CHAPTER 8

Cyclopropyl homoconjugation —Experimental facts and interpretations

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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 derivatives. Building on the considerable work then underway on neighbouring group participation in ionization reactions, Shoppee suggested that the double bond in the cholesteryl system could function in a similar manner to Lewis base containing groups such as acetate or alkoxyl, etc.

Further studies on the cholesteryl/1-cholesteryl system were reported by Dodson and Reigel and particularly by Weinstein and his coworkers. This early work showed that the interconversion of the two cholesteryl derivatives, one of which has an open or 'homoallyl' form and the other a 'cyclopropylcarbinyll' form, could be understood in terms of the intermediate (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.

\[
\begin{align*}
\text{(1)} & \quad \text{X} \quad \equiv \quad \text{X} \\
\text{(2)} & \quad \equiv \quad \text{X} \\
\text{(3)} & \quad \equiv \quad \text{X}
\end{align*}
\]

In 1950 both Weinstein, Walborsky and Schreiber and Roberts, Bennett and Armstrong independently broadened the concept from the cholesteryl system starting point to a range of other examples including the norbornenyl cations. Weinstein 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 Weinstein made early use of theory in the form of Hückel calculations to explore the phenomenon.
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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 cation. Doering and colleagues suggested that the cycloheptatriene carboxylic acids could be regarded as planar pseudo-aromatic type structures with a homoconjugative interaction between C(1) and C(6). Based on the results of solvolytic studies on the bicyclo[3.1.0]hexyl system, Weinsein set out the general concept of homoaromaticity in 1959.

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.

The concept of homoconjugation is now over 45 years old. Like many models in organic chemistry, while not without some original sceptics, 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 important.

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, I, 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 tautom. 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.

\[ \begin{align*}
\text{X} \quad \rightleftharpoons \quad \text{Y} \\
\end{align*} \]

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 coworkers\textsuperscript{25-28} 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 bonding\textsuperscript{29} and a careful determination of molecular properties with the aid of high-level \textit{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 follows\textsuperscript{25-28}.

(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 \( \pi \)-orbitals of the cyclic system,
(b) bond orders and \( \pi \)-character indices that are approaching those of an aromatic \( \pi \)-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 \( \pi \)-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\textsuperscript{25,27,28} that should lead to:
(a) significant equalization of \( ^{13} \text{C} \) chemical shifts in the cyclic system,
(b) the magnetic susceptibility, \( \chi \), 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 \textit{endo}- and \textit{exo}-oriented protons when the system in question possesses a \( \text{CH}_2 \) group properly located above the ring.

In the case of bond (cyclopropyl) homoconjugation, Cremer and coworkers found that potentially homoantiaromatic 4\( q \) electron systems prefer to delocalize along the periphery of the bicyclic system, thus increasing the number of electrons involved in cyclic delocalization from 4\( q \) to 4\( q + 2 \).\textsuperscript{26,30} Hence, in line with orbital descriptions suggested by Hehre\textsuperscript{31}, homoantiaromaticity seems to result from an antiaromatic Möbius 4\( q + 2 \) electron system\textsuperscript{32} rather than an antiaromatic Hückel 4\( q \) electron system\textsuperscript{25-28}. In any case, homoantiaromaticity is reflected by a destabilizing resonance energy\textsuperscript{25-28}.

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 (4\( q + 2 \) \( \pi \)-electrons. The cyclic delocalization should also be reflected in the stability of a system and its spectro-
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Scopistic 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 area. 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 years, the two concepts are inextricably linked. This is most evident when pericyclic reactions are considered from the perspective of aromatic or antiaromatic transitions states and the Hückel/Möbius concept. The inter-relationship can be demonstrated by the electrocyclic reaction shown in Scheme 1.

\[
\text{(CH)}_n \xrightarrow{\text{disrot.}} (\text{CH})_n \xrightarrow{\#} (\text{CH})_{n-2}
\]

4q + 2 homoaromatic
4q antihomoaromatic

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. 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 systems, leads to a fundamentally different set of properties and reactions of these systems as compared to the potentially homoaromatic 4q + 2 cases.
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 accounts.

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 \( \pi \)-system or, alternatively, starting with an open-chain \( \pi \)-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 Charton,\(^{40}\) Story and Clark,\(^{17}\) de Meijere,\(^{41}\) and an extensive overview of more recent work has been prepared by Tidwell.\(^{42}\) Recent updates on this topic have been provided by Cremer and colleagues.\(^{26,43,24}\)

Studies on the ability of a cyclopropane to conjugate have involved a wide variety of approaches including spectroscopic, thermochemical, structural and theoretical examinations.\(^{42}\) 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 chromophore.\(^{42}\)

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 cyclopropane\textsuperscript{45-47}. 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 \(\pi\)-electron acceptor groups such as the carbonyl group\textsuperscript{45}. 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).

![Diagram](image)

(7) \(3\) 
(8) \(R = H\)
(9) \(R = \text{Me}\)

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 \(\pi\)-system of the acceptor group\textsuperscript{45,48}. Similar conclusions have also been reached on the basis of UV studies\textsuperscript{42,49} and theoretical calculations\textsuperscript{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 bond\textsuperscript{45}. This estimate is consistent with the 60\% figure derived by Pete on the basis of an analysis of the UV spectra of cyclopropyl-containing systems\textsuperscript{53}.

The geometric changes resulting from conjugation of a cyclopropane with a conventional \(\pi\)-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 exist\textsuperscript{54}, 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 ion\textsuperscript{55} with a strong cross-ring interaction\textsuperscript{56-58}. Both of these ions are significantly more stable than the corresponding homosallyl 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 reported\textsuperscript{59-61}. Of these structures some five represent relatively simple systems and in each of these cases a bisected or close to

<p>| TABLE 1. Internuclear distances (Å) of some cyclopropyl compounds and cations |
|---------------------------------|-----|-----|-----|-----|</p>
<table>
<thead>
<tr>
<th>Bond</th>
<th>(7^a)</th>
<th>(8^a)</th>
<th>(9^a)</th>
<th>(10^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)—O</td>
<td>—</td>
<td>1.256(8)</td>
<td>1.268(8)</td>
<td>—</td>
</tr>
<tr>
<td>C(1)—C(2)</td>
<td>—</td>
<td>1.405(10)</td>
<td>1.461(9)</td>
<td>1.343</td>
</tr>
<tr>
<td>C(2)—C(3)</td>
<td>1.517</td>
<td>1.516(8)</td>
<td>1.529(9)</td>
<td>2.159</td>
</tr>
<tr>
<td>C(2)—C(4)</td>
<td>—</td>
<td>1.516(8)</td>
<td>1.545(8)</td>
<td>1.543</td>
</tr>
<tr>
<td>C(3)—C(4)</td>
<td>1.478</td>
<td>1.418(12)</td>
<td>1.448(9)</td>
<td>1.453</td>
</tr>
</tbody>
</table>

\textsuperscript{a}References 43-45.
\textsuperscript{b}References 59–61.
\textsuperscript{c}Reference 56.
bisectioned 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 homocoujugation and homoaromaticity in general is whether conjugation can be transmitted through a cyclopropane ring.

Early work based on the solvolysis of substituted cyclopropylcarbiny1 systems 62,63, spectroscopic studies 64, calculations 65 and the structural work analysed by Allen 65,46 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 conjugation 66. 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 substituents 67.

In cations the situation would appear to be somewhat different. Wiberg and colleagues have examined the effect of substituents on the cyclobutenium/cyclopropylcarbiny1 homoallyl cation energy surface using ab initio calculations at the MP2/6-31G(d) level 68. In general, π-donor substituents at the 3-position were found to favour a cyclopropylcarbiny1 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’.

```
+1
CH₂
2
₄
OH
(10)
```

SCHEME 3. The 3-hydroxycyclopropylcarbiny1 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 situation 68.

III. MONOHOMOAROMATIC AND HOMOANTIAROMATIC CATIONS

A. Homotropeny1 ions

In many respects the homotropeny1 ion can be considered to be the archetype 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 homotropeny1 cation have now been reported 69. 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 homotropeny1 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 homotropenylum ions can be achieved by two general routes. The first involves the addition of an electrophile to a cyclocatetraene 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 access\(^{75-78}\).

![Scheme 4. Routes to the homotropenylum ion](image)

The original report of the preparation of the homotropenylum 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\(_8\)H\(_9\)\(^+\) cation that exhibited remarkable properties\(^{79}\). Apart from its stability, which allowed for the isolation of its salts as solids, the key feature noted was its unusual \(^1\)H NMR spectrum in which the resonances attributable to the two protons of a methylene group were non-equivalent and separated by 5.86 ppm\(^{80}\). 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 view\(^{23}\).

![Chemical shifts](image)

Since Pettit’s original report, the homotropenylum ion has been studied extensively. The resulting large body of work has previously been reviewed\(^{14-22}\). The account given here highlights the different lines of evidence for the electronic nature of the cation.

1. **NMR and magnetic properties of homotropenylum ions**

Subsequent to the initial work outlined above, high field \(^1\)H and \(^{13}\)C NMR studies of 11 and model compounds supported the original suggestion for its structure\(^{90,83}\). In terms of model compounds one of the key approaches taken was to use the metal carbonyl complexes of the homotropenylum 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 $\pi$-system to the metal, was suggested to have a localized structure\textsuperscript{84}.

A distinctive feature of the $^1\text{H}$ NMR spectra of homotropenylum ion derivatives is that the magnitude of the chemical shift difference ($\Delta \delta$) between the 8-\textit{exo} and 8-\textit{endo} proton resonances is found to be dependent on the nature and position of substituents on the ‘seven-membered’ ring\textsuperscript{2,78,85,86}. 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 homotropenylum ions, 16 and 17, have $\Delta \delta$ values only some 50–55% of that found for the parent cation\textsuperscript{27,85}. Systematic variation in the donor properties of the oxygen substituent using the Lewis acid scale developed by Childs and colleagues\textsuperscript{87} led to a linear change in $\Delta \delta$\textsuperscript{69}.

\[ \text{(16)} \quad \text{OH} \]

\[ \text{(17)} \quad \text{OH} \]

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 current\textsuperscript{86}. However, as will be shown later, substitution also results in some fairly major changes in the structure of the homotropenylum 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 homotropenylum systems is that there is an induced ring current when the ions are in a magnetic field and that this affects 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 ion\textsuperscript{88}.

Winstein and colleagues carried out a ring current calculation for 11 using the Johnson–Bovey\textsuperscript{89} approach and by assuming that atoms C(1)–C(7) adopted a planar configuration\textsuperscript{14}. This planar configuration was subsequently shown to be incorrect and a further ring current calculation was undertaken by Childs, McGlinchey and Varadarajan in 1984\textsuperscript{90}. This second calculation used as a starting point the known geometry of the 2-hydroxyhomotropenylum ion\textsuperscript{91}. 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-\textit{exo} and 8-\textit{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 homotropenylum ion and showed that its long-wavelength absorption band ($\lambda_{\text{max}}$ 313 nm) was intermediate between that of the tropylium ($\lambda_{\text{max}}$ 273.5 nm) and heptatrienyl ($\lambda_{\text{max}}$ 470 nm) cations\textsuperscript{70}. 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 homotropenylum or closely related systems determined using X-ray crystallographic techniques have been reported. These ions are 18\(^{91}\), 19\(^{92}\), 20\(^{19}\), 21\(^{19}\) and 22\(^{94}\).

![Structural diagrams of various ions](image)

Up to this time there has been no report of the experimental determination of the structure of the parent homotropenylum 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 cation\(^{99}\).

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>
<thead>
<tr>
<th>Bond</th>
<th>19</th>
<th>18</th>
<th>20</th>
<th>21</th>
<th>22</th>
<th>11</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)–C(7)</td>
<td>2.284(5)</td>
<td>1.626(8)</td>
<td>1.474(11)</td>
<td>1.544(8)</td>
<td>2.293(3)</td>
<td>1.906</td>
</tr>
<tr>
<td>C(1)–C(8)</td>
<td>1.480(5)</td>
<td>1.488(7)</td>
<td>1.498(11)</td>
<td>1.515(9)</td>
<td>1.487(3)</td>
<td>1.478</td>
</tr>
<tr>
<td>C(7)–C(8)</td>
<td>1.506(6)</td>
<td>1.488(7)</td>
<td>1.497(12)</td>
<td>1.471(9)</td>
<td>1.487(3)</td>
<td>1.478</td>
</tr>
<tr>
<td>C(1)–C(2)</td>
<td>1.407(5)</td>
<td>1.422(12)</td>
<td>1.488(10)</td>
<td>1.439(10)</td>
<td>1.373(5)</td>
<td>1.397</td>
</tr>
<tr>
<td>C(2)–C(3)</td>
<td>1.359(5)</td>
<td>1.372(2)</td>
<td>1.395(10)</td>
<td>1.425(10)</td>
<td>1.416(6)</td>
<td>1.396</td>
</tr>
<tr>
<td>C(3)–C(4)</td>
<td>1.420(5)</td>
<td>1.378(13)</td>
<td>1.402(10)</td>
<td>1.341(8)</td>
<td>1.375(5)</td>
<td>1.404</td>
</tr>
<tr>
<td>C(4)–C(5)</td>
<td>1.364(6)</td>
<td>1.378(13)</td>
<td>1.400(10)</td>
<td>1.446(7)</td>
<td>1.375(5)</td>
<td>1.404</td>
</tr>
<tr>
<td>C(5)–C(6)</td>
<td>1.429(7)</td>
<td>1.37(2)</td>
<td>1.393(11)</td>
<td>1.413(7)</td>
<td>1.416(6)</td>
<td>1.396</td>
</tr>
<tr>
<td>C(6)–C(7)</td>
<td>1.337(5)</td>
<td>1.422(12)</td>
<td>1.495(11)</td>
<td>1.484(7)</td>
<td>1.373(5)</td>
<td>1.397</td>
</tr>
<tr>
<td>(\Delta \delta) (ppm)</td>
<td>3.10</td>
<td>3.10</td>
<td>0.18</td>
<td>—</td>
<td>5.86</td>
<td></td>
</tr>
</tbody>
</table>

References: 92, 91, 69/19, 93, 94, 27

\(^{a}\Delta \delta\) is the chemical shift difference between the two resonances of the bridging (C\(_3\)) 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 Å (see also Chapter 2 of this volume)\textsuperscript{45}, 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)\textsuperscript{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 homotropenylium ion](image)

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\textsuperscript{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 distance\textsuperscript{91}. 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 structure\textsuperscript{92}. 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\textsuperscript{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 \textsuperscript{1}H 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 \textsuperscript{13}C NMR spectroscopy that there were no fundamental differences in the structure or charge distribution of the cation in solution or the solid state\textsuperscript{91,92}.
8. Cyclopropyl homoconjugation—Experimental facts and interpretations

The structure of 20 was suggested to be fully consistent with a 5C/4π 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\(^{99,92}\).

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 delocalization\(^{93}\). 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 homotropenylium ions. The earliest of these involved measurement of the barrier to ring inversion of stereoselectively labelled homotropenylium 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)\(^ {99}\). The barrier to this process was found to be 22.3 kcalmol\(^{-1}\). Winstein’s postulate that the process involved a ring inversion process and the planar cyclooctatrienyl cation 23 was later confirmed by Berson and Jenkins\(^ {99}\). 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 homotropenylium 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 homotropenylium ring](image)

The reported barriers to the inversion of C(8) of substituted homotropenylium 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>
<thead>
<tr>
<th>Cation</th>
<th>Barrier to inversion (kcalmol(^{-1}))</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>24a: R8 = D, R1 = R2 = H</td>
<td>22.3</td>
<td>70</td>
</tr>
<tr>
<td>24b: R8 = Cl, R1 = R2 = H</td>
<td>22.6</td>
<td>72</td>
</tr>
<tr>
<td>24c: R8 = D; R1 = OMe, R2 = H</td>
<td>19.6</td>
<td>101</td>
</tr>
<tr>
<td>24d: R8 = Me, R1 = OH, R2 = H</td>
<td>17.1</td>
<td>77</td>
</tr>
<tr>
<td>24e: R8 = R1 = H, R2 = OH</td>
<td>&gt;27.0</td>
<td>77</td>
</tr>
<tr>
<td>25</td>
<td>9.5</td>
<td>100</td>
</tr>
</tbody>
</table>
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 FSO₂H were measured\textsuperscript{102}. Of particular interest are the differences in heats of protonation for the various ketones and these data are summarized in Scheme 7.

\[
\begin{align*}
\text{(26)} &\xrightarrow{\Delta \Delta H = 3.7} \text{(27)} \\
(28) &\xrightarrow{\Delta \Delta H = 0.8} \text{(29)} \\
(30) &\xrightarrow{\Delta \Delta H = 0.2} \text{(31)}
\end{align*}
\]

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 kcal mol\(^{-1}\). As excepted, the effect of introducing a second double bond is much smaller (27 → 28 or 27 → 30). There is, however, a major effect on introduction of the third double bond, 28 → 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 ion\textsuperscript{39}. 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 colleagues\textsuperscript{102} that the 2-hydroxyhomoctropenium 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-hydroxyhomotropenium ion was less clear-cut. This has been confirmed by \textit{ab initio} calculations carried out by Cremer and Colleagues\textsuperscript{103}.

A further, less direct way in which homoaromatic stabilization of substituted homotropenium ions has been assessed is by measurement of their rates of interconversion and equilibrium positions between isomeric homotropenium 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 8\textsuperscript{77}. 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 hydroxyhomotropenium ions being relatively small (total spread being \textit{ca} 2 kcal mol\(^{-1}\)), while 36 was found to be 15.5 kcal mol\(^{-1}\) more stable than 33\textsuperscript{77,69}. The surprising feature of this series of rearrangements was the finding
that 36, formally a bishomoantiaromatic ion, was more stable than any of the isomeric homotropenylium ions.

The position of the equilibrium between the 8,8-dimethylhomotropenylium ions and the bicyclo[3.2.1]octadienyl system was shown to be very dependent on the nature of any additional substituents. 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 homotropenylium ions.

5. Theoretical calculations

A number of different groups have undertaken theoretical examinations of the structure and properties of the homotropenylium ion. These include Hehre, Goldstein and Hoffmann, Jorgensen, Haddon, Cremer, Bader and coworkers, Barzaghi and Gatti, Schleyer, Cremer and coworkers, and Cremer and coworkers (see Section IV. B of Chapter 7).

The underlying reason for the large number of studies is that the calculated ground state structure of the homotropenylium 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 Haddon\textsuperscript{106} in 1988 (HF and MP2 single-point calculations) and Cremer and coworkers\textsuperscript{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 homotropenylum 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 $^1$H and $^{13}$C NMR chemical shifts as a function of the C(1)–C(7) distance\textsuperscript{25,27}. Comparison of these calculated and observed shift values of the homotropenylum ion confirmed a C(1)–C(7) distance of 2 Å. At this distance the chemical shift difference between the \textit{exo} and \textit{endo} C(8) protons became a maximum. In addition the calculated magnetic susceptibility adopted a maximum value, i.e., a distinct susceptibility extaltation was found for the C(1)–C(7) equilibrium distance of 2 Å\textsuperscript{25,27}.

Analysis of the MP2 electron density distribution of the homotropenylum 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\textsuperscript{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 $\pi$-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 $^{13}$C 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 homotropenylum cation suggest that it is the prototype of a no-bond homoaromatic molecule\textsuperscript{25,27}. However, this conclusion seems to be at odds with the estimates of the homoaromatic resonance energy\textsuperscript{27,106}. Using a bicyclic form of the homotropenylum 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 homotropenylum ion\textsuperscript{27}. 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 Cremer\textsuperscript{27} and Haddon\textsuperscript{106} 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 homotropenylum 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 \textit{ab initio} calculations on hydroxy-substituted homotropenylum ions\textsuperscript{103}.

Scott and Hashemi have examined the effect of constraining the C(1)–C(7) distance in the homotropenylum ring by linking these two atoms by a three carbon bridge (termed a ‘molecular caliper’), 40\textsuperscript{112}. While the structure of 40 has not been determined, the C(1)–C(7)
8. Cyclopropyl homoconjugation—Experimental facts and interpretations

![Image of molecular structure](image)

(40)

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 homotropenylium 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\(^{10,11}\). 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 ions\(^{39}\).

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 methods\(^{14-21}\). The approaches employed parallel those used with the homotropenylium system and include an early examination of the UV spectra of the ions\(^{114}\). 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 work\(^{110}\). 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](image)

SCHEME 10. Cations on the C\(_2\)H\(_3\)⁺ 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 \(^1\)H 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 process\(^{116}\).
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 homotropenylium ion\(^{70}\). Olah suggested that the energy barrier for inversion of 41 was a measure of its homoaromatic stabilization\(^{115}\). 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) \(\pi\)-interaction and that the system can be classified as homoaromatic\(^{115}\). 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 \(^{13}\)C 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 \(^{13}\)C NMR chemical shifts of C(1)/C(3) and C(2) of the homocyclopropenium cations\(^{115}\). 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 colleagues[121] 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>
<thead>
<tr>
<th>Ion or compound</th>
<th>Reference</th>
<th>Method used</th>
<th>C(1)–C(3) distance (Å)</th>
<th>Fold angle (°)</th>
<th>α (°)</th>
<th>δ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>41 (bent)</td>
<td>111</td>
<td>MP2/6-31G(d)</td>
<td>1.735</td>
<td>35.5</td>
<td>18.2</td>
<td></td>
</tr>
<tr>
<td>41 (planar)</td>
<td>111</td>
<td>MP2/6-31G(d)</td>
<td>1.972</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>119</td>
<td>X-ray</td>
<td>2.032(10)</td>
<td>4.4</td>
<td>3.1/2.5</td>
<td>38.6</td>
</tr>
<tr>
<td>47</td>
<td>120</td>
<td>X-ray</td>
<td>1.775(4)</td>
<td>31.5</td>
<td>13.8</td>
<td>2.3</td>
</tr>
<tr>
<td>48</td>
<td>121</td>
<td>X-ray</td>
<td>1.806(6)</td>
<td>37.3</td>
<td>11.4</td>
<td>-40.0</td>
</tr>
<tr>
<td>49</td>
<td>121</td>
<td>X-ray</td>
<td>1.833(4)</td>
<td>36.4</td>
<td>10.1/16.6</td>
<td>-23.4</td>
</tr>
<tr>
<td>52</td>
<td>128</td>
<td>X-ray</td>
<td>1.915(4)</td>
<td>31.2</td>
<td>na&quot;</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>131</td>
<td>X-ray</td>
<td>1.792(15)</td>
<td>32.9</td>
<td>na&quot;</td>
<td></td>
</tr>
</tbody>
</table>

*Not 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)\(^{122}\).

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 coworkers\(^{111}\). As has been described for the homotropenylium 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 colleagues\(^{115}\). 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 1.A above (see also Chapter 7\(^{25}\)). 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 homoaromatic\(^{127}\). This sensitivity of homoaromatic delocalization to substitution parallels that demonstrated with the homotropenylium 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.

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 interaction\(^{130}\). More recent \textit{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 coworkers\(^{134}\). 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 reported. 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 cyclobutenyI/homocycloprenium 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 cyclooctatetraene⁹, the 4n-electron homologues of benzene, it is instructive to compare the formally homoantiaromatic bicyclo[3.1.0]hexenyl/cyclohexadienyl cation systems with the homocycloprenium and homotropenylium 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 4n-electron systems.

![Scheme 14](image)

**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 Köpfig⁶ and Barkhash⁷. Numerous reviews on the cyclohexadienyl cations have appeared.

The initial work on the bicyclo[3.1.0]hexenyl system was reported by de Vries¹⁵ and Weinstein and Battiste in 1960¹⁶. It was shown that acetylation of the tosylate 55 occurred with a 10¹⁰-fold acceleration over neopentyl tosylate. The ionization of 55 was found to be anehimically assisted with the predominant kinetic product of the reaction being the homofulvene 56. Small amounts of the acetate 57 were also present. Pentamethylnitrene, 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 Weinstein in 1968¹⁷. 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 electrolytic ring-opening reaction and not a more deep-seated rearrangement process. 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 Weinstein also showed that irradiation of 59 led to a clean photoisomerization and the formation of a photostationary state consisting of 58 and 59\textsuperscript{139–141}. Thus, in contrast to the homotropylium or homocyclopropenium ion systems, the ‘open’ and ‘closed’ forms of these 4π 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\textsubscript{2}Cl\textsubscript{2} as well as a transient species under solvolytic conditions\textsuperscript{142}. 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 benzene\textsuperscript{143}.

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\textsuperscript{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-
8. Cyclopropyl homoconjugation—Experimental facts and interpretations

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 review.\textsuperscript{25}

![Scheme 17](image)

SCHEME 17. Isomerization of 62 (energies in kcal/mol\textsuperscript{17})

Information on electron delocalization in the bicyclo[3.1.0]hexenyl cations is available from their reported NMR spectra\textsuperscript{137-145}. 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 $^{13}$C NMR spectrum of the parent ion\textsuperscript{114}, 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](image)

SCHEME 18. $^{13}$C NMR shifts (ppm)
There have been a large number of studies of the NMR spectra of cyclohexadienyl cations\(^{47,132,133}\). 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 \(62^{48}\), \(63^{49}\) and \(64^{50}\) 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.

![Chemical structures](image)

\( (62) \text{ R = Me} \quad (63) \text{ R = Ph} \quad (64) \text{ R = H; X = ClO}_4^- \quad \text{Pyrr} = N\text{-Pyrryl} \)

In terms of the bicyclo[3.1.0]hexenyl ions, the structure of the protonated ketone \(65\) was determined by Childs, Lock and colleagues\(^{60}\). 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 (\textit{vide supra}) and

![Chemical structures](image)

\( (65) \text{ OH} \quad \text{SbCl}_6^- \quad \text{H}_2\text{O} \quad (66) \text{ OH} \quad \text{SbCl}_6^- \)

<table>
<thead>
<tr>
<th>Compound</th>
<th>C1–C2</th>
<th>C2–C3</th>
<th>C3–C4</th>
<th>C4–C5</th>
<th>C5–C6</th>
<th>C1–C6</th>
<th>C1–C5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(65)</td>
<td>1.474</td>
<td>1.410</td>
<td>1.351</td>
<td>1.510</td>
<td>1.501</td>
<td>1.547</td>
<td>1.511</td>
</tr>
<tr>
<td>(66)</td>
<td>1.403</td>
<td>1.502</td>
<td>1.433</td>
<td>1.534</td>
<td>1.559</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(61)</td>
<td>1.492</td>
<td>1.392</td>
<td>1.392</td>
<td>1.492</td>
<td>1.535</td>
<td>1.535</td>
<td>1.501</td>
</tr>
</tbody>
</table>

*Numbering scheme for \(66\) is non-standard as shown on the structure.
*Average \(\sigma\) is 0.008 Å.
*Average \(\sigma\) is 0.011 Å.
*Calculated structure STO-3G\(^{30}\).
other protonated cyclopropyl ketones, e.g. 60, 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 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 out105,151 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 coworkers26,30 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 homoaromatic 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 homocyclopropenium ions and the bicyclo[3.1.0]hexenyl cations result in fundamentally different reactions of these cations. As was noted earlier, the homotropenylium and homocyclopropenium 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 ring137–143,145,152.

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-cyclohexadienones134.

Childs and Weinstein 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

Subsequently went on to show the remarkably high stereoselectivity associated with these reactions\(^{140}\). Rearrangements of the parent ion have been examined by Berson and colleagues\(^{142}\) (Scheme 21).

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 circumambulations\(^{155}\). 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.
8. Cyclopropyl homoconjugation—Experimental facts and interpretations

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 radical\(^{156}\).

Berson and Jenkins have looked for a comparable circumambulation in the parent homotropenylum 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 homotropenium ions which can be attributed to the difference in electron delocalization of the two systems.

\[
\text{D} + \xrightarrow{65^\circ\text{C}} \text{FSO}_3\text{H} \xrightarrow{\Delta G^\neq > 27 \text{ kcal mol}^{-1}} \text{D}
\]

SCHEME 23. Examination of circumambulation in 11D

It is possible to detect thermally induced circumambulations in certain substituted homotropenium ions. Hehre in his theoretical study (HF/STO-3G) of 11 suggested that the placement of methyl substituent at C(8) of the homotropenium 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 homotropylum ion, 68 (Scheme 25)\(^{159}\).

Circumambulation of the bridging methylene carbon of the homocyclopropenium 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 pathway\(^{160}\). Koptyug and colleagues have reported that a circumambulation of the bridg-
SCHEME 24. Rearrangement of 8,8-dimethylhomotropenyl ion

\[
\begin{align*}
\text{I} & \xrightarrow{\text{Ag}^+ \text{ acetone}} \text{[D]} & \xrightarrow{\Delta \text{ D$_2$SO$_4$}} & \text{[D]} \\
\text{D} & \xrightarrow{\Delta \text{ D$_2$SO$_4$}} & \text{D} & \xrightarrow{\text{H}^+} \text{D}
\end{align*}
\]

SCHEME 25. Rearrangement involving the bridged homotropenyl ion 68

SCHEME 26. Degenerate rearrangement of a homocyclopropenium 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 process$^{162}$.

The different electronic properties of the bicyclo[3.1.0]hexenyl, homotropenyl and homocyclopropenium 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 symmetry$^{163}$. 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 homotropenyl 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 27$^{164}$.

In concluding this section on the homoaromatic and homeantiaromatic cations, it should be pointed out that in the case of both the homotropenyl and bicyclo[3.1.0]
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 Hogveen and Volger\textsuperscript{165} and Paquette, Olah and colleagues\textsuperscript{166}, this has been shown not to be the case. Thermochemical measurements by Childs, Mulholland and Nixen\textsuperscript{87} have shown that the bicyclo[2.1.1] ions are less stable (ΔH = 7.8 kcal mol\textsuperscript{-1}) than the bicyclo[3.1.0]systems (Scheme 28).

![Diagram](image_url)

**SCHEME 28.** Thermochemical relationship between bicyclohexenyl cations (all values are enthalpies except for a ΔG\textsuperscript{o} value marked with* and are in kcal mol\textsuperscript{-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 cyclopropenium 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.
cis-1,4-bishomotropenylium ion  \[ \text{trans-1,4-bishomotropenylium ion} \]

SCHEME 29. *Cis* and *trans* bishomotropenylium ions

A further general point needs to be made before specific systems are examined. In the introduction, we laid out the two general approaches to homocconjugative 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 homocconjugative 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. Bishomotropenylium Ions**

Early work on the bishomotropenylium ions has been reviewed by Paquette\(^*\) and a more recent account given by Williams and Kurtz\(^*\). 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 bishomotropenylium ions\(^*\). 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 work\(^*\). The initially formed unsubstituted barbaralyl cation rearranges to \(71\) at \(-125\, ^\circ\text{C}\).

\[
\begin{array}{c}
\text{R} \quad \text{OH} \\
\text{FSO}_3\text{H} \\
\text{SO}_2\text{CIF} \\
\text{–135 \,^\circ\text{C}}
\end{array} \rightarrow (\text{CH})_9^+ \stackrel{\Delta}{\rightarrow} \text{R} \quad \text{–125 \,^\circ\text{C}} \\
\text{R} = \text{H or Me} \\
\text{R} = \text{H or Me} \quad \text{(71) R = H} \quad \text{(72) R = Me}
\]

SCHEME 30. Formation of bridged bishomotropenylium ions

Since these original reports, a variety of different routes have been used to prepare these ions.\(^*\) A related 1,4-bishomotropenylium ion, \(73\), was prepared independently by Roberts, Hamberger and Winstein\(^*\) and Schröder and colleagues\(^*\).

\[
\text{(73)}
\]

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-
8. Cyclopropyl homoconjugation—Experimental facts and interpretations

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 chapter)\(^\text{25}\)?

![Scheme 31. Bishomotropenylion potential energy surface](image)

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 \(^1\)H NMR spectrum of 71 provided comparatively little definitive information on its structure and electron delocalization\(^\text{171}\). In particular, the absence of \textit{exo} and \textit{endo} protons on the bridging carbons meant that the difference in their chemical shifts, the traditional but overly simplistic indicator of homocyclic delocalization, could not be used. Detailed analyses of the \(^1\)H NMR spectra of the cations suggested that their structures could be understood in terms of a bishomotropenylion 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 constants\(^\text{177}\). 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 bishomotropenylion formulation of the structure of 71\(^\text{171–178}\).

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 conclusions\(^\text{179}\). The most recent calculations of the potential energy surface linking the two ions were reported by Cremer, Ahlberg and colleagues in 1993\(^\text{38}\). 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 results\(^\text{180}\), that 71-D rather than 71-O is the energy minimum. However, the homocyclic aromatic 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 $^{71}_{28,169,180}$.

<table>
<thead>
<tr>
<th>Bond</th>
<th>$^{71}$-D$^{a}$</th>
<th>$^{71}$-D$^{b}$</th>
<th>$^{71}$-O$^{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(2)—C(3)/C(4)—C(5)</td>
<td>1.380 Å</td>
<td>1.348 (Å)</td>
<td>1.357 (Å)</td>
</tr>
<tr>
<td>C(3)—C(4)</td>
<td>1.411</td>
<td>1.427</td>
<td>1.442</td>
</tr>
<tr>
<td>C(7)—C(8)/C(8)—C(9)</td>
<td>1.393</td>
<td>1.378</td>
<td>1.390</td>
</tr>
<tr>
<td>C(2)—C(9)/C(5)—C(7)</td>
<td>2.147</td>
<td>2.075</td>
<td>2.356</td>
</tr>
<tr>
<td>Fold angle (deg)</td>
<td>100.0</td>
<td>93.2</td>
<td>113.8</td>
</tr>
</tbody>
</table>

$^{a}$Geometry at calculated [MP4(SDQ)-MP2/6-31G(d)] energy minimum.
$^{b}$Geometry calculated [MP2/6-31G(d)] for fold angle of 93° obtained from best fit of IGLO calculated chemical shifts.
$^{c}$MP2/6-31G(d) calculated geometry.

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

<table>
<thead>
<tr>
<th>Carbon</th>
<th>$^{71}$-D</th>
<th>$^{71}$-O</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(1)/C(6)</td>
<td>45.9</td>
<td>46.4</td>
<td>52.6</td>
</tr>
<tr>
<td>C(2)/C(5)</td>
<td>121.5</td>
<td>121.2</td>
<td>117.2</td>
</tr>
<tr>
<td>C(3)/C(4)</td>
<td>145.4</td>
<td>141.9</td>
<td>140.2</td>
</tr>
<tr>
<td>C(7)/C(9)</td>
<td>176.9</td>
<td>227.4</td>
<td>155.5</td>
</tr>
<tr>
<td>C(8)</td>
<td>145.4</td>
<td>148.3</td>
<td>144.0</td>
</tr>
</tbody>
</table>

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 review.$^{25}$

Overall, it is clear that $^{71}$ can rightly be considered to be abishomoaromatic 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 bishomotropenylen ions exist which lack such a framework.

Protonation of $^{74}$ in FSO$_2$H at low temperatures was shown by Warner and Weinstein to give a cation which was suggested to be the cis-1,3-bishomotropenylen cation, $^{75}_{181}$. The main evidence for the structure of $^{75}$ was its $^1$H and $^{13}$C NMR spectra.$^{18,182}$ However, the $^1$H 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 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 $^{13}$C NMR spectrum of $^{75}$ with the model compounds raises in our minds serious questions as to the validity of these claims. Apart from the $^{13}$C 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 $^{13}$C 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 systems. 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 \(^{13}\)C NMR shift values exclude the possibility of a closed form, it would appear that Warner and Winston prepared 76 rather than 75. Cremer and coworkers also pointed out that agreement between the calculated and experimental \(^{13}\)C NMR spectrum can only be obtained by re-assigning the shifts assigned to C(1) and C(2). 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).

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

Cremer and colleagues concluded the 76 is non- or only very weakly, bishomoaromatic. 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 ketones. It was concluded on the basis of \(^1\)H NMR studies that neither cation could be regarded as being homoaromatic. It would appear that in the *cis*-isomer, steric interactions between the two ethylene 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 ethylene groups is absent. However, it is not possible for the cation to adopt a boat-type conformation, as has been found for the parent homotropenylion, 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-bishomotropenylium ions.

There have been several attempts to prepare trishomotropenylium ions. However, these have all been unsuccessful\textsuperscript{185}.

\section*{B. Bishomocyclopropenium Ions}

A large amount of work has been reported on potentially bis- or trishomocyclopropenium ions. Many reviews exist including those by Weinstein\textsuperscript{14,16}, Story and Clark\textsuperscript{17}, Williams and Kurtz\textsuperscript{21}, Koptyug\textsuperscript{132}, Hogeveen and Kwant\textsuperscript{156}, Lenoir and Siehl\textsuperscript{157} and a particularly full account by Barkhash\textsuperscript{133}. The topic also overlaps that of the pyramidal cations and related boranes\textsuperscript{186}. 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\textsuperscript{-1} lower in energy than the planar form, 81\textsuperscript{189}. More recent high-level calculations of Szabo, Kraka and Cremer revealed that MP2 seriously exaggerates the energy difference\textsuperscript{190}. At MP4/DZ+P using MP2 geometries, the non-planar form 80 is 6 kcal mol\textsuperscript{-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\textsuperscript{189}. This means that the energy difference of 6 kcal mol\textsuperscript{-1} provides only a lower limit to the true homoaromatic resonance energy of 80.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{scheme33.png}
\caption{Ring inversion of 80}
\end{figure}

Despite the seeming stability of 80, all attempts to prepare the cation as a stable species in super-acid media have been unsuccessful\textsuperscript{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\textsuperscript{192,193}. 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 forms\textsuperscript{192}.

\[
\begin{array}{c}
\text{B—H} \\
(82)
\end{array}
\]

There have been a larger number of reports on the preparation of bridged bishomocyc-
clopropenium ions in which the homoconjugative bridges are linked together by an appro-
priate 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.

\[
\begin{array}{c}
\text{(83) } n = 1-4 \\
(84) \\
(85)
\end{array}
\]

The initial report on the formation of 84 was by Winsten and colleagues in 1955\textsuperscript{194}. 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 accelerations\textsuperscript{195}. These
unusually large rate accelerations were attributed to neighbouring group participation or
homoconjugation. Later these ions were called bishomocyclopropenium ions\textsuperscript{196}. Brown
and Bell offered a contrary view and suggested that 84 could be considered to be a rapidly
equilibrating pair of cyclopropylcarbinyl cations (Scheme 34)\textsuperscript{197}.

\[
\text{SCHEME 34. Equilibrating cyclopropylcarbinyl cations}
\]

Both 84 and 85 have been prepared as stable ions in super-acid media and their NMR
properties studied\textsuperscript{198-201}. 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). Winsten and coworkers were able to place a lower limit of 19.6 kcal mol\textsuperscript{-1} on

\[
\begin{array}{c}
(85) \\
\Delta G^\ddagger > 19.6 \\
\text{kcal mol\textsuperscript{-1}} \\
\text{FSO}_3\text{H}
\end{array}
\]

\[
\text{SCHEME 35. Interconversion of 7-norbornadienyl cations}
\]
TABLE 8. Structures of 7-norbornenyl cations and related compounds

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

*All distances given in Å.

the barrier to this process\textsuperscript{198}. 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 inversions.

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

While \textsuperscript{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 \textsuperscript{85} and an even more distorted structure for \textsuperscript{84}. The calculated \textsuperscript{13}C 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.

![Structures of 7-norbornenyl cations and related compounds](image)

Recently, work has been reported on the 7-boranorbornene (89) and 7-boranorbornadiene (90) systems related to \textsuperscript{84} and \textsuperscript{85}. Schleyer and colleagues have examined the parent molecules \textsuperscript{87} and \textsuperscript{88} theoretically [MP2(FU)/6-31G(d)] and concluded that they have very similar structures and electron delocalizations to the related cations (Table 8)\textsuperscript{203,204}. X-ray structures of substituted derivatives of \textsuperscript{89} and \textsuperscript{90} have been determined and these have very similar distorted conformations to those of \textsuperscript{84}, \textsuperscript{85} and \textsuperscript{86}\textsuperscript{205}. Calculated (IGLO) NMR chemical shifts of \textsuperscript{87} and \textsuperscript{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\textsuperscript{208}. 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 media\textsuperscript{207}, a preparation later repeated by Olah and colleagues\textsuperscript{192,208} and Kelly and coworkers (Scheme 36)\textsuperscript{509}.

\[ \text{SbF}_3/\text{SO}_2\text{ClF} \rightarrow \]

\[ X = \text{Cl} \]

\[ \text{(92)} \]

\[ \text{(93)} \]

SCHEME 36. Formation of trishomocyclopropenium ion

The key feature of the NMR spectra of 91 is its simplicity. Thus the $^{13}$C 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 $^{13}$C NMR resonances of the cation strongly suggested the formulation of its structure as the trishomocyclopropenium ion, 93\textsuperscript{210}. This conclusion was reinforced by the preparation of the deuterated cation and examination of the isotopic perturbation of its $^{13}$C chemical shifts\textsuperscript{208,211}, and measurement of the $^{13}$C–$^1$H coupling constants\textsuperscript{209}.

\[ \text{+} \leftrightarrow \text{+} \leftrightarrow \text{+} \]

SCHEME 37. Equilibration between classical bicyclohexyl cations

Szabo, Kraka and Cremer have recently carried out an extensive \textit{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-
tions. In addition, they studied the mechanisms of formation and decomposition of \( \text{93} \) and several hetero analogues. According to MP2 optimizations, \( \text{93} \) 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 \( \text{80} \). The authors concluded on the basis of the calculated energetic, structural, electronic and magnetic properties that \( \text{93} \) fulfills the criteria for homooaromaticity given above in Section I. A and in the preceding chapter. As such \( \text{93} \) is clearly the prototype of a trishomoaromatic cation.

Cremer and colleagues pointed out that an exact determination of the homooaromatic resonance energy of \( \text{93} \) is not possible because of strong hyperconjugative, strain and inductive effects present in the cation. 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 \( \text{93} \) than in any other homooaromatic system studied thus far. The high-field shift of the \( ^{13} \text{C} \) NMR signals by about 350 ppm and the magnetic susceptibility exaltation found by Cremer and coworkers confirm this description.

Cremer and colleagues found that \( \text{93} \) 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 \( \text{93} \). This envelope conformation provides a reasonable reference for estimating the homooaromatic resonance energy of \( \text{93} \). 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 \( \text{trans} \) hydrogen atom at C(2) (energy barrier 1 kcal mol\(^{-1}\)) (Scheme 38).

\[
\text{SCHEME 38. Isomerization of the envelope form of 93}
\]

Replacement of C(6) of \( \text{93} \) by various heteroatoms was found by Cremer and coworkers to decrease the homooaromatic 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). Silicon atoms in positions 1, 3 and 5 were found to give homooaromatic analogues of \( \text{93} \); however, it was found difficult to segregate homooaromatic stabilization and Si–C–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 \( \text{94} \) and \( \text{95} \). 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.

\[
\text{(94) and (95)}
\]
Szabo and Cremer have also investigated the possibility of cyclobutyl homoconjugation in 96 by determining its structure, conformation and energetics. 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 kcal mol⁻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-norboryl 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 formed. Recently Bremer, Schleyer and colleagues have produced and characterized the stable dication 100 from the difluoride 101. 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 aromaticity) 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 delocalization.

The clearest example is that of 104 described by Weinstein and colleagues. This cation, which rearranges to the isomeric 1- and 5-methyl-7-norbornadienyl ions at -125°C,
exhibits a $^1$H NMR spectrum which is typical of a cyclopentenyl cation and an isolated cyclobutene.

\[
\begin{align*}
\text{(102) } R &= \text{ H} \\
\text{(104) } R &= \text{ Me}
\end{align*}
\]

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 homocoujugation. 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 systems. Perhaps as a result of the difficulties in this area, a large amount of work has been reported.

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. 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$^{-1}$. 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 chapter. 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 extensively. The seven-membered ring of 105 adopts a boat-type conformation with C(7) forming the ‘prow’ of the boat. 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). Cycloheptatriene is related to 106 by a thermally allowed disrotatory process involving an aromatic transition state. 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. Attempts have been made by Dunitz and coworkers to map the course of the ring closure of bridged derivatives of 105 to 106. 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 literature. 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. This result is consistent with the results of Roth and his coworkers, who have given a value of 4.5 kcal mol⁻¹ as the homoaromatic resonance energy of 105. 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 chapter. 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 (10⁴ cm³ mol⁻¹). 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 substituent. The largest exaltation found was for 7-t-butylcycloheptatriene, 107, Λ = −14.8, a value which, surprisingly, is larger than that found for benzene itself (−13.7). 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 4-cycloheptadienes and showed that there was a considerable upfield shift of the resonance of the former protons.

---

*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 position. 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 investigations and recent high-level ab initio calculations [MP2 and CCSD(T)]. This recent theoretical work qualifies and corrects older or less reliable ab initio or semi-empirical calculations.

The boat conformation of 105 is appropriate for a C(1)–C(6) interaction. Cremer, Dick and Christen 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 Cremer 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 pr 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 Å.

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] shows that a considerable degree of bond equalization is present in 105. Cremer and Kraka suggest that this is the consequence of homo-conjugative electron delocalization. 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.

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 estimated a resonance energy of 5.6 kcal mol⁻¹ for 106 based on an assumed heat of formation ΔH⁰ of 49.6 kcal mol⁻¹ derived from ab initio calculations of Cremer and Dick and Schulman, Disch and Sabio. Experimental estimates of the enthalpy difference between 105 and 106 range from 4 to 4.5 kcal mol⁻¹. However, these estimates are too low in view of the recent CSSD(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⁻¹. 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. G.25). 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, values which are comparable to that calculated by Kraka and Cremer.

![Diagram](image)

Calculations of the geometry of 106 have been reported by a number of groups. The most accurate data are those from the calculations of Kraka and Cremer based on MP2/DZ+P and CCSD(T)/DZ+P calculations. 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 \( \pi \)-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 cyclo-
propyl compounds such as 111 and 112. They argued that the chemical shifts of 110 could
be accounted for on the basis of an induced ring current.

\[
\begin{align*}
\delta 1.65 & \quad \text{OBCl}^- \\
& \quad \text{OMe}
\end{align*}
\]

\[
\begin{align*}
\delta 3.48 & \quad \text{H}
\end{align*}
\]

(110)

\[
\begin{align*}
\delta 2.76 & \quad \text{OBCl}^- \\
& \quad \text{OMe}
\end{align*}
\]

\[
\begin{align*}
\delta 1.65 & \quad \text{H}
\end{align*}
\]

(111)

\[
\begin{align*}
\delta 2.56-2.83 & \quad \text{OBCl}^- \\
& \quad \text{OMe}
\end{align*}
\]

\[
\begin{align*}
\delta 2.56-2.83 & \quad \text{H}
\end{align*}
\]

(112)

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 systems. 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 equal-
ization 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.

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 \( 1 \times 10^3 \) times greater than that of 114. 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/cyclohepta-
triene-like transition state is only possible with the anti-isomer 113.

\[
\begin{align*}
\text{O} & \quad \text{O}
\end{align*}
\]

(113)

(114)

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. The ratio \( k(115-\text{endo})/k(115-\text{exo}) \) was found to be \( 8.9 \times 10^3 \) at 164.5 °C which
corresponds to a \( \Delta \Delta G^\circ = 7.9 \) kcal mol\(^{-1}\). These authors also attribute the high reactivity
of the anti-isomer 115 to the possibility of \( \pi \)-electron delocalization in the developing nor-
caradiene component of the transition state.

In the case of 116 the work of Roth and coworkers suggests that cyclopropyl homocon-
jugation leads to destabilization of 10 kcal mol\(^{-1}\). This result has been confirmed by
ab initio calculations as described in the preceding chapter.\textsuperscript{25} The magnitude of the difference between the resonance energies of 106 and 116 is startling. Jørgensen noted the unique properties of 116 on the basis of a MO theory analysis of the molecule.\textsuperscript{249}

The structure of 116 has been calculated by Karka and Cremer\textsuperscript{26} at the HF/6-31G(d) level of theory and by Skancke and coworkers at a lower level.\textsuperscript{250} 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 Cremer\textsuperscript{26} 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 electrons.\textsuperscript{251}

Bicyclo[2.1.0]pentene, 116, can be considered to be the prototype of a neutral homoastrionic 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 4$q$ systems will likely be rewarding in terms of fully understanding the nature of cyclopropyl homoastrionicity and homoastrionicity.

Neutral homoastrionicity has also been invoked for 117 by Wilcox and coworkers.\textsuperscript{251} 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 homoastrionicity 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 homoastrionicity.

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) protons.\textsuperscript{252} The more recent work of Mackay and colleagues using acyl derivatives nicely reinforces the induced ring current model for the anomalous chemical shifts.\textsuperscript{253} 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

Homotropyliene (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 system\textsuperscript{254}. 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 rearrangements\textsuperscript{255}. With semibullvalene it would appear that a homoaromatic transition state is of lower energy than one possessing diradical character\textsuperscript{256}.

As is shown in Scheme 40, the activation enthalpy of the degenerate valence isomerization in 120 is only 5.2 kcal mol\textsuperscript{-1}\textsuperscript{257}. Recent \textit{ab initio} calculations by Szabo and Cremer give values of 4.0 (MP2/DZ+P+ZPE) and 6.5 kcal mol\textsuperscript{-1} (MP4/DZ+P+ZPE) for this barrier\textsuperscript{258}. 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 Å (MP2). These results confirm the earlier expectations based on MO theory and semi-empirical calculations.

Hoffmann and Stohrer\textsuperscript{231}, using MO theory, and Dewar and Lo, using MINDO/2\textsuperscript{256}, 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 symmetric 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\textsuperscript{252,259}. If this could indeed be demonstrated experimentally, then 126 could be regarded as a frozen transition state\textsuperscript{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 \textit{ab initio} calculations (MP2 and MP4)\textsuperscript{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'\textsuperscript{262}. However, the \textit{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

\[ \Delta H^\circ = 5.2 \text{ kcal mol}^{-1} \] 

\[ \text{CCl}_2\text{F}_2 \] 

\[ \text{(129') \rightarrow} \]


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 Farey\(^{242,259}\), **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 chapter\(^{25}\).

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 \(^{13}\)C NMR has shown that the earlier work did not take into account the presence of two valence tautomers\(^{263}\).

The C(2)–C(8) distances of substituted semibullvalenes are typically found to be ca. 1.58 Å\(^{264}\), a distance which is longer than that of a typical cyclopropane bond\(^{45-47}\). While AM1 calculations reported by Dewar and Jie\(^{266}\) do not replicate this long internal cyclopropane bond, the recent calculations of Szabo and Cremer discussed above give a value of 1.58 Å\(^{258}\). These latter authors also find evidence of significant \(\pi\)-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 systems\(^{21}\). 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 systems\(^{266}\).

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
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\textsuperscript{25,26}.

Considerable attention has been paid to the thermochemical results obtained by Paquette and coworkers for 129 in which homoaromatic stabilization was suggested\textsuperscript{267} and later supported by Rogers and colleagues\textsuperscript{284}. However, more recent work has shown that this is not the case\textsuperscript{268}. Similarly, Scott and coworkers have shown that any resonance stabilization in 130, $R = \text{Me}$, if present, is small and cannot be quantified given the accuracy of the thermochemical methods available with these large molecules\textsuperscript{269}.

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.

\section*{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 homoaromatic\textsuperscript{31}. 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, \textit{vide supra}. However, with the corresponding anion 131 and its derivatives, there is no experimental or theoretical evidence to suggest that homoconjugation is important\textsuperscript{270}. 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 factor\textsuperscript{271}. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\caption{Diagrams illustrating homoaromatic systems.}
\end{figure}
The bridged bicyclic system 133 represents the earliest example of an anion that was claimed to be homoaromatic. 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 properties. However, this explanation was challenged in 1981 by two different groups. On the basis of calculations Grutzner and Jorgensen (MINDO/3) as well as Mayr, Schleyer and colleagues (MNDO and STO-3G) concluded independently that the properties of 133 could be accounted for 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 fragment. Christl and coworkers provided further NMR evidence to support the claim for homoaromatic stabilization of 133 and its phenyl-substituted derivatives. NMR evidence supporting some degree of charge delocalization was presented by Köhler and Hertkorn while Trimitis and Zimmermann cautioned against the use of chemical shifts to probe for homoconjunctive interactions in 133 and its derivatives. 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 Washburn and measurements in the gas phase were undertaken by Lee and Squires. These latter results showed that 134 possesses a very high gas-phase acidity that is nearly 10 kcal mol⁻¹ greater than that of 135.

![Diagram of 134 and 135](image)

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 structure. 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](image)

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 interactions. 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 important. 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 Trimitis and his group examining the rates of deuterium exchange, which led them to conclude that there was no special stability of derivatives of 133. A counter-view was expressed by Tuncay and colleagues, also based on exchange experiments. 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 salts. Hertkorn and Köhler 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 homoaromatic.

Squires, in a recent review, examines and dismisses the explanations put forward by Schleyer and colleagues and Lindh and coworkers 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 extensively. 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 chapter. 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 carbochyclic systems. The recent developments with the boron analogues of the cyclobutanyl/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.

VIII. ACKNOWLEDGEMENTS

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IX. REFERENCES

25. D. Cremer, R. F. Childs and E. Kraka, see the preceding chapter (Chapter 7) in this volume and references cited therein.
8. Cyclopropyl homoconjugation—Experimental facts and interpretations

8. Cyclopropyl homoconjugation—Experimental facts and interpretations