and H. Hogeveen, *J. Am. Chem. Soc.*, **100**, 1193 (1978).
163. R. B. Woodward and R. Hoffmann, in *The Conservation of Orbital Symmetry*, Academic Press, New York, 1969.
164. R. F. Childs and C. V. Rogerson, *J. Am. Chem. Soc.*, **98**, 6391 (1976); **100**, 649 (1978); **102**, 4159 (1980).
165. H. Hogeveen and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **87**, 385, 1042 (1968); **88**, 353 (1969).
166. L. A. Paquette, G. R. Krow, J. M. Bollinger and G. A. Olah, *J. Am. Chem. Soc.*, **90**, 7147 (1968).
167. P. Ahlberg, D. L. Harris and S. Winstein, *J. Am. Chem. Soc.*, **92**, 2146, 4454 (1970).
168. C. Engdahl, G. Jonsäll and P. Ahlberg, *J. Am. Chem. Soc.*, **105**, 891 (1983).
169. D. Cremer, P. Svensson, E. Kraka and P. Ahlberg, *J. Am. Chem. Soc.*, **115**, 7445 (1993)
170. M. B. Huang, O. Goscinski, G. Jonsäll and P. Ahlberg, *J. Chem. Soc., Perkin Trans. 2*, 305 (1983); J. Bella, J. M. Poblet, A. Demoulliens and F. Volatron, *J. Chem. Soc., Perkin Trans. 2*, 37 (1989).
171. P. Ahlberg, J. B. Grutzner, D. L. Harris and S. Winstein, *J. Am. Chem. Soc.*, **92**, 3478 (1970).
172. P. Ahlberg, D. L. Harris, M. Roberts, P. Warner, P. Seidl, M. Sakai, D. Cook, A. Diaz, J. P. Dirlam, H. Hamberger and S. Winstein, *J. Am. Chem. Soc.*, **94**, 7064 (1972).
173. P. Ahlberg, G. Jonsäll and C. Engdahl, *Adv. Phys. Org. Chem.*, **19**, 223 (1983).
174. C. Engdahl and P. Ahlberg, *J. Chem. Res. (S)*, 342 (1977).
175. M. Roberts, H. Hamberger and S. Winstein, *J. Am. Chem. Soc.*, **92**, 6346 (1970).
176. G. Schröder, U. Prange, N. S. Bowman and J. F. M. Oth, *Tetrahedron Lett.*, 3251 (1970); G. Schröder, U. Prange, B. Putzl, J. Thio and J. F. M. Oth, *Chem. Ber.*, **104**, 3406 (1971).
177. G. Jonsäll and P. Ahlberg, *J. Am. Chem. Soc.*, **108**, 3819 (1986).
178. D. Cook, A. Diaz, J. P. Dirlam, D. L. Harris, M. Sakai, S. Winstein, J. C. Barborak and P. v. R. Schleyer, *Tetrahedron Lett.*, 1405 (1971).
179. S. Yaneda, S. Winstein and Z. Yoshida, *Bull. Chem. Soc. Jpn.*, **45**, 2510 (1972); M. B. Huang and G. Jonsäll, *Tetrahedron*, **41**, 6055 (1985).
180. P. Svensson, F. Reichel, P. Ahlberg and D. Cremer, *J. Chem. Soc., Perkin Trans. 2*, 1463 (1991).
181. P. Warner and S. Winstein, *J. Am. Chem. Soc.*, **93**, 1284 (1971).
182. L. A. Paquette, M. J. Broadhurst, P. Warner, G. A. Olah and G. Liang, *J. Am. Chem. Soc.*, **95**, 3386 (1973).
183. K. J. Szabo, E. Kraka and D. Cremer, *J. Org. Chem.*, to appear.
184. R. F. Childs and H. A. Corver, *J. Am. Chem. Soc.*, **94**, 6201 (1972).
185. K. Ohkata and L. A. Paquette, *J. Am. Chem. Soc.*, **102**, 1082 (1980); R. B. Du Vernet, M. Glanzmann and G. Schröder, *Tetrahedron Lett.*, 3071 (1978); L. A. Paquette, P. B. Lavrikand and R. H. Summerville, *J. Org. Chem.*, **42**, 2659 (1977).
186. H. Hogeveen and P. W. Kwant, *Acc. Chem. Res.*, **8**, 413 (1975).
187. D. Lenoir and H.-U. Siehl, in Houben-Weyl's *Method. Org. Chemie*. (Ed. M. Hanack), Vol. 19c, Thieme Verlag, Stuttgart, 1990, p. 1.
188. H. Schwarz, *Angew. Chem., Int. Ed. Engl.*, **20**, 991 (1981); G. A. Olah, G. K. S. Prakash, R. E. Williams, L. D. Field and K. Wade, in *Hyperecarbon Chemistry*, Wiley, New York, 1987.

189. P. v. R. Schleyer, T. W. Bentley, W. Koch, A. J. Kos and H. Schwarz, *J. Am. Chem. Soc.*, **109**, 6953 (1987).
190. K. J. Szabo, E. Kraka and D. Cremer, *J. Am. Chem. Soc.*, to appear.
191. M. Saunders and R. J. Berger, *J. Am. Chem. Soc.*, **94**, 4049 (1972).
192. G. A. Olah, G. K. S. Prakash, T. N. Rawdah, D. Wittaker and J. C. Rees, *J. Am. Chem. Soc.*, **101**, 3935 (1979).
193. J. B. Lambert, R. B. Finzel and C. A. Belec, *J. Am. Chem. Soc.*, **102**, 3281 (1980); J. B. Lambert and R. B. Finzel, *J. Am. Chem. Soc.*, **105**, 1954 (1983).
194. S. Winstein, M. Shatavsky, C. Norton and R. B. Woodward, *J. Am. Chem. Soc.*, **77**, 4183 (1955).
195. S. Winstein and C. Ordronneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).
196. W. G. Woods, R. A. Carboni and J. D. Roberts, *J. Am. Chem. Soc.*, **78**, 5653 (1956).
197. H. C. Brown and H. M. Bell, *J. Am. Chem. Soc.*, **85**, 2324 (1963).
198. M. Brookhart, A. Diaz and S. Winstein, *J. Am. Chem. Soc.*, **88**, 3135 (1966); H. G. Richey and R. K. Lustgarten, *J. Am. Chem. Soc.*, **88**, 3136 (1966).
199. P. R. Story and M. Saunders, *J. Am. Chem. Soc.*, **84**, 4876 (1962).
200. M. Brookhart, R. K. Lustgarten and S. Winstein, *J. Am. Chem. Soc.*, **89**, 6352 (1967); R. K. Lustgarten, M. Brookhart and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2437 (1972).
201. G. Olah and G. Liang, *J. Am. Chem. Soc.*, **97**, 6803 (1975).
202. T. Laube, *J. Am. Chem. Soc.*, **111**, 9224 (1989).
203. J. M. Schulman, R. L. Disch, P. v. R. Schleyer, B. Bühl, M. Bremer and W. Koch, *J. Am. Chem. Soc.*, **114**, 7897 (1992).
204. M. Bremer, K. Schlötz, P. v. R. Schleyer, U. Fleischer, M. Schindler, W. Kutzelnigg, W. Koch and P. Pulay, *Angew. Chem., Int. Ed. Engl.*, **28**, 1042 (1989).
205. P. J. Fagan, E. G. Burns and J. C. Calabrese, *J. Am. Chem. Soc.*, **110**, 2979 (1988); P. J. Fagan, Results cited in Reference 35.
206. S. Winstein, J. Sonnenberg and L. de Vries, *J. Am. Chem. Soc.*, **81**, 6523 (1959).
207. S. Masamune, S. Sakai, A. V. K. Jones and T. Nakashima, *Can. J. Chem.*, **52**, 855, 857 (1974); S. Masamune, M. Sakai and A. V. K. Jones, *Can. J. Chem.*, **52**, 858 (1974).
208. G. K. S. Prakash, M. Arvanghi and G. A. Olah, *J. Am. Chem. Soc.*, **107**, 6017 (1985).
209. D. P. Kelly, J. J. Giansiracusa, D. R. Leslie, I. D. McKern and G. C. Sinclair, *J. Org. Chem.*, **53**, 2497 (1988).
210. P. v. R. Schleyer, D. Lenoir, P. Mison, G. Liang, G. K. S. Prakash and G. A. Olah, *J. Am. Chem. Soc.*, **102**, 683 (1980).
211. H.-U. Siehl, *Adv. Phys. Org. Chem.*, **23**, 63 (1987).
212. H. Tanida, T. Tsuji and T. Irie, *J. Am. Chem. Soc.*, **89**, 1953 (1967); J. S. Haywood-Farmer and R. E. Pincock, *J. Am. Chem. Soc.*, **91**, 3020 (1969); M. Battiste, C. L. Deyrup, R. E. Pincock and J. Haywood-Farmer, *J. Am. Chem. Soc.*, **89**, 1854 (1967).
213. R. M. Coates and J. L. Kirkpatrick, *J. Am. Chem. Soc.*, **92**, 4883 (1970); R. M. Coates and E. R. Fretz, *J. Am. Chem. Soc.*, **97**, 2538 (1975); M. Saunders and M. R. Kates, *J. Am. Chem. Soc.*, **102**, 6867 (1980); W. L. Jorgenson, *Tetrahedron Lett.*, 3033 (1976).
214. K. J. Szabo and D. Cremer, *J. Org. Chem.*, **60**, 2257 (1995).
215. W. R. Scott and R. E. Pincock, *J. Am. Chem. Soc.*, **95**, 2040 (1973).
216. M. Bremer, P. v. R. Schleyer, K. Schötz, M. Kausch and M. Schindler, *Angew. Chem., Int. Ed. Engl.*, **26** 761 (1987).
217. R. K. Lustgarten, M. Brookhart and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7364 (1968).
218. H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **97**, 2459 (1975).
219. H. Hogeveen and E. M. G. A. van Kruchten, *Recl. Trav. Chim. Pays-Bas*, **96**, 61 (1977); *J. Org. Chem.*, **42**, 1472 (1977).
220. A. Diaz, M. Sakai and S. Winstein, *J. Am. Chem. Soc.*, **92**, 7477 (1970).
221. E. Kaufmann, H. Mayr, J. Chandrasekhar and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 1375 (1981).
222. J.-H. Shin, *Bull. Korean Chem. Soc.*, **3**, 66 (1988).
223. K. N. Houk, R. W. Gandour, R. W. Strozier, N. G. Rondan and L. A. Paquette, *J. Am. Chem. Soc.*, **101**, 6797 (1979).
224. L. T. Scott, *Pure Appl. Chem.*, **58**, 105 (1986); R. Gleiter and W. Schafer, *Acc. Chem. Res.*, **23** 369 (1990); M. F. Falcetta, K. I. Jordan, J. E. McMurry and M. N. Paddon-Row, *J. Am. Chem. Soc.*, **112**, 579 (1990).

225. W. R. Roth, O. Adamczak, R. Breuckmann, H.-W. Lennartz and R. Boese, *Chem. Ber.*, **124**, 2499 (1991).
226. W. R. Roth, M. Böhm, H.-W. Lennartz and E. Vogel, *Angew. Chem.*, **95**, 1011 (1983); W. R. Roth, F.-G. Klärner, G. Siepert and H.-W. Lennartz, *Chem. Ber.*, **125**, 217 (1992).
227. G. Maier, *Angew. Chem., Int. Ed. Engl.*, **6**, 402 (1967); E. Vogel, *Pure Appl. Chem.*, **20**, 237 (1969).
228. M. Traetteberg, *J. Am. Chem. Soc.*, **86**, 4265 (1964); S. S. Butcher, *J. Chem. Phys.*, **42**, 1833 (1965).
229. F. A. L. Anet, *J. Am. Chem. Soc.*, **86**, 458 (1964); F. R. Jensen and L. A. Smith, *J. Am. Chem. Soc.*, **86**, 956 (1964).
230. E. Ciganek, *J. Am. Chem. Soc.*, **89**, 1454, 1458 (1967).
231. R. Hoffmann, *Tetrahedron Lett.*, 2907 (1970); R. Hoffmann and W.-D. Stohrer, *J. Am. Chem. Soc.*, **93**, 6941 (1971).
232. J. F. Liebman and A. Greenberg, *Chem. Rev.*, **89**, 1225 (1989).
233. H. B. Bürgi, E. Shefter and J. D. Dunitz, *Tetrahedron*, **31**, 3089 (1975).
234. D. W. Rogers, A. Podosenin and J. F. Liebman, *J. Org. Chem.*, **58**, 2589 (1993); D. W. Rogers, S. A. Loggins, S. D. Samuel, M. A. Finnerty and J. F. Liebman, *Struct. Chem.*, **1**, 481 (1990).
235. H. J. Dauben, Jr., J. D. Wilson and J. L. Laity, in *Non-benzenoid Aromatics*, Vol. 2. (Ed. J. P. Snyder), Academic Press, New York, 1971, p. 167.
236. R. F. Childs and I. Pikulik, *Can. J. Chem.*, **55**, 259 (1977).
237. I. Pikulik and R. F. Childs, *Can. J. Chem.*, **55**, 251 (1977).
238. E. Kraka and D. Cremer, *J. Am. Chem. Soc.*, to appear.
239. D. Cremer, B. Dick and D. Christen, *J. Mol. Struct.*, **110**, 277 (1984).
240. D. Cremer and B. Dick, *Angew. Chem., Int. Ed. Engl.*, **21**, 865 (1982).
241. J. M. Schulman, R. L. Disch and M. L. Sabio, *J. Am. Chem. Soc.*, **106**, 7696 (1984).
242. R. V. Williams, Jr., A. Kurtz and B. Farley, *Tetrahedron*, **44**, 7455 (1988).
243. T.-H. Tang, C. S. Q. Lew, Y.-P. Cui, B. Capon and I. G. Csizmadia, *J. Mol. Struct.*, **305**, 149 (1994).
244. A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).
245. T. Tsuji, S. Teretake and H. Tanida, *Bull. Chem. Soc. Jpn.*, **42**, 2033 (1969); R. Huisgen, *Angew. Chem., Int. Ed. Engl.*, **9**, 751 (1970); P. M. Warner and S.-H. Lu, *J. Am. Chem. Soc.*, **102**, 331 (1980).
246. I. Pikulik and R. F. Childs, *Can. J. Chem.*, **53**, 1818 (1975).
247. H. Tanida, T. Tsuji and T. Irie, *J. Am. Chem. Soc.*, **89**, 1953 (1967); B. Halton, M. A. Battiste, R. Rehberg, C. L. Deyrup and M. E. Brennan, *J. Am. Chem. Soc.*, **89**, 5964 (1967); M. A. Battiste and J. W. Nebzdyosky, *J. Am. Chem. Soc.*, **92**, 4450 (1970); S. C. Clarke and B. L. Johnson, *Tetrahedron Lett.*, 617 (1967); D. M. Birney and J. A. Berson, *Tetrahedron*, **42**, 1561 (1986).
248. A. Bertsch, W. Grimme, G. Reinhardt, H. Rose and P. M. Warner, *J. Am. Chem. Soc.*, **110**, 5112 (1988).
249. W. L. Jörgensen, *J. Am. Chem. Soc.*, **97**, 3082 (1975).
250. P. N. Skancke, K. Yamashita and K. Morokuma, *J. Am. Chem. Soc.*, **109**, 4157 (1987).
251. C. F. Wilcox, Jr., D. A. Blain, J. Clardy, G. Van Duyne, R. Gleiter and M. Eckert Maksic, *J. Am. Chem. Soc.*, **108**, 7693 (1986).
252. A. Counotte-Potman, H. C. van der Plas and B. van Veldhuizen, *J. Org. Chem.*, **46**, 2138 (1981); C. H. Stam, A. Counotte-Potman and H. C. van der Plas, *J. Org. Chem.*, **47**, 2856 (1982).
253. C. P. R. Jennison, D. Mackay, K. N. Watson and N. J. Taylor, *J. Org. Chem.*, **51**, 3043 (1986).
254. G. Schröder, J. F. M. Oth and R. Merényi, *Angew. Chem., Int. Ed. Engl.*, **4**, 752 (1965); L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972).
255. W. v. Doering, V. G. Toscano and G. H. Beasley, *Tetrahedron*, **27**, 5299 (1971).
256. M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, **93**, 7201 (1971).
257. A. K. Cheng, F. A. L. Anet, J. Mioduski and J. Meinwald, *J. Am. Chem. Soc.*, **96**, 2887 (1974).
258. K. J. Szabo and D. Cremer, to appear.
259. R. V. Williams and H. A. Kurtz, *J. Org. Chem.*, **53**, 3626 (1988); *J. Chem. Soc., Perkin Trans. 2*, 147 (1994).
260. M. J. S. Dewar and C. Jie, *Tetrahedron*, **44**, 1351 (1988).
261. H. Quast, R. Janiak, E.-M. Peters, K. Peters and H. G. v. Schnering, *Chem. Ber.*, **125**, 969 (1992).
262. L. S. Miller, K. Grohmann and J. J. Dannenberg, *J. Am. Chem. Soc.*, **105**, 6862 (1983).

263. L. M. Jackman, A. Benesi, A. Mayer, H. Quast, E.-M. Peters, K. Peters and H. G. v. Schnering, *J. Am. Chem. Soc.*, **111**, 1512 (1989).
264. Y. C. Wang and S. H. Bauer, *J. Am. Chem. Soc.*, **94**, 5651 (1972); L. A. Paquette, W. E. Volz, M. A. Beno and G. G. Christoph, *J. Am. Chem. Soc.*, **97**, 2562 (1975).
265. S. A. Weisman, S. G. Baxter, A. M. Arif and A. H. Cowley, *J. Am. Chem. Soc.*, **108**, 529 (1986).
266. A. B. McEwan and P. v. R. Schleyer, *J. Org. Chem.*, **51**, 4357 (1986).
267. J. F. Liebman, L. A. Paquette, J. R. Peterson and D. W. Rogers, *J. Am. Chem. Soc.*, **108**, 8267 (1986).
268. M. A. Miller, J. M. Schulman and R. L. Disch, *J. Am. Chem. Soc.*, **110**, 7681 (1988); M. J. S. Dewar and A. J. Holder, *J. Am. Chem. Soc.*, **111**, 5384 (1989); A. J. Holder, *J. Comput. Chem.*, **14**, 251 (1993); J. W. Storer and K. N. Houk, *J. Am. Chem. Soc.*, **114**, 1165 (1992).
269. L. J. Schaad, B. A. Hess, Jr. and L. T. Scott, *J. Phys. Org. Chem.*, **6**, 316 (1993); L. T. Scott, M. J. Cooney, D. W. Rogers and K. Dejroongruang, *J. Am. Chem. Soc.*, **110**, 7244 (1988).
270. G. A. Olah, G. Ascensio, H. Mayr and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **100**, 4347 (1978); A. J. Birch, A. L. Hinde and L. Radom, *J. Am. Chem. Soc.*, **102**, 6430 (1980).
271. L. M. Tolbert and A. Rajca, *J. Org. Chem.*, **50**, 4805 (1985).
272. J. M. Brown and J. L. Occolowitz, *J. Chem. Soc., Chem. Commun.*, 376 (1965); *J. Chem. Soc. (B)*, 411 (1968); J. M. Brown, *J. Chem. Soc., Chem. Commun.*, 638 (1967); S. Winstein, M. Ogliaruso, M. Sakai and J. M. Nicholson, *J. Am. Chem. Soc.*, **89**, 3656 (1967).
273. E. Kaufmann, H. Mayr, J. Chandrasekhar and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **103**, 1375 (1981).
274. J. M. Brown, R. J. Elliott and W. G. Richards, *J. Chem. Soc., Perkin Trans. 2*, 485 (1982).
275. M. Christl, H. Leininger and D. Brückner, *J. Am. Chem. Soc.*, **105**, 4843 (1983); M. Christl and D. Brückner, *Chem. Ber.*, **119**, 2025 (1986).
276. F. H. Köhler and N. Hertkorn, *Chem. Ber.*, **116**, 3274 (1983).
277. G. B. Trimitsis and P. Zimmermann, *J. Chem. Soc., Chem. Commun.*, 1506 (1984).
278. W. N. Washburn, *J. Org. Chem.*, **48**, 4287 (1983).
279. R. E. Lee and R. R. Squires, *J. Am. Chem. Soc.*, **108**, 5078 (1986).
280. N. Hertkorn, F. H. Köhler and G. Müller, *Angew. Chem., Int. Ed. Engl.*, **25**, 468 (1986).
281. P. v. R. Schleyer, E. Kaufmann, A. J. Kos, H. Mayr and J. Chandrasekhar, *J. Chem. Soc., Chem. Commun.*, 1583 (1986).
282. R. Lindh, B. O. Roos, G. Jonsäll and P. Ahlberg, *J. Am. Chem. Soc.*, **108**, 6554 (1986).
283. G. Trimitsis, F.-T. Lin, R. Eaton, S. Jones, M. Trimitsis and S. Lane, *J. Chem. Soc., Chem. Commun.*, 1704 (1987); G. Trimitsis, J. Rimoldi, M. Trimitsis, J. Balog, F.-T. Lin, A. Marcus, K. Somayajula, S. Jones, T. Hendrickson and S. Kincaid, *J. Chem. Soc., Chem. Commun.*, 237 (1990).
284. A. Tuncay, M. A. Caroll, L. A. Labeots and J. M. Pawlak, *J. Chem. Soc., Chem. Commun.*, 1590 (1990).
285. M. Christl and H. Müller, *Chem. Ber.*, **126**, 529 (1993).
286. N. Hertkorn and F. H. Köhler, *Z. Naturforsch.*, **45b**, 848 (1990).
287. M. Christl, R. Less and H. Müller, *J. Chem. Soc., Chem. Commun.*, 153 (1994).
288. R. R. Squires, *Acc. Chem. Res.*, **25**, 461 (1992).