Chem. Rev. **2001,** *101,* 1185−1204 **1185**

Homoaromaticity

Richard Vaughan Williams

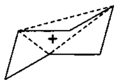
Department of Chemistry, University of Idaho, P.O. Box 442343, Moscow, Idaho 83844-2343

Received October 4, 2000

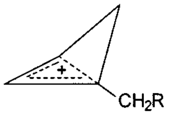
Contents

I. Introduction

In 1959 Winstein introduced the term “homoaromatic” to describe compounds that display aromaticity despite one or more saturated linkages interrupting the formal cyclic conjugation.[1] He suggested that the tris-homocyclopropenyl cation **1**[2] should be classed as homoaromatic.[1] Earlier, Roberts and Applequist noted the “homo” relationship between the cyclobutenyl cations **2**[3] and the aromatic cyclopropenyl cation (**3**) and Doering et al. invoked “pseudo-aromaticity” for the Buchner acids (**4**).[4] In the same year, Roberts et al. proposed unusual stability for the “bis-homocyclopropenyl” cation **5** to rationalize the high solvolytic reactivity of *anti*-7-substituted norbornenes.[5] Each of these compounds would be regarded as homoaromatic should they exhibit the properties of aromaticity.

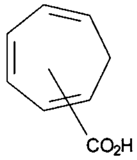


1

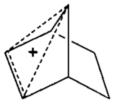


2

3



4



5

In the intervening 41 years since the introduction of Winstein’s terminology, the study of homoaromaticity has flourished as witnessed by the numerous review articles on[6−14] and sections of monographs devoted to[15] various aspects of this topic. Homoaromaticity is well-established in cationic systems where delocalization of charge provides an additional driving force for homoaromaticity. The weight of evidence supports the designation of the cationic systems **1**, **2**, and **5** as homoaromatic. Similarly, it might be anticipated that charge delocalization would enhance the possibilities of homoaromaticity in anionic systems. In general, this has not proved to be the case. Neutral radicals do not participate in homoconjugation and are not expected to exhibit homoaromaticity.

10.1021/cr9903149 CCC: $36.00

Richard Williams was born in Prestatyn, North Wales. He earned his B.Sc. degree in Chemistry from the University of Leeds (1975) and his Ph.D. degree in 1978 under the tutelage of Ian Fleming at the University of Cambridge, England. Following postdoctoral appointments with Reg Mitchell at the University of Victoria, Canada, and Leo Paquette at the Ohio State University, he was apppointed to an assistant professorship at Memphis State University in 1983. He was promoted to Associate Professor in 1988, and in 1989 he moved to the University of Idaho, where he is currently a Professor of Chemistry. His research interests include the synthesis and study of theoretically interesting molecules especially novel (homo)aromatics and highly strained small ring compounds.

Homoaromaticity in neutral molecules, just as in anions, is controversial and is an area of continuing intense activity.[6−14, 16−20]

The most recent of the earlier reviews cover the literature on homoaromaticity through 1994.[12−14] The present contribution will continue coverage from 1995 to the beginning of 2000. Naturally, sufficient background will be provided to set the new material in an appropriate context.

II. Aromaticity

It is impossible to discuss homoaromaticity without first considering aromaticity. The field of aromaticity continues to be controversial. The central theme of this controversy is the definition of aromaticity itself.[21] Although a universally applicable and acceptable definition of aromaticity may never exist, there is general agreement that aromaticity is an exceedingly useful concept and that the term should not be abandoned.[26] No doubt, there will be detailed discussions of the fundamentals of aromaticity elsewhere in this thematic issue of *Chemical Reviews*. Here, only a brief overview of aromaticity is provided with selected citations (to review articles where possible). The first guide to designating a molecule as aromatic is Hückel's rule, which suggests a planar monocyclic hydrocarbon with complete cyclic delocalization of $(4n + 2)$ π-electrons, where n is an integer, will be aromatic.[27] Planar monocyclic systems involving the cyclic delocalization of $4n$ π-electrons are predicted to be antiaromatic. Various diagnostic properties result from these cyclic delocalizations and these properties have been used to establish indices of aromaticity.

A. Energetic Considerations—“Resonance Energy”[21]

The usual measure of aromaticity is in terms of thermodynamics. In Hückel's definition, the aromatic molecule enjoys a *special stability*, relative to a nonaromatic reference molecule, as a result of its cyclic delocalization of the π-electrons. The special stability is generally expressed as resonance energy. The choice of reference has a profound effect upon the resonance energy. In the Hückel model, the aromatic compound with q formal double bonds is compared with q ethylenes. The resonance energy thus determined is a measure of the total stabilization resulting from both the regular conjugation (as found in acyclic polyenes) and the cyclic delocalization (characteristic of aromaticity). In this model, no account is taken of geometric factors which may have significant energetic consequences. A better model would use as a reference a hypothetical compound with an identical geometry and the same number of formal but strictly localized double bonds as the aromatic species. For example, the reference for benzene would be the localized and hexagonal 1,3,5-cyclohexatriene. Again, the resonance energy would measure the total stabilization from both regular and cyclic delocalization. Yet another model, due to Dewar and Gleicher,[28] defines a resonance energy relative to a hypothetical delocalized system with the same number of $C{=}C$ double bonds, $C{-}C$ single bonds, and $C{-}H$ bonds as the aromatic compound but not cyclically conjugated. In this case, the resonance energy represents the extra stabilization due to the cyclic delocalization only. Many variations on these basic models have been proposed, each leading to a different resonance energy. The individual energies used to calculate the resonance energy may come from experiment, theory, group additivity approaches, or a combination of these. Various isodesmic and homodesmotic schemes have also been used to determine resonance energies. No matter the details of the method used, the Dewar model generally leads to a relative ordering of resonance energies more closely aligned with experimental orders of aromaticity. Depending on the model, some $4n$ antiaromatic systems may show destabilization relative to the chosen reference. Although thermodynamics is the prime discriminator for aromaticity, other factors, such as bond length equalization and magnetic properties, are viewed as manifestations of aromaticity and have been used in the construction of scales of aromaticity.

B. Geometric Considerations—Bond Length Equalization[21]

The $C\overset{---}{=}C$ bonds around the periphery of an aromatic molecule are of approximately equal length. The closer each bond is to identical in length, the more aromatic the compound, and conversely, the more the bond lengths alternate around the periphery, the less aromatic the compound. Various indices of aromaticity were developed based on the degree of bond alternation in the molecule under scrutiny. However, as Schleyer pointed out,[23] bond length equalization should not be used alone as a criterion for aromaticity as some bond-equalized systems are not aromatic. Traditionally, this bond length equalization is attributed to the cyclic delocalization of the

π-electrons. More recently, the σ-framework was credited with enforcing the bond equalization while the π-system was claimed to favor an alternating single- and double-bond pattern. This latter view has been questioned, and the debate as to the origin of the bond equalization continues today.[29] The bond lengths around the periphery of antiaromatic molecules strongly alternate.

C. Magnetic Effects[21]

While aromaticity is difficult to define, experimentally it is often easily detected. As a result of the cyclic delocalization in an aromatic, an external magnetic field induces a “ring current” in the aromatic molecule. This ring current leads to anomalous magnetic properties such as large magnetic anisotropy and magnetic susceptibility exaltation. Garratt defined molecules with an induced diamagnetic ring current as diatropic and those with a paramagnetic ring current as paratropic.[32] Diatropicity and paratropicity, which are most easily detected by proton NMR spectroscopy, are manifestations of aromaticity and antiaromaticity, respectively. Schleyer proposed that diamagnetic susceptibility exaltation is the only measurable property uniquely associated with aromaticity and went on to define aromaticity in terms of this exaltation.[23] Schleyer and others also contend that the various indices of aromaticity are well correlated, whereas Katritzky and others maintain that aromaticity is multidimensional and, in particular, that magnetic susceptibility is orthogonal to the classical criteria for aromaticity.[23,26] Recently, Schleyer et al. introduced nucleus-independent chemical shifts (NICS),[33] the negative of the absolute magnetic shieldings, as a means of evaluating the aromaticity/antiaromaticity of a system.

D. Chemical Reactivity[21]

In general, aromatic compounds tend to react in such a fashion as to retain the aromatic nucleus by undergoing substitution rather than addition reactions. This unusual (for unsaturated systems) pattern of reactivity is taken as an indication of the special stability of aromatics. Chemical reactivity is not a particularly good criterion for aromaticity as it is difficult to quantify and for many aromatics the preferred reaction motif is addition.

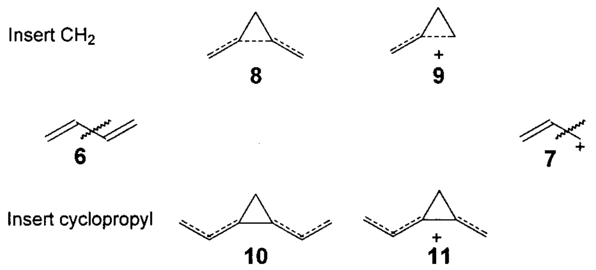
E. Concluding Remarks

It is absolutely vital to continue to explore the fundamental aspects of aromaticity, to strive for a widely applicable definition, to probe the uni- or multidimensionality of the phenomenon, to discover whether the σ- or π-systems are responsible for the bond-equalized structures, and to develop as widely applicable quantitative scale of aromaticity as possible. Much progress has been made in these endeavors, but much remains to be done. However, from a pragmatic stance, recognizing a compound as (qualitatively) aromatic is usually easily achieved by a combination of the criteria surveyed above. As pointed out in numerous review articles,[21] relying on just one criterion in assigning aromaticity, or not, is perilous and may lead to errors. No matter how the π-system is brought into proximity, by virtue of the σ- or π-framework, delocalization will result and the properties usually associated with aromaticity will be observed for $(4n + 2)$ electron species.

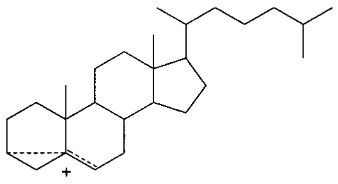
Theory and experiment have always been closely linked in the study of aromaticity. With the advent of both better hardware and software, it is now practical to carry out high-order calculations on large and complex systems. It is well-recognized that calculations lacking electron correlation, e.g., Hartree−Fock (HF), do not adequately represent systems possessing extended conjugation. Electron-correlated calculations, such as density functional theory (DFT) using the B3LYP functional and second-order Möller−Plesset perturbation theory (MP2) both using at least a 6-31G* basis set, are generally considered to yield reliable results in all but the most challenging of systems. The relative energy ordering of the various conformations of [10]annulene were found to depend on the level of theory used. B3LYP and MP2 methods incorrectly ordered the energies of the various conformers in comparison with the computationally much more expensive coupled cluster theory.[34] However, it should be noted that the geometries of the minima found by each method were comparable. Similarly, in calculations on *syn*- and *anti*-bismethano[14]annulene, it was found, as is usual, that HF calculations overemphasized the stability of the localized forms whereas MP2 and DFT using the BLYP functional overestimate the extent of delocalization.[35] The B3LYP method was the most accurate, providing results closely aligned with experiment. Calculated magnetic data have proved to be extremely dependable, and in particular, calculated NMR chemical shifts are in close agreement with experimentally determined shifts. The better fit of the calculated chemical shifts, for one of the higher energy minima (B3LYP and MP2) of [10]annulene, with the experimental NMR spectrum was the first indication that B3LYP and MP2 may have given incorrect energy ordering for the conformers of [10]annulene.[34] NICS, whether they are calculated at the ring centroid or slightly out of the mean plane (to reduce the local paramagnetic contributions of the σ-bonds) or dissected into σ- and π-contributions,[36] are well-defined and free from the arbitrariness of a chosen reference system. As such, they provide an excellent means for the confirmation of aromaticity or antiaromaticity.

III. Homoaromaticity: General Features

Formally, homoconjugation results when the direct conjugative linkage between adjacent centers (e.g., as in **6** and **7**) is interrupted by insertion of a saturated unit. The saturated unit is generally a CH_2 group but can be a larger alkyl residue or even a heteroatomic moiety. As well as through-space homoconjugation (referred to as no-bond homoconjugation by Cremer and Childs et al.[13,14]), e.g., as in **8** and **9**, σ-homoconjugation (or more descriptively, bond homoconjugation[13,14]), e.g., as in **10** and **11**, is also possible.[6−14]

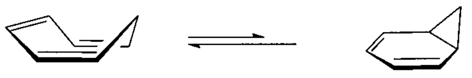


The first suggestion of a delocalized homoconjugated system is due to Winstein and Adams.[37] They invoked participation by the remote double bond of cholesteryl *p*-toluenesulfonate to form the "homoallylic"[38] cation **12**. Earlier Shoppee proposed that a classical intermediate resulted from a similar interaction between the double bond and the incipient cationic center in 3-cholesteryl derivatives.[39]

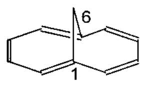


12

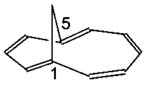
Homoaromaticity refers to the special case in which the homoconjugative interaction(s) completes an energy lowering cyclic delocalization of ($4n + 2$) electrons and results in the properties of aromaticity.[6−14] Similarly, homoantiaromaticity ensues when the homoconjugative interaction(s) completes the cyclic delocalization of $4n$ electrons. Just as there is bond and no-bond homoconjugation, the same options are possible in homoaromaticity. Often the potential no-bond and bond homoaromatics are related by a rearrangement as illustrated in the valence tautomerism between 1,3,5-cycloheptatriene (**13**) and norcaradiene (**14**).[40,41] Both **13** and **14** are well set up for homoconjugation, while their homoaromaticity or otherwise has been a matter of some controversy (vide infra). Should **13** and **14** prove to be homoaromatic, then, in Winstein's terminology,[6] they are *mono*homoaromatic and each could be referred to as monohomobenzene as there is one interruption to the direct aromatic conjugation of benzene. Multiple homoconjugative insertions into an aromatic may result in bis-, tris-, tetrahomoaromatics, etc.



In no-bond and bond (σ-) homoaromaticity, the cyclic delocalization is completed by one or more energy lowering through-space or through-bond interactions. A third type of homoaromaticity is possible. In this type the cyclic delocalization of the aromatic system is not interrupted; instead, a transannular homoconjugative interaction(s) perturbs the aromatic delocalization.[12,14] This type of homoaromaticity is exemplified in the bridged annulenes such as Vogel's **15**[42] and Massamune's **16**[43] bridged [10]-annulenes.[44,45] As a consequence of the significant transannular homoconjugation in **15** (C1,C6) and **16** (C1,C5), they are more appropriately referred to as homonaphthalene and homoazulene, respectively.



15



16

A. Criteria for Homoaromaticity

Homoaromaticity not only requires the presence of homoconjugation, but also the observation of "aromaticity" as described in section II and characterized by satisfying a range of these criteria. Childs and Cremer et al. presented a very thorough examination of the criteria for classification as homoaromatic, and they summarized their requirements for homoaromaticity as follows.[13,14] "(1) The system in question should possess one or more homoconjugative interactions (either through-bond or through-space) closing cyclic conjugation. (2) The bond or interaction indices of the homoconjugative interactions should be significantly greater than zero, thus indicating either a partial bond (cyclopropyl homoconjugation) or substantial through-space interactions (no-bond homoconjugation). (3) Electron delocalization in the closed cyclic system should be characterized by (a) effective overlap between the π-orbitals of the cyclic system, (b) bond orders and π-character indices that are approaching those of an aromatic π-system, (c) delocalization of positive or negative charge throughout the cyclic system in case of charged molecules, (d) a relatively large degree of bond equalization with bond lengths differing from those of normal single or double bonds. (4) For either cyclopropyl or no-bond homoaromatic systems, the number of π-electrons participating in cyclic electron delocalization should be close to $4q + 2$. (5) Homoaromaticity should lead to a stabilizing resonance energy >2 kcal mol^{-1}. (6) No-bond homoaromatic systems should possess exceptional magnetic properties that should lead to (a) significant equalization of ^{13}C chemical shifts in the cyclic system, (b) the magnetic susceptibility, χ, adopting a maximum value for an unconstrained homoaromatic system, i.e., the exaltation of the magnetic susceptibility indicates homoaromatic electron delocalization, (c) a large chemical shift difference between the *endo*- and *exo*-oriented protons when the system in question possesses a CH_2 group properly located above the ring".

Cremer and co-workers extended and widely applied the Bader topological analysis of "atoms in molecules"[46] to a range of (potential) homoaromatic molecules.[47] The recommended bond or interaction indices of item 2 are derived from such an analysis and are based on the electron densities calculated at the bond critical point (for bond homoaromaticity) or at the midpoint of the homoconjugative internuclear gap (for no-bond homoaromaticity where no bond critical point exists). Williams, Kurtz, and Farley developed semiempirical discriminators for the confirmation of homoaromaticity based on two-center energy partitioning terms (a negative value indicates a favorable interaction between centers) and a considerable drop in energy between the SCF and correlated, via simple 2 × 2 or 4 × 4 configuration interactions (CI2 and CI4 respectively), levels of theory.[48] These discriminators have proved to be effective in assessing homoaromatic interactions in a variety of systems and provide results in complete agreement with other discriminators for homoaromaticity.[48−50] Although two-center energy partitioning only furnishes qualitative bond or interaction indices, an advantage of these discriminators is that their determination requires very modest computational resources. The π-character indices (item 3b) are related to the bond ellipticities as defined by Bader. The determination of resonance energies for homoaromatic molecules is as problematic as it is for aromatics (vide supra). Once again the choice of references strongly influences the calculated resonance energies and can lead to significant errors. Due to these problems with resonance energies, extreme caution is recommended in their use. The exceptional magnetic properties referred to in item 6 result from an induced diamagnetic ring current in the homoaromatic species. Evidence for this ring current is usually available from NMR spectroscopy, which is frequently used to confirm the homoaromaticity of a compound. Bond homoaromaticity, which is less well-studied than its no-bond counterpart, is currently confined to consideration of cyclopropyl (and its heteroatomic analogues) homoaromaticity. Recently, Houk et al.[51] using high-level theory obtained evidence in support of earlier conclusions by Haddon[52] and Jorgensen[53] that only cyclopropyl and not cyclobutyl conjugation is effective in homoaromaticity. Although the magnetic properties of bond (cyclopropyl) homoaromatics have not been extensively studied, they probably parallel those of the no-bond homoaromatics but will be perturbed by the presence of the (stretched) three-membered ring. Again, demonstration of a diamagnetic ring current affords good evidence for homoaromaticity.

B. Assignment as Homoaromatic

Certainly, almost any molecule satisfying all of the Childs and Cremer et al. requirements is homoaromatic.[13,14] However, a subset of these conditions can be used to confidently assign a candidate as homoaromatic in the majority of cases. This subset consists of the Childs and Cremer et al. items 1, 3d, and 4 and in addition a characteristic homoconjugative gap and evidence for an induced diamagnetic ring current. For no-bond homoaromatics, the homoconjugative gap should range between 1.8 and 2.2 Å and is ideally approximately 2 Å.[12−14,50] Potential cyclopropyl homoaromatics are comparatively rare. They should have a stretched cyclopropyl bond characterized by a bond critical point.[12−14,50] Evidence for a ring current is most conveniently obtained experimentally from NMR spectroscopy.[21] Alternatively, a large magnetic susceptibility exaltation, determined by comparing the measured or calculated magnetic susceptibilities with the corresponding increment values,[21] or a large negative NICS value[33,50] confirm the existence of a ring current. In the absence of NMR verification, NICS is perhaps the best method to demonstrate the presence of a ring current as it is a well-defined method not requiring the use of an arbitrary model.

C. Concluding Remarks

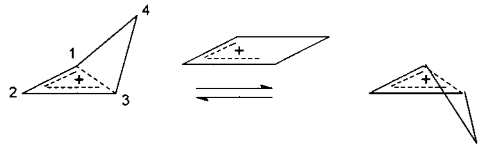
Theory plays an even more important role in homoaromaticity than it does in aromaticity. The interruption of the direct aromatic delocalization in a homoaromatic results in an attenuation of the properties of aromaticity. It may be more difficult to detect these attenuated properties, and consequently, the experimental data may be ambiguous. The determination of experimental parameters, especially structural information, is often difficult or even impossible as many homoaromatics are not isolable in a pure state, are transient species, are not solids, and/or do not give good crystals. More tractable derivatives of the parent system may be sufficiently perturbed by the substituent(s) so as to further attenuate the attributes of homoaromaticity or even change the fundamental character from homoaromatic to nonhomoaromatic.[54] It is feasible to use high-order theoretical methods to determine the properties associated with (homo)aromaticity, discussed above and in previous reviews.[6−15] These theoretically determined data are dependable and can be confidently used to predict that a compound is homoaromatic. However, in this reviewer's opinion, to designate a compound as homoaromatic it is essential to also obtain experimental data supporting homoaromaticty. Experiment should be augmented by theory, and it is perfectly reasonable to use theory to supplement an incomplete set of experimental data in confirming the homoaromaticity of a compound. A particularly powerful combination of theory and experiment is seen in the comparison of calculated and experimentally measured NMR chemical shifts, vide supra. Excellent agreement between the theoretically determined and experimentally measured NMR chemical shifts is strong evidence that the calculated geometry is accurate.[13,34]

IV. Cationic Homoaromaticity

A. Two-Electron Systems

1. Monohomocyclopropenium Cations

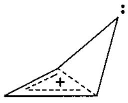
The homocyclopropenium cation (**17**) is the simplest homoaromatic, and a derivative (**2**) was the first system proposed to be homoaromatic.[3] In their long history, the parent and various substituted homocyclopropenium cations have been extensively investigated. The results of these investigations are summarized in previous reviews.[6−15] The parent **17** and most of the derivatives examined were convincingly demonstrated to be homoaromatic. These homoaromatic cations adopt a puckered geometry with a relatively short nonbonded 1,3 distance(~1.8 Å, consistent with homoaromaticity), a high barrier to inversion (**17a** $\rightleftharpoons$ **17b**, ~8 kcal mol^{-1}) through a planar nonhomoaromatic transition state and a significant build up of positive charge at C2. The size of the barrier to inversion is taken as an indicator of the degree of homoaromaticity.



17a **17b**

Several theoretical studies of the homocyclopropenium ion (**17**) have appeared since the very detailed investigation by Schleyer and Otto et al.[55] These more recent studies do not provide any further insights into the undisputed homoaromaticity of **17**. In a full exploration of the potential energy surface of $C_4H_5^+$, Hopkinson et al. found 14 minima at HF/6-31G** and 9 minima at MP2(full)/6-311G** and determined that **17** was the second lowest energy species, only 9.1 kcal mol^{-1} higher in energy than the aromatic methylcyclopropenyl cation.[56] Notario and Elguero used the G2 method to determine the proton affinity of tetrahedrane and concluded that its superbasicity results from its high strain energy and the stability of the homocyclopropenium cation, the product of protonation.[57] In another theoretical study, Maksić et al. used the G2 and other ab initio methods (many the same as in the earlier work by Schleyer and Otto et al.[55]) to investigate **17**, the lowest energy cation produced upon protonation of cyclobutadiene.[58]

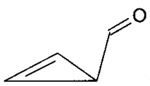
A computational study, prompted by an earlier experimental observation of the formation of $C_6N_2H_2^{+\bullet}$ dimers in ion molecule reactions of cyanoacetylene, revealed the stabilizing effect of homoaromaticity in the cationic cyclo-$C_4H_3^+$ carbene **18**.[59] The homoaromatic singlet cation (**18a**) has a puckered geometry and is 19.5 kcal mol^{-1} lower in energy than the planar triplet species (**18b**).[59b] Sequentially replacing the hydrogen atoms in **18** with nitrile groups lowers the singlet−triplet energy gap, but even in the corresponding trinitrile, the singlet is favored over the triplet by 8.3 kcal mol^{-1}.



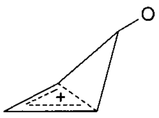
18a

18b

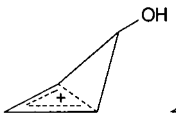
As part of their studies designed to elucidate the mechanism for the circumambulatory rearrangements of substituted cyclopropenes, Minkin and coworkers presented evidence for the formation of a homoaromatic hydroxycyclobutenyl cation. The barrier to rearrangement of **19** is calculated to be high, and the homoaromatic **20** is disfavored (42.6 kcal mol^{-1} higher in energy than **19**).[60a] The circumambulatory rearrangement is predicted to be accelerated by protonation of the carbonyl group, and the hydroxymonohomocyclopropenium cation **21** is the lowest energy species found (3.7 kcal mol^{-1} lower than the energetically nearest cation **22**).[60]



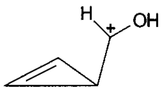
19



20



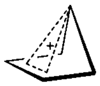
21



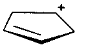
22

2. Bishomocyclopropenium Cations

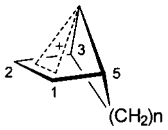
Despite considerable effort to prepare the parent bishomocyclopropenium ion (**23**),[6−15] it remains unknown experimentally. **23** is calculated to be puckered (pucker angle ~90°) and 6 kcal mol^{-1} (MP4SDQ/6-31G*//MP2/6-31G*) more stable than the nonhomoaromatic, but less strained, planar conformation **24**.[61] Since Roberts et al.[5] first proposed the enhanced stability of the bishomocyclopropenyl cation **5**, numerous 3,5-bridged derivatives (**25**) were prepared and fully characterized as homoaromatic both by experiment and theory.[6−15]



23

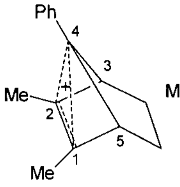


24

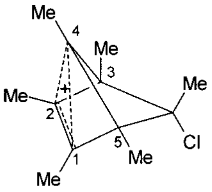


25

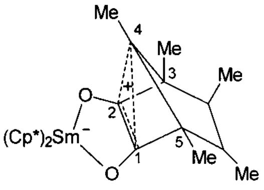
Recently Laube et al. and Evans et al. reported X-ray structures for the three different 3,5-bridged bishomocyclopropenyl cations **26**−**28**.[62,63] In each case, the formal double bond is elongated (C1−C2 ~1.41 Å) compared with a normal double bond and C4 leans toward this former double bond (average C1−C4 and C2−C4 distances ~1.75−1.88 Å). These results are in excellent agreement with calculated structures for related bishomocyclopropenyl cations with both experiment and theory strongly supporting the homoaromaticity of these systems.



26

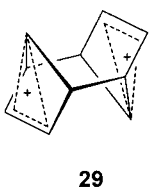


27

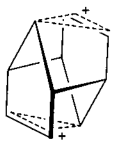


28

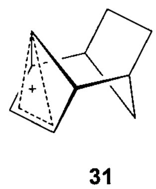
The dication **29** could be considered a sandwich bishomoaromatic dication or a 4 π-electron longicyclic aromatic system or as the alternative homoaromatic species **30**.[64] To resolve this problem, Olah and Prakash et al. undertook a theoretical study of these compounds and also, for comparison, monocation **31**. Using HF/6-31G* and B3LYP/6-31G* methods, they obtained optimized structures for **29**−**31**. There is no evidence for longicyclic stabilization in **29**, and both **29** and **31** are clearly bishomoaromatics. The dication **30** is less stable than **29** by 34.2 kcal mol^{-1}. Supporting these conclusions, the calculated ^{13}C NMR chemical shifts for **29** are in excellent agreement with the with those obtained experimentally[65] from treatment of diol **32** with SbF_5/SO_2ClF.



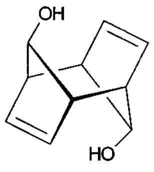
29



30



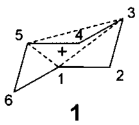
31



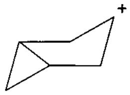
32

3. Trishomocyclopropenium Cations

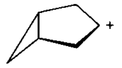
The trishomocyclopropenium cation **1** was one of the first species proposed and convincingly demonstrated to be homoaromatic.[6−15] In a comprehensive theoretical study of this and related cations, Cremer et al. reaffirmed the homoaromaticity of this ring system.[61] They again stressed the role played by ^{13}C NMR chemical shifts as a link between theory and experiment noting that good agreement between these values indicated an accurate calculated geometry. The homoconjugative distances are all equal in **1** (C1−C3 = C1−C5 = C3−C5 = 1.82 Å), and the positive charge is evenly distributed over C1, C3, and C5. Exactly as in other (homo)aromatic systems, finding a suitable reference for calculating resonance energies is difficult. Cremer et al. reported that **1** is more stable than **33** and **34** by 12 and 12.6 kcal mol^{-1}, respectively. However, neither **33** nor **34** are good models for the determination of the resonance energy of **1** as in both some homoconjugative interactions remain and the strain energies are very different compared with **1**. In addition to the Cremer et al. study, Prakash and Olah et al. also calculated the ^{13}C NMR chemical shifts of **1**. Both groups obtained close agreement with the experimental values.[61,64]



1

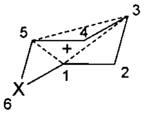


33

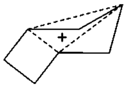


34

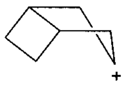
The effect of substituting a heteroatom for C6 in **1** depends, as expected, on the electronegativity of the atom. Electronegative atoms (N and O) reduce the effectiveness of the homoconjugation and result in reduced homoaromaticity in **35** and **36** compared with **1**, while electron donation, e.g., by B as in **37**, has the opposite effect.[61] These changes are clearly reflected in the C1−C5 homoconjugative internuclear distances of 1.74, 1.706, and 1.995 Å in **35**, **36**, and **37**, respectively. Similarly in **38**, which is perturbed by insertion of a CH$_2$ group, homaromaticity is unimportant (C1−C5 = 1.647 Å). At the HF level of theory, **38** is calculated to be 8.8 kcal mol^{-1} less stable than **39**. However, on the electron-correlated MP2 surface, **38** is no longer at a stationary point.[61]



35 X = NH
36 X = O
37 X = BH

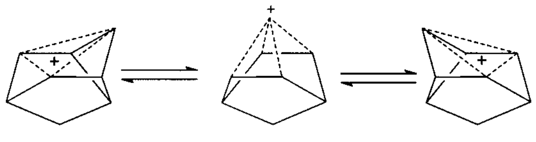


38



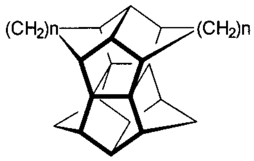
39

Prakash, Olah, and Rasul found that the trishomocyclopropenium cations **40** are ~0.2 kcal mol^{-1} more stable than the corresponding hypercoordinate square-pyramidal cation **41**.[66] From their calculated ^{13}C NMR chemical shifts, they determined that these ions exist as a rapidly equilibrating mixture (**40**:**41** = 2:1) in superacid solution. In other related hypercoordinate square-pyramidal cations, the potential trishomocyclopropenium cations were not stable species.

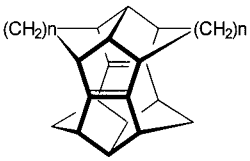


4. Pagodane Dications

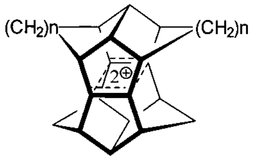
The pagodanes **42** (*n* = 1 or 2) and **48**, isopagodanes **45** (*n* = 1 or 2), and related dienes **43** and **46** (*n* = 1 or 2) and **49** can each be oxidized to the corresponding dications **44** and **47** (*n* = 1 or 2) and **50**.[67−70] The dications **44** and **47** are fully characterized by experiment, ^{13}C NMR spectroscopy, and by theory as 4-center 2-electron (4c/2e) bishomoaromatic dications.[67,70] Prinzbach et al. proposed that the persistent species formed upon two-electron oxidation (cyclic voltametry) of **48** or **49** is the homoaromatic 4c/2e dication **50**.[69] The central 4c/2e moiety has a rectangular geometry with calculated (B3LYP/6-31G*) bond/interatomic distances ranging from *a* = 2.357 to 2.419 Å and *b* = 1.424 to 1.432 Å for **44** and **47**.[70] While these distances are not ideal, they certainly do not preclude homoaromaticity.



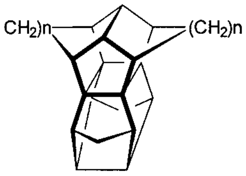
42



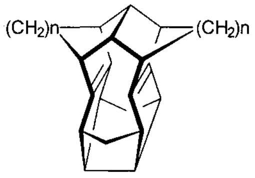
43



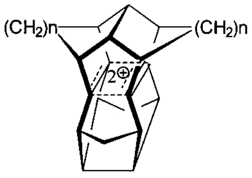
44



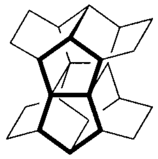
45



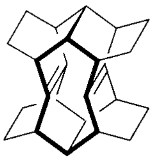
46



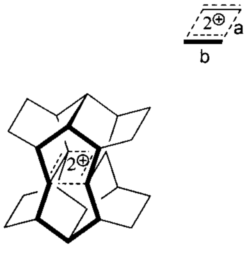
47



48



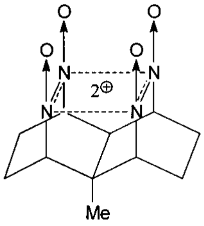
49



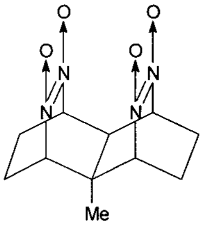
50

5. Syn-Periplanar Bisdiazene–Tetroxide Dication

Another 4c/2e dication **51**, related to the pagodane dications, was proposed to be formed during electrochemical oxidation of the tetroxide **52**.[71] B3LYP/6-31G* calculations support the homoaromatic delocalization in **51** and indicate an average homoconjucative N−N distance of 2.55 Å, which is similar to that found in the pagodane dications.



51

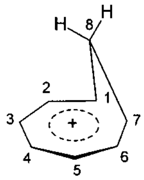


52

B. Six-Electron Systems

1. Monohomotropylium Cation

The homotropylium cation (**53**) and its numerous derivatives are the most extensively studied and well-established homoaromatics.[6−15] Experiment and theory clearly demonstrate that **53** and many of its derivatives satisfy the criteria for homoaromaticity (Section III.A). **53** is the archetype no-bond homoaromatic species. It adopts a boat-shaped conformation with the "seven-membered" ring (C1 to C7) not greatly deviating from planarity. There is no bond critical point linking C1−C7, but there is a significant build up of electron density between these carbon atoms which mediates effective (through-space) delocalization. The ellipticities and bond orders of the "seven-membered" ring are close to those of benzene and the bond lengths are equalized (average 1.400 ± 0.004 Å). The positive charge is evenly distributed over the "seven-membered" ring as evidenced by calculation and the very similar ^{13}C NMR chemical shifts for C1−C7. In estimating the resonance energy of **53**, the usual problem of choice/availability of a suitable reference compound is encountered. All estimates indicate that the homotropylium cation is more stable than the reference compound used and, therefore, support its homoaromaticity. The calculated magnetic susceptibility of **53** varies as the C1−C7 distance is scanned (optimizing all other geometric parameters), reaching a maximum at the equilibrium geometry (C1−C7 ~2.0 Å) at which point there is also a large magnetic susceptibility exaltation. In the ^{1}H NMR spectrum of **53**, both C8 protons are shielded with the 8-*endo* proton resonating at higher field than tetramethylsilane. The NMR chemical shift difference between the 8-*endo* and 8-*exo* protons is large (5.86 ppm).



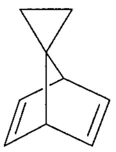
53

Reindl et al. developed a new force field method, based on MMP2, to allow calculations on delocalized carbocations.[72] They demonstrated the efficacy of this method with calculations on benzylic and cyclically delocalized cations including the homotropylium cation. The results obtained for **53** were in agreement with those obtained using ab initio (MP2 and MP4) and DFT (B3LYP) methods. They concluded that the homoconjugative stabilization in **53** is large (−13.4 kcal mol^{-1}) and comparable to the aromatic stabilization energies of the tropylium cation and benzene (−15.7 and −16.4 kcal mol^{-1}, respectively). They also reported a NICS value for the homotropylium cation of −11.1 ppm. Their results, once more, strongly support the homoaromaticity of **53**.

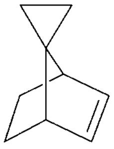
C. Miscellaneous Cationic Systems

1. Homobicycloaromaticity

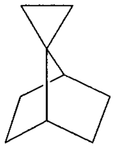
X-ray and calculated (HF/6-31G* and MP2/6-31G*) structures for the series of spirocyclic norbornyl compounds **54**−**56** revealed significant cyclopropyl homoconjugation in **54** and **55** as well as hyperconjugation in all three compounds.[73] Boese et al. interpreted the experimental electron densities and calculated dipole moments as indicating an important contribution from the homobicycloaromatic resonance form **57** in determining the electronic and structural properties of **54**.



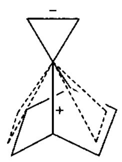
54



55



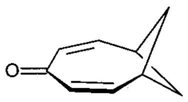
56



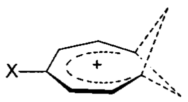
57

2. Potential Homoaromatics

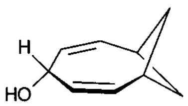
Paquette et al. prepared the dihomotropone **58** and concluded from its IR, UV, and NMR spectra that there was no evidence for the homoaromatic charge-separated species **59**.[74] Again, upon protonation, the dihomotropylium cation **60** was not detected. Acid treatment of the alcohol **61** from reduction of **58** gave facile Wagner−Meerwein rearrangement and no indication of the desired dihomotropylium cation **62**.



58

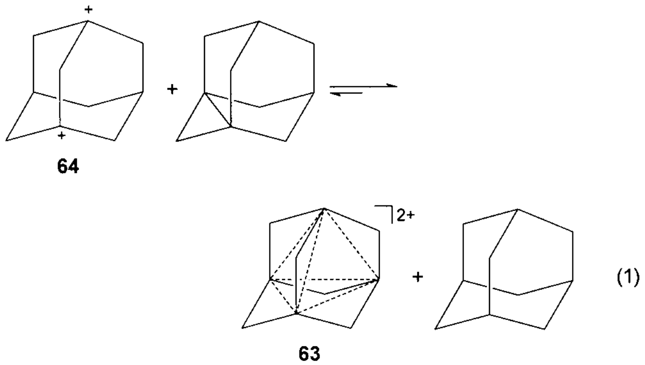


59 X = O$^-$
60 X = OH
62 X = H

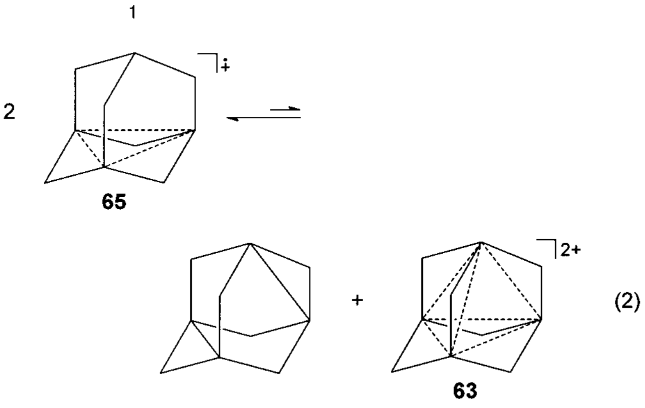


61

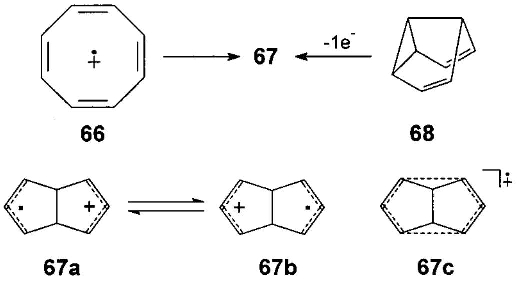
Schleyer et al. prepared, and fully characterized as three-dimensionally homoaromatic (tetratrishomoaromatic), the 4c/2e dehydroadamantyl dication **63**.[75] They also determined, from the isodesmic reaction 1, that **63** is stabilized by 47 kcal mol^{-1} (MINDO/3) relative to **64**. Calculated and observed magnetic



properties, ^{13}C NMR chemical shifts,[75] magnetic susceptibility exaltation[23,33] and NICS[33] confirm the homoaromaticity of **63**. Arnold and Chan reinvestigated the isodesmic reaction 1 and other features of this system using ab initio and DFT methods.[76] These workers obtained a relative stabilization for **63** of 36.8 kcal mol^{-1} (HF/6-31G*) and a homoconjugative gap (2.074 Å B3PW91/6-31G*) not far removed from the ideal for no-bond homoaromaticity. In addition, they found using the isodesmic reaction 2 that the radical cation **65** is 164.4 kcal mol^{-1} (HF/6-31G*) more stable than **63**. Interestingly, the spin density is located predominantly on C1 while the charge is delocalized facilitating the formation of the trishomocyclopropenyl cation moiety shown in **65**.

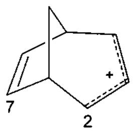


Photorearrangement of the radical cation **66**, formed on oxidation of cyclooctatetraene, produces the bicyclo[3.3.0]octa-2,6-diene-4,8-diyl radical cation **67**.[77] **67** is also obtained directly upon oxidation of semibullvalene **68**.[78] The nature of this cation, localized **67a** $\rightleftharpoons$ **67b** or bishomoaromatic delocalized **67c**, has been the subject of some debate. Williams et al. proposed, based on cryogenic ESR studies, that **67** has a delocalized ground state.[78] However, in a computational and experimental (CIDNP) reinvestigation of **67**, Roth and Lakkaraju suggested that from the available data it was not possible to distinguish between rapidly equilibrating localized radical cations (**67a** $\rightleftharpoons$ **67b**) and the delocalized **67c**.[79] Several more recent papers have appeared on this matter, and each concludes that the delocalized homoaromatic **67c** is the ground state.[80] A recent review has appeared on conjugated and homoconjugated radical cations.[81]



3. Potential Homoantiaromatics

Jiao and Schleyer calculated a large positive magnetic susceptibility for the bicyclo[3.2.1]octadienyl cation **69** indicative of homoantiaromaticity.[82] Again, consistent with homoantiaromaticity, they found a large C2−C7 internuclear separation (2.452 Å at RMP2/6-31G*).



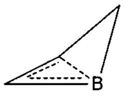
69

V. Neutral Homoaromaticity

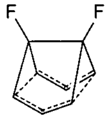
The area of neutral homoaromaticity remains controversial with few well-accepted examples of neutral homoaromatic molecules.[12,64] Indeed, several investigators concluded that the existence of neutral homoaromatic compounds was very unlikely or even impossible.[12] In an early theoretical investigation on the trimerization of acetylene to give benzene, Houk and Paquette et al. concluded that homoconjugative interactions in neutral systems were normally destabilizing.[83] However, a recent reinvestigation of the same system at a much higher level of theory identified a weak aromatic stabilization of the planar D_{3h} transition state.[84] Jiao and Schleyer demonstrated that the D_{3h} transition state is aromatic from its large magnetic susceptibility exaltation (slightly greater than benzene's) and its NICS values.[85] NICS$_{\text{(total)}}$ is found to be a maximum, along the intrinsic reaction coordinate, at the transition state. Similarly, Morao and Cossío classify this transition state as in-plane aromatic from a consideration of the variation of its NICS values and diamagnetic shielding constants with distance (perpendicular to the transition structure plane).[86]

Childs, Cremer, and Elia maintain that there are several examples of neutral homoaromatics.[14] They suggest that 1,2-dihydroborete (**70**) and some of its derivatives are neutral homoaromatics. This electron-deficient system is isoelectronic with the monohomocyclopropenium cation (**17**). It has been investigated by both theory and experiment, and its classification as homoaromatic is justified.[12,14,87] In addition to **70**, Childs, Cremer, and Elia propose that certain semibullvalenes, barbaralanes, bridged annulenes, cycloheptatrienes, and norcaradienes are homoaromatic.[14] They draw particular attention to the semibullvalenes **71**−**75** and consider that **74** and **75** are the best candidates for experimental work.

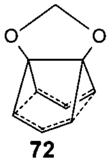
Despite this reviewer's obvious bias toward supporting the homoaromaticity of **74**,[50,88] he does not believe that any of these semibullvalenes, which only exist in theory and have yet to be studied experimentally, should be considered homoaromatic. The calculations on **71**−**75** are of high quality and are extremely reliable. However, in the absence of experimental confirmation of homoaromaticity, these fascinating semibullvalenes must remain only candidates for this elusive classification. Childs, Cremer, and Elia did not designate any specific barbaralane as homoaromatic,[14] although Quast has come remarkably close to achieving this goal (vide infra).[89] As mentioned previously, the bridged annulenes belong to a different class of homoaromatics in which the cyclic delocalization is not interrupted by insertion of a saturated unit. Instead, the system is perturbed by transannular homoconjugation. This type of homoaromaticity is well-founded and well-established in several bridged annulenes.[12] The homoaromaticity of the cycloheptatrienes, which remains controversial, is discussed below.



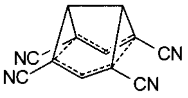
70



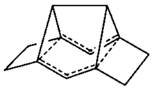
71



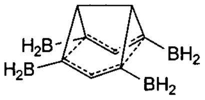
72



73



74



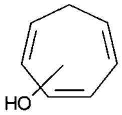
75

A. Six-Electron Systems

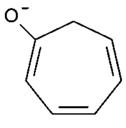
1. Cycloheptatrienes (and Norcaradienes)

The cycloheptatrienes and norcaradienes, especially the parent hydrocarbons **13** and **14**, are very thoroughly investigated species.[40,41] Childs, Cremer, and Elia provide an excellent review of the status (regarding homoaromaticity) of these compounds up to 1995.[14] Early studies conflicted in their conclusions, while the majority of recent investigations support minimal homoaromatic stabilization in **13**.[12,14,90−92] Roth et al. reparametrized the MM2 force field to include contributions from regular (acyclic polyenes) and cyclopropyl conjugation.[93] This new MM2ERW force field yields accurate heats of formation for polyenes and cyclopropyl polyenes. However, the MM2ERW heats of formation do not take any account of cyclic delocalization; thus, the difference in energy between the experimental and MM2ERW heats of formation of (homo)aromatics affords a resonance energy. Using this method, Roth et al. obtained a homoaromatic resonance energy for **13** of 4.1 kcal mol^{-1} (and similarly estimated a resonance energy of 5.8 kcal mol^{-1} for norcaradiene **14** using an ab initio heat of formation for comparison with the MM2ERW value).[90] Rogers, Liebman, and Podosenin arrived at similar stabilization energies for **13** from consideration of adjusted heats of formation and isodesmic and thermoneutral heats of formation.[91]

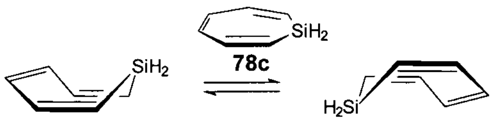
The most recent experimental and theoretical studies *do not* support the existence of any significant homoaromaticity in cycloheptatriene (**13**) and its derivatives.[94,95] The isomeric cycloheptatrienols **76** react very differently toward electrophiles, and the enolate **77**, derived from one of these trienols, has a much lower activation barrier to coupling with powerful electrophiles (*p*-substituted benzenediazonium ions) than does the phenoxide ion. Lew and Capon interpreted these results as indicating the lack of any significant homoaromatic stabilization in cycloheptatrienes.[94] Nishinaga, Izukawa, and Komatsu optimized the boat and planar (transition state for ring inversion) forms of cycloheptatriene (**13**) and silepin (**78**) using the B3LYP/6-31G* method[96] and determined the NICS values for each of these species at HF/6-31+G*.[95] Silepin showed no evidence for an induced ring current and is not homoaromatic (boat, **78a,b**) nor aromatic (planar, **78c**, potentially using the silicon d orbitals to complete the aromatic delocalization). However, Nishinaga, Izukawa, and Komatsu considered the NICS of −4.2 ppm in the boat cycloheptatriene to indicate "a weakly aromatic species". These authors do, however, point out that their NICS value for boat-**13** is very similar to that for cyclopentadiene (−3.2 ppm),[33] which Schleyer and Tidwell et al. classify as "At best, the aromaticity of cyclopentadiene is borderline"[97] and Nyulászi and Schleyer even more negatively as "Cyclopentadiene exhibits a somewhat enhanced diamagnetic susceptibility anisotropy, but there is no convincing energetic, geometric, or NICS (nucleus-independent chemical shift) evidence for aromaticity".[36]



76



77



78c

78a **78b**

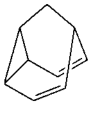
Obviously, whether the cycloheptatrienes should be classified as homoaromatic or not is still being debated. In this reviewer's opinion, cycloheptatriene (**13**) enjoys very weak homoaromatic stabilization which can be easily overwhelmed by other factors.

2. Semibullvalenes and Barbaralanes

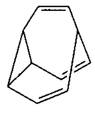
In his efforts to lower the activation energy for the Cope rearrangement, Doering designed the first fluxional molecule homotropilidine (**79**).[98] Barbaralane (**80**), bullvalene (**81**), and semibullvalene (**68**) are each related to **79** as homotropilidines locked in the appropriate "Cope conformation" (**79b**). As a conse-

79a **79b** **79c**

quence of the significant cyclopropane-induced ring strain and the locked conformation, the activation barriers to the degenerate Cope rearrangement in **68**, **80**, and **81** are reduced even further than in **79**.[98]



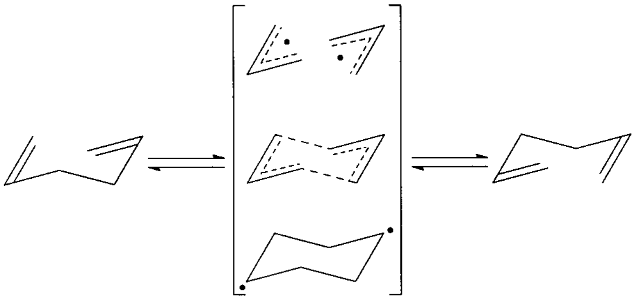
80



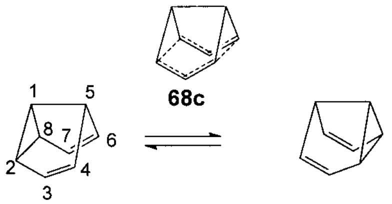
81

There is substantial current interest in the mechanism of the Cope rearrangement with many recent experimental and high-order theoretical studies of this reaction.[99] There are three mechanistic extremes (Scheme 1) for the Cope rearrangement involving the following intermediates/transition states: (1) a pair of interacting allyl radicals, (2) an aromatic species, or (3) a 1,4-cyclohexanediyl diradical. All recent investigations are in agreement that the Cope rearrangement of 1,5-hexadiene is concerted and proceeds via an aromatic chair transition state. Substituents have a profound effect on the mechanism, and as concluded much earlier by Gajewski,[107] there is a mechanistic continuum between the radical and aromatic pathways with the exact mechanism depending on the nature and position of the substituents.[99]

Scheme 1



Zimmerman et al.[108] were the first to prepare and study semibullvalene (**68**), which undergoes the degenerate Cope rearrangement **68a** $\rightleftharpoons$ **68b** with a very small activation barrier ($\Delta G^{\ddagger} \sim 6$ kcal mol^{-1}).[109,110]

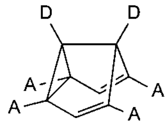


68c

68a

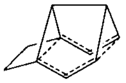
68b

The low-lying transition state for the Cope rearrangement of semibullvalene is the bishomoaromatic C_{2v} species **68c**.[50,111] The semibullvalenes have long been recognized as the system most closely approaching the goal of neutral homoaromaticity.[49,112] Dewar and Hoffmann independently predicted that the activation barrier to the Cope rearrangement of semibullvalene could be reduced, and perhaps even eliminated, by introducing electron-withdrawing substituents (A) at the 2, 4, 6, and 8 positions and electron-donating groups (D) at the 1 and 5 positions (**82**).[113,114] These substitution patterns result in a stabilization of the transition state. A recent review on studies directed toward achieving homoaromatic semibullvalenes and a detailed study of the effects of substituents on the Cope equilibrium in semibullvalenes and barbaralanes have appeared.[49,115] Numerous Dewar–Hoffmann semibullvalenes and barbaralanes have been prepared, and even though their Cope barriers are reduced compared with **68** and **80**, respectively, none have a homoaromatic ground state.[12,14,49,115,116] Recent ab initio calculations reaffirm the previously predicted[117,118] homoaromaticity of the substituted semibullvalenes **71** and **73** and also indicate that **75** will be homoaromatic.[14]

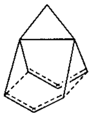


82

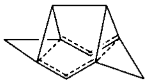
An alternative approach to realizing a ground-state homoaromatic semibullvalene is through strain-induced destabilization of the localized forms **68a** and **68b** effected through small ring annelation.[12,49,116] Earlier predictions of homoaromatic ground states for the annelated semibullvalenes **74**,[88] **83**,[119] and **84**[117] based on semiempirical calculations were confirmed by recent high-order ab initio (HF, MP2, CASSCF, CASPT2N) and DFT methods.[50] In the same study, in which structural, energetic, and magnetic criteria were used in assessing the homoaromaticity of each candidate, the semibullvalene **85** was also predicted to be strongly homoaromatic.[50] The monoannelated **86**, which is calculated to display only partial bond equalization in the "homoaromatic" ring and relatively small diamagnetic susceptibility exaltation and NICS, is considered moderately homoaromatic.[50] Childs, Cremer, and Elia report in their review that the annelated semibullvalenes **72** and **74** are homoaromatic.[14]



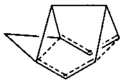
83



84

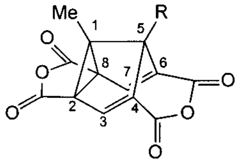


85

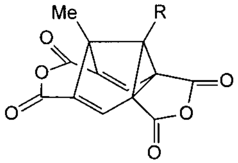


86

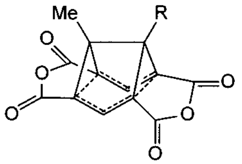
Semiempirical ab initio and DFT investigations on the dianhydride **87** all indicate that it should possess a homoaromatic ground state.[116,120] Using correlated ab initio (MP2/6-31G*) and DFT (B3LYP/6-31G*) methods, only the C_{2v} homoaromatic **87c** ground-state species could be found. The C_s-localized **87a,b** are not at stationary points on the correlated potential energy surface. Initial experimental results supported the homoaromaticity of **87**. X-ray structures at 293, 243, and 163 K showed C_2 symmetry, and the solution- and solid-phase ^{13}C NMR spectra also indicated C_2 symmetry and were temperature invariant down to 190 and 223 K, respectively.[121] However, closer examination of the X-ray data suggested dynamic disorder resulting from Cope rearrangement. X-ray analysis at lower temperatures (148–40 K) revealed that symmetry was broken (C2–C8 = 1.679(4) Å and C4–C6 = 2.197(4) Å at 123 K) and the structural parameters varied with temperature.[120–122] Quast et al. showed that the variation of semibullvalene structure with temperature results from the skewed equilibrium between nondegenerate (as a consequence of the crystal environment) tautomers, e.g., **87a** ⇌ **87b**.[123–125] Below 40 K there is no evidence of disorder in the X-ray structures of **87**. These structures must correspond with that of a single localized tautomer **87a** or **87b**.[122] The solution-phase nature (delocalized homoaromatic or localized) of **87** was probed using a modification of the Saunders' isotopic perturbation method[126] pioneered by Gompper et al.[127] In Gompper's procedure, the degeneracy of equilibrating semibullvalene tautomers is lifted by substitution at the 1 and 5 positions with two different alkyl groups. The time- and population-averaged chemical shifts in the NMR spectra will vary with temperature for equilibrating localized ground states but be temperature invariant for a delocalized homoaromatic species. The ^{13}C NMR spectra of **88** showed a clear equilibrium-driven variation of chemical shift with temperature, indicating that **88** and, by analogy, **87** are not homoaromatic in the solution phase.[120,121] A similar conclusion was reached regarding the bisimides **89** and **90**.[116]



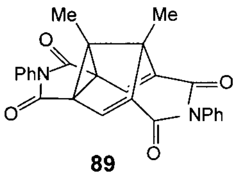
87a R = Me
88a R = Et



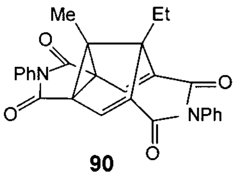
87b R = Me
88b R = Et



87c R = Me
88c R = Et



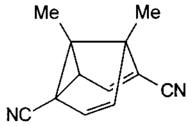
89



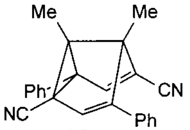
90

The results for dianhydride **87** present an interesting dichotomy. From experiments in the condensed phases, **87** is unequivocally shown not to be homoaromatic. However, calculations of a quality generally considered sufficient for such systems (vide supra) yield a single minimum surface corresponding with a homoaromatic ground state. It is possible that matrix effects may account for this discrepancy between experiment (condensed phases) and calculation (isolated molecule gas phase).[116,128]

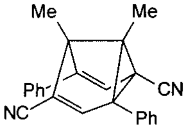
The most fluxional semibullvalenes and barbaralanes tend to be thermochromic.[49,89,120,129,130] Quast attributes this thermochromism to a flat potential energy surface with an exceedingly low barrier to the Cope rearrangement.[89,129,130] He suggests that the colored, high-temperature species are in a vibrationally excited level above the Cope barrier and are homoaromatic.[89,130] Support for Quast's model comes from calculations by Zilberg et al. based on the valence-bond-derived "twin-state" concept.[131] Quast and Seefelder recorded the variable-temperature UV–vis spectra of four of their semibullvalenes and barbaralanes (**91**–**94**) in a range of solvents of widely varying dipolarity.[89,130] They concluded from the results of this study that the colored homoaromatic species enjoyed greater relative stabilization in the more dipolar solvents. In addition, in the most highly dipolar solvents, e.g., *N*,*N*′-dimethylpropylene urea (DMPU), the homoaromatic **92c** and **93c** were found, in contrast to the results in less dipolar solvents, to be *more* stable than the corresponding localized forms **92a,b** and **93a,b**. Similarly, Quast et al. proposed, from a NMR study extending the Saunders' isotopic perturbation method, that **95c**, a deuterated analogue of **93**, is 0.38–0.53 kcal mol^{-1} more stable than the localized forms in DMPU.[132] X-ray crystallography revealed that there is appreciable steric strain in **93** and **94** due to the proximity of the substituents on the "cyclopropane" ring.[133] Quast et al. suggest that these steric interactions are alleviated in the corresponding Cope transition states and that this contributes to the lowering of the activation barrier in such barbaralanes (and semibullvalenes).



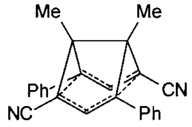
91



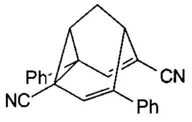
92a



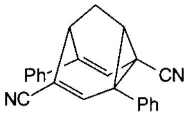
92b



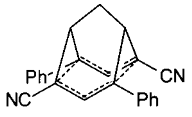
92c



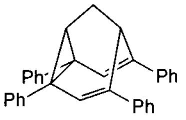
93a



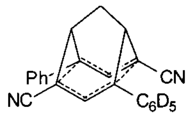
93b



93c



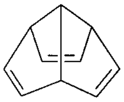
94



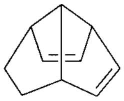
95c

3. Potential Trishomobenzenes

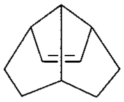
Triquinacene (**96**) has an interesting history. It was first prepared in 1964 by Woodward et al., who concluded that there was no evidence for delocalization of the π-system.[134] Since that time there have been many other studies on triquinacene, almost all of which conclude that there is no significant trishomoaromatic stabilization of **96**.[12] Two thermochemical studies comparing the heats of hydrogenation of **96** and di- and tetrahydrotriquinacenes (**97** and **98**) resulted in a small resonance energy of about 4.5 kcal mol^{-1} for **96** and the claim of homoaromaticity.[135,136] Several groups subsequently reinvestigated this system, and each determined that triquinacene was not homoaromatic.[12] Most recently, a definitive experimental and theoretical study firmly established that triquinacene is not homoaromatic.[137] In this investigation Rüchardt, de Meijere, and Schleyer et al. determined calorimetrically the standard heat of formation of **96** to be 4.0 kcal mol^{-1} *higher* than the value, derived from its heat of hydrogenation and the heat of formation of hexahydrotriquinacene (**99**), used in the earlier thermochemical studies. This 4 kcal mol^{-1} difference essentially eliminates the previously determined resonance energy of **96** and clearly demonstrates its lack of homoaromaticity. In addition to these new experimental results, high-level calculations provided structural, magnetic, and energetic evidence refuting the homoaromaticity of **96**.[137]



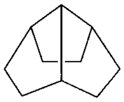
96



97

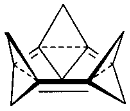


98

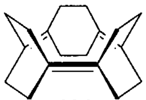


99

Schleyer and Jiao predicted that the novel compound **100** is an "in-plane" homobezene in which the π-overlap is in the plane of the "six-membered" ring rather than orthogonal to it, as in benzene.[23] The calculated geometric, energetic, and magnetic properties of **100** lend strong support to its trishomoaromaticity. The related triene **101**, prepared and studied much earlier by McMurry et al., is not homoaromatic.[138] It was shown, by photoelectron spectroscopy, to have little through-space interaction of the double bonds.



100

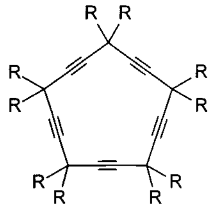


101

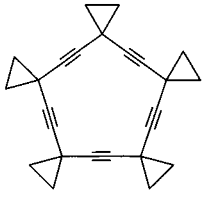
B. 10-Electron Systems

1. [5]Pericyclyne

Two different modes of cyclic homoconjugation, in-plane and out-of-plane, can be envisaged for the pericyclynes. If either or both modes operate, then the pericyclynes will be homoaromatic or homoantiaromatic depending on the order of the pericyclyne. The proposed homoaromaticity of decamethyl [5]-pericyclyne (**102**), involving 10 in-plane and/or 10 out-of-plane π-electrons, is closely related to that of triquinacene. Several studies indicated that there is some homoconjucative interaction in the pericyclynes but that these interactions do not lead to homoaromaticity.[12] However, in a thermochemical investigation of **102**, analogous to that in triquinacene, Scott and Rogers et al. estimated a small aromatic stabilization energy of about 6 kcal mol^{-1} for **102** and from this they considered **102** to be homoaromatic.[139] Recent studies of the pericyclynes and other macrocyclic oligoacetylenes are summarized in two review articles.[140,141] High-level ab initio and DFT calculations clearly showed, by means of magnetic, geometric, and energetic criteria, that the pericyclynes **103** and **104** are not homoaromatic and it is very unlikely that any of the pericyclynes will prove to be so.[142]



102 R = Me
103 R = H



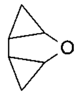
104

C. Miscellaneous Neutral Systems

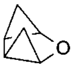
1. σ-Homobenzenes and σ-Homofurans

The σ-homobenzenes have been the subject of extensive investigation. The results of these investigations, to 1994, are summarized in the review by Williams and Kurtz.[12] Several other *formal* bond homoaromatics have been prepared and/or studied since 1994. No claim is made for aromatic stabilization of their ground states nor that these compounds should be categorized as homoaromatic. Klärner et al. extended their earlier mechanistic work on the σ-homofurans **105**, **106**, and **107**[143] to the thermolysis of the bridged bishomofuran **108**.[144]

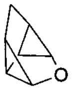
105



106

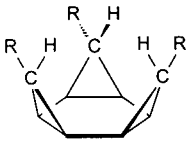


107

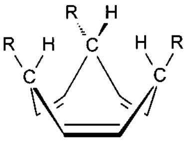


108

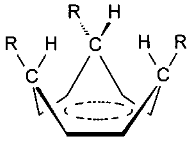
Prinzbach et al. continued their investigations of a variety of σ-trishomobenzenes (**109**, e.g., R = CO_2R, CN, C≡C−TIPS), their conversions to the corresponding π-trishomobenzenes **110**, and the exploration of the potential for these compounds in synthesis.[145,146] In the case of these all-cis compounds (**109**), a concerted pathway is generally followed to the corresponding π-trishomobenzenes through the trishomoaromatic-stabilized transition state **111**. In the ultimate bond homobenzenes, Vollhardt et al. prepared the novel compounds **112**, **113**, and **114**.[147]



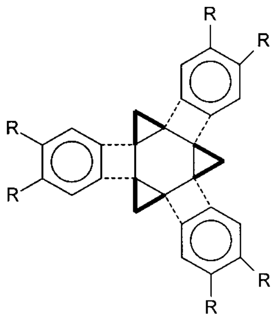
109



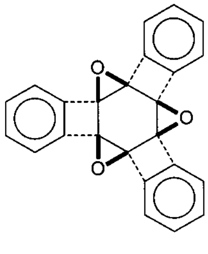
110



111



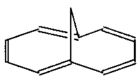
112 R = H
113 R = $SiMe_3$

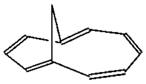


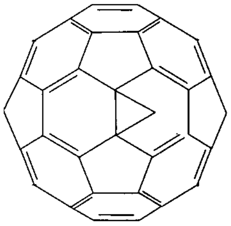
114

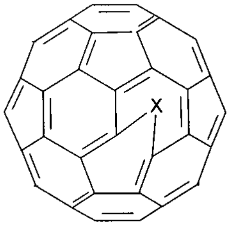
2. Homofullerenes (Fulleroids)

Insertion reactions into C_{60} fullerenes can lead to ring-closed products formed at a 6−6 fullerene ring junction (termed methanofullerenes), e.g., **115**, and ring-opened products formed at a 6−5 ring junction (termed homofullerenes or fulleroids), e.g., **116**−**118**. As already discussed (vide supra), certain bridged annulenes are homoaromatic as a result of significant transannular homoconjugation. A similar transannular homoconjugation is possible in the homofullerenes.[148] Haddon and Raghavachari compared the results of the π-orbital axis vector (POAV) analysis of the homofullerenes **116**−**118** with those for the bridged [10]annulenes **15** and **16** and concluded that there is appreciable homoconjugation in the homofullerenes and that perhaps, like **15** and **16**, they are homoaromatic.[149] Homofullerenes are also possible from insertion at the 6−5 ring junction of C_{70} fullerenes. Haddon, Meier, and Brock et al. prepared such an adduct (**119**) by dichlorocarbene addition to C_{70} and determined its X-ray structure.[150] Using the X-ray geometry, they calculated reduced resonance integrals for the transanular homoconjugative interaction in **119**, **15**, and **16**. They concluded that the homoconjugative interaction in **119** is greater than that in **15** and **16**, supporting a homoaromatic designation for **119**. The term homofullerene was originally rejected by Wudl in favor of "fulleroid" on the grounds of the unwieldy nature of the homofullerene nomenclature for polybridged fullerenes.[151] However, Haddon et al. suggest the adoption of the more descriptive homofullerene terminology.[149,150]

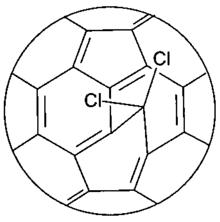

15


16


115



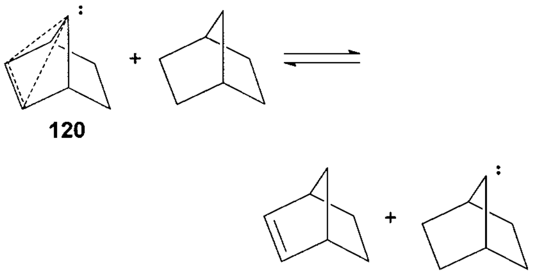
116 X =CH_2
117 X = O
118 X = NH



119

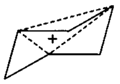
3. Homoaromatic Carbenes

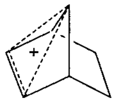
Freeman used DFT methods (B3LYP/6-31G*) to study the carbene analogues **120**−**122**[152] of the isoelectronic homoaromatic cyclopropenium cations **1**, **5** (vide supra), and **124**.[12] Isodesmic reactions (e.g., reaction 3 for **120**) revealed appreciable homoaromatic stabilization for the singlet carbenes **120** and **121** (15.56 and 14.06 kcal mol^{-1}) and only moderate stabilization for the corresponding singlet **122** (3.27 kcal mol^{-1}). The stabilization of **120** and **121** is comparable to that of **5** (20.91 kcal mol^{-1}) calculated using the same isodesmic scheme (eq 3) as for **120**, substituting the cationic species for the carbene intermediate.

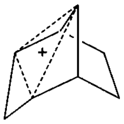


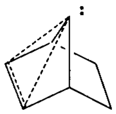
(3)

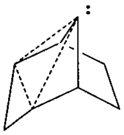
Comparison of the geometries for singlet and triplet **120** and **121** showed large differences indicative of homoaromaticity in the singlet. The calculated geometries of singlet and triplet **122** are very similar. Freeman also calculated the singlet−triplet energy gaps for **120**−**122**. He found that the **120** and **121** singlets demonstrated substantially enhanced relative stabilization when compared with the corresponding singlet−triplet gap in the carbenacyclohexane reference, while the gap in **122** shows only moderate enhancement. In a very recent extension of this work, Freeman and Pugh refined the calculated energies for the above species using the B3LYP/6-311+G(3df,2p)//B3LYP/6-31G* method and also investigated the bicyclic carbene **123**.[153] They concluded from the consideration of energetic, geometric, and magnetic properties that the singlet carbenes **120** and **121** are homoaromatic while **122** is not and **123**, analogous to the cation **69**, is perhaps homoantiaromatic.

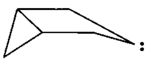

1

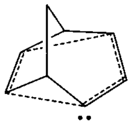

5


124


120


121

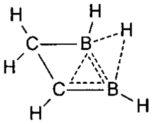

122

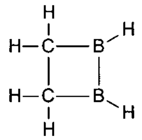

123

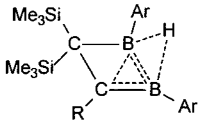
4. Nonclassical 1,2-Diboretanes and 1,2-Diborolanes

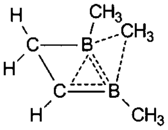
Berndt et al. demonstrated that 1,2-diboretanes with electron-deficient boron atoms prefer the nonclassical **125a** to the classical **125b** structure.[154] The nonclassical structure is characterized by two 3c/2e interactions, one for the hydrogen-bridged B−H−B and one for the homoaromatic B−C−B "three-membered ring" (isoelectronic with the homocyclopropenium cation). Berndt et al. prepared three derivatives (**126**) of 1,2-diboretane. They obtained an

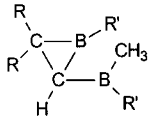
X-ray structure on **126a** and compared this and the experimental chemical shifts of **126a**−**c** with the calculated structural and NMR parameters obtained for **125a** and **125b**. The fit of the experimental data with the corresponding calculated quantities for **125a** (and *not* **125b**) is very convincing. The methyl-bridged compound **127** was predicted to be formed from **128a**, although this cyclization was not observed experimentally in the highly substituted derivative **128b**. The absence of cyclization was attributed to extreme steric hindrance.

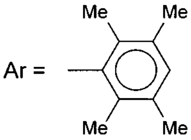

125a


125b

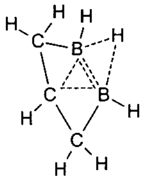

126a R = $\mathrm{SiEt_3}$
126b R = $\mathrm{SnMe_2H}$
126c R = H

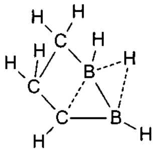

127

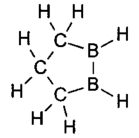

128a R = H, R' = $\mathrm{CH_3}$
128b R = $\mathrm{SiMe_3}$, R' = Ar



Berndt et al. also calculated (MP2/6-31G*) the relative stabilizations of the classical and nonclassical forms of 1,2-diborolane **129**.[154] They found that the hydrogen- bridged bishomoaromatic **129a** is 18.9 kcal $\mathrm{mol^{-1}}$ lower in energy than the classical **129c** and that **129b** is 2.5 kcal $\mathrm{mol^{-1}}$ more stable than **129c**.

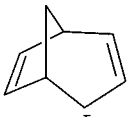

129a

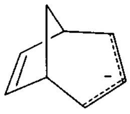

129b

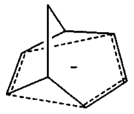

129c

VI. Anionic Homoaromaticity

Williams and Kurtz, in their 1994 review, found no evidence to support the unequivocal assignment of homoaromaticity to an anionic system.[12] Childs, Cremer, and Elia considered that there may be examples of anionic homoaromatics.[14] They favored the bicyclo[3.2.1]octadienyl anion **130** as the most likely contender for homoaromaticity (**130c**). Indeed, **130** has been the best studied of the potential homoaromatic anions, and interest in and controversy over this system continues today (vide infra).[12,14] Other intriguing molecules, rich in heteroatoms, have recently and convincingly been advanced as candidates for anionic homoaromaticity.


130a

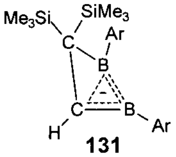

130b

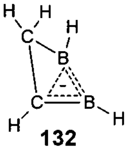

130c

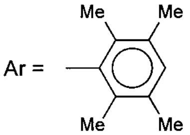
A. Two-Electron Systems

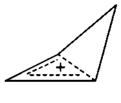
1. Monoanions of 1,2-Diboretanes

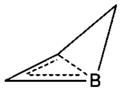
Reaction of 1,2-diboretane **126c** with lithium in diethyl ether yields the homoaromatic 1,2-diboretanide **131**, which is isoelectronic with the monohomocyclopropenium cation (**17**).[155] The X-ray structure of **131** is very similar to the structure of **126c** and also that calculated (MP2/6-31G*) for **132**. Compared with the structure of **126c**, the bridging hydrogen is replaced by the coordinated lithium ion, $\mathrm{Li^+OEt_2}$, in **131**. However, contrary to **126c** in which the bridging hydrogen is part of a 3c/2e unit, in **131** the lithium ion is only electrostatically bound. The calculated (**132** and **132**−$\mathrm{Li^+}$) and observed (**131**) NMR chemical shifts are in reassuring agreement. Berndt et al. determined the barrier to inversion for **131** (19.5 kcal $\mathrm{mol^{-1}}$) and compared this value with those calculated for **132** and **132**−$\mathrm{Li^+}$ (17.5 and 20.4 kcal $\mathrm{mol^{-1}}$, respectively) and a range of other homocyclopropenium analogues: **17a** $\rightleftharpoons$ **17b** (11.5 kcal $\mathrm{mol^{-1}}$), **70** (5.1 kcal $\mathrm{mol^{-1}}$), **133** (7.2 kcal $\mathrm{mol^{-1}}$), **134** (31.0 kcal $\mathrm{mol^{-1}}$), and **135** (15.5 kcal $\mathrm{mol^{-1}}$). The barrier to inversion, which is considered to be a measure of the degree of homoaromaticity,[12,14] of **131** (**132**) is noticeably higher than all of the other compounds considered except for **134**. By all experimental and calculated criteria, compounds **131** (**132**) are homoaromatic.

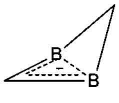

131

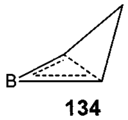

132

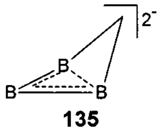



17


70


133

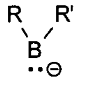

134

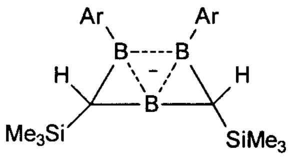

135

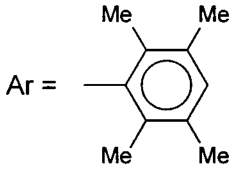
2. Mono- and Dianions of Triboracycloalkanes

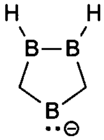
Borenate anions **136** are the boron analogues of carbenes. These species were only known in the gas phase until Berndt et al. prepared the borenate ion **137** which they characterized, as the $\mathrm{Li^+(THF)_3{\cdot}Et_2O}$

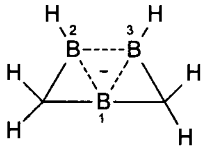
salt, by X-ray crystallography.[156] Like the pericyclynes (vide supra), **137** and **138** are capable of in-plane and out-of-plane homoconjugation. The electron pair, formally in a boron (B1) p-orbital, may interact with the vacant p-orbitals of the other two borons (B2 and B3) resulting in a 3c/2e π-system, while the vacant hybrid orbital on B1 can interact with the B2−B3 σ-bond to give a 3c/2e σ-system. If these interactions occur, then the molecules are 2-fold bishomoaromatic and termed by Schleyer et al. "doubly aromatic".[157] Geometric, energetic, and magnetic properties calculated for the unsubstituted parent borenate ion **138** strongly support a bishomoaromatic designation (**138b**).[156] The observed structure and NMR chemical shifts of **137** are in good agreement with those calculated for **138b** and confirm its "double" bishomoaromaticity. Carbene **139** is similarly predicted to favor the bishomoaromatic **139b** over the classical **139a**. No experimental evidence unambiguously revealing the nature of the ground state (homoaromatic or not) of the known derivatives **139c**−**e** is available.[156]

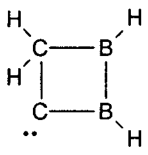

136

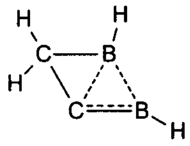

137

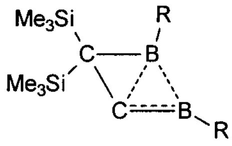


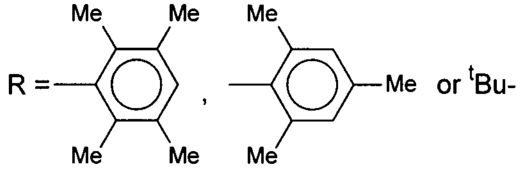

138a


138b


139a

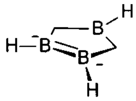

139b

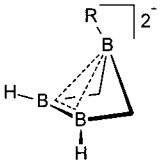

139c-e

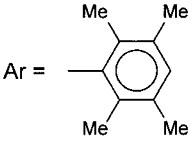


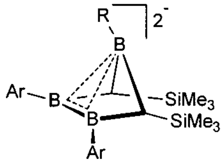
The parent 1,2,4-triboracyclopentane dianion **140** may adopt a classical conformation **140a** or a bishomoaromatic geometry **140b** analogous to the isoelectronic (experimentally unknown) prototype bishomocyclopropenium cation **23**. Berndt et al. prepared the derivatives **141a**−**d** and obtained X-ray structures of the corresponding salts of **141a**−**c**.[158] The calculated and experimental structures of **140c**−**e** and **141a**−**c**, respectively, are in accord as are the calculated and measured NMR chemical shifts for **140c**−**f** and **141a**−**d**. The compounds **140b**−**f** and **141a**−**c** have puckered geometries with all internuclear distances fully supporting bishomoaromaticity. The bishomoaromatic **140b** is calculated to be 39 kcal mol^{-1} more stable than the classical **140a**, which is significantly greater than the corresponding stabilization of **23** over the planar classical **24**.


23

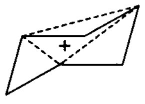

140a


140b R = H
140c R = Ph
140d R = OH
140e R = NH$_2$
140f R = Me

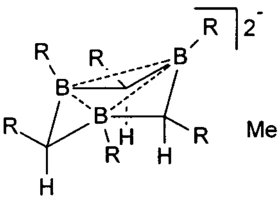



141a R = Ph
141b R = OEt
141c R = NEt$_2$
141d R = Me

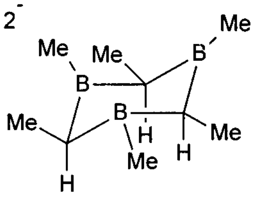
The 1,3,5-triboracyclohexane dianions are closely related to the 1,2,4-triboracyclopentane dianions. The former dianions can exist as the trishomoaromatic species **142a** related to the trishomocyclopropenium cation **1**. Schleyer and Siebert found that two-electron lithium reduction of **143** in THF gave the trishomoaromatic **142b**, which crystallized, after tetrahydropyran (THP) or crown ether treatment, to give tetrameric aggregates in each case.[159] The aggregate formed after THP treatment gave a disordered X-ray structure of poor quality. However, the crystals from the crown ether route resulted in a good X-ray structure indicative of homoaromaticity in the monomeric units. The ^{11}B NMR chemical shift of **142b** is in excellent agreement with the corresponding value calculated for the C_{3v}-symmetric **142a**−Li$_3^+$. **142a** has a large negative NICS and very appreciable homoaromatic stabilization energies calculated from isodesmic reactions and by comparison of the energies of the "open" and "closed" (homoaromatic) forms. Thus, by geometric, energetic, and magnetic criteria, **142b** is judged to be a trishomoaromatic dianion. Schleyer and Siebert also examined the associated trishomoaromatic **1** and the potential trishomoaromatics **144** and **145**. They found, from the same methods of calculating stabilization energies as used for **142a**, that **1** and **144** prefer the closed homoaromatic form while **145** prefers the open form. **1**, **143**, and **145** are each predicted to be trishomoaromatic from their NICS values.



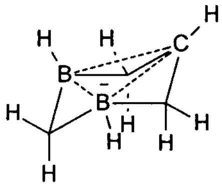
1



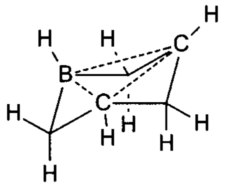
142a R = H
142b R = Me



143



144

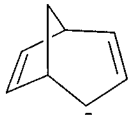


145

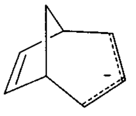
B. Six-Electron Systems

1. The Bicyclo[3.2.1]octadienyl Anion

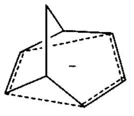
Anionic homoaromaticity is repeatedly invoked to explain the unusual properties of the bicyclo[3.2.1]-octadienyl anion **130**, and just as often, evidence is presented denying the importance of homoaromaticity in this system.[12,14] The controversy continues today. Jiao and Schleyer calculated the magnetic properties of **130c** (at the RMP2/6-31G* level with and without a lithium counterion).[82] They concluded, principally from the large diamagnetic susceptibility exaltation and stability of **130c**, that **130** is bishomoaromatic. These results and conclusion are supported by the very recent calculations of Freeman and Pugh.[153] On the contrary, Werstiuk and Ma, from a detailed analysis of the calculated magnetic properties including vector current densities, do not find a ring current to support the homoaromaticity of **130**![160] They studied **130** and its lithium salt (**130**−Li) using RHF/6-31+G* and determined magnetic properties using IGAIM (Jiao and Schleyer used IGLO). Their calculated geometries[161] and magnetic susceptibilities are in qualitative agreement with those of Jiao and Schleyer and the X-ray structure of **130**−Li. However, Jiao and Schleyer's electron-correlated calculations, not surprisingly, provide a better fit with the X-ray structure. The NMR chemical shifts calculated by Werstiuk and Ma are in good agreement with the experimental values for **130**−Li.



130a



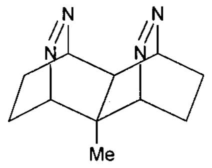
130b



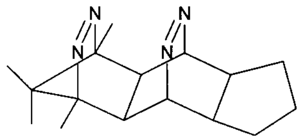
130c

2. Radical Anions and Dianions from Bisdiazenes

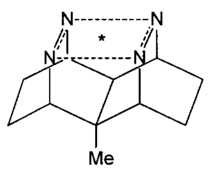
Gescheidt and Prinzbach reduced the proximate bisdiazenes **146** and **147** with alkali metals to give the corresponding radical anions and dianions.[162] They characterized these ions as the bishomoaromatic 4c/5e and 4c/6e **148**−**151**. They based their assignments of homoaromaticity on the formation of deeply colored solutions, the high stability of each of these ions in solution, calculated and measured ESR hyperfine splittings for **148** and **150**, and ^1H and ^{13}C NMR spectra consistent with the symmetrical dianions **149** and **151**. In addition, calculations (B3LYP/6-31G*) on **150** and **151** indicate energetic favoring of the delocalized species and geometries supportive of homoaromaticity.



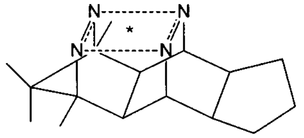
146



147



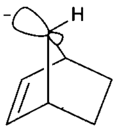
148 * = •−
149 * = 2-



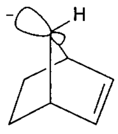
150 * = •−
151 * = 2-

C. Miscellaneous Anionic Systems

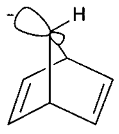
In a theoretical study (HF/6-31+G*, B3LYP/6-31++G* and MP2/6-31+G**) of the 7-norbornyl anions **152**−**155**, Sauers found no evidence for bishomoantiaromaticity in **152** or **154**.[163] There is negligible difference in absolute energies between **152** and **153** and in their respective destabilization energies calculated from homodesmotic reaction schemes. The proton affinities of **152**−**155** are all very similar and slightly less than that of the methyl anion. An interesting feature of the anions **152**−**155** is that they are not homoantiaromatic but they are delocalized. The negative charge is delocalized into the C−C σ-framework, helping to account for their relative stabilization compared with the methyl anion.



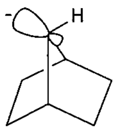
152



153

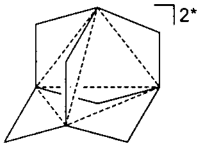


154

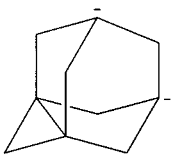


155

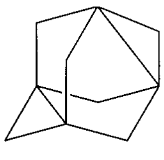
Assuming Hückel's ($4n + 2$) rule applies to three-dimensional aromaticity, following from the dehydroadamantyl dication **63**, the next aromatic member of this series should have six delocalized electrons and correspond with the dianion **156**. In their calculations, Chan and Arnold were not able to locate the delocalized dianion **156**.[76] They found the essentially localized dianion **157** as a high-energy species considerably less stable than the corresponding radical anion or "parent" pentacycle **158**. Chan and Arnold predict that the next closed-shell (aromatic?) system, with the tetratrishomoaromatic dication **63**'s T_d symmetry, will require eight (*not* six) electrons. Their prediction is based on an analysis of the frontier orbitals of the T_d symmetric **63** in which the LUMO is triply degenerate.



63 * = +
156 * = -



157



158

VII. Conclusion

In the conclusion to their 1994 review of homoaromaticity,[12] Williams and Kurtz noted that there were many well-accepted examples of cationic homoaromatics while there were no such examples for neutral or anionic systems. Much progress has been made since that time, particularly in the area of anionic homoaromaticity. Recently, many anionic compounds have been fully characterized as homoaromatic. There remains a dearth of neutral homoaromatics. The 1,2-boretanes provide the most convincing examples of neutral homoaromaticity. Recent studies continue to dispute the homoaromaticity of cycloheptatriene (**13**), although this reviewer is now convinced that **13** is marginally homoaromatic. Quast reports observing vibronically excited homoaromatic semibullvalenes and barbaralanes under ordinary conditions. Even more exciting is his evidence for homoaromatic semibullvalenes and barbaralanes being of lower energy than the corresponding localized forms in highly dipolar solvents. Surely ground-state homoaromatic semibullvalenes and barbaralanes cannot be far away.

Major advances in hardware now allow high-order theoretical calculations to be carried out, relatively routinely, on large and complex molecules. The area of homoaromaticity has particularly benefited in this respect. New theoretical methods have been introduced and widely applied in the characterization of homoaromaticity. Calculated NMR chemical shifts are in excellent agreement with experimental shifts provided that the calculated and experimental geometries are a close match. This link between experiment and theory has been extensively exploited in verifying molecular structures of potential homoaromatics.

VIII. References

(1) Winstein, S. *J. Am. Chem. Soc.* **1959**, *81*, 6524.
(2) Winstein, S.; Sonnenberg, J.; deVries, L. *J. Am. Chem. Soc.* **1959**, *81*, 6523.
(3) Applequist, D. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 4012.
(4) Doering, W. v. E.; Laber, G.; Vonderwahl, R.; Chamberlain, N. F.; Williams, R. B. *J. Am. Chem. Soc.* **1956**, *78*, 5448.
(5) Woods, W. G.; Carboni, R. A.; Roberts, J. D. *J. Am. Chem. Soc.* **1956**, *78*, 5653.
(6) Winstein, S. *Chem. Soc. Spec. Publ.* **1967**, *21*, 5.
(7) Winstein, S. *Q. Rev. Chem. Soc.* **1969**, *23*, 1411. (Reprinted in *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, p 965.)
(8) Story, P. R.; Clark, B. C., Jr. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1972; Vol. III, p 1007.
(9) Warner, P. In *Topics in Nonbenzenoid Aromatic Chemistry*; Nozoe, T., Breslow, R., Hafner, K., Ito, S., Murata, I., Eds.; Hirokawa Publishing Co.: Tokyo, 1977; Vol. II, p 283.
(10) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106.
(11) Childs, R. F. *Acc. Chem. Res.* **1984**, *17*, 347.
(12) Williams, R. V.; Kurtz, H. A. *Adv. Phys. Org. Chem.* **1994**, *29*, 273.
(13) Cremer, D.; Childs, R. F.; Kraka, E. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; J. Wiley & Sons: Chichester, 1995; Vol. 2, p 339.
(14) Childs, R. F.; Cremer, D.; Elia, G. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; J. Wiley & Sons: Chichester, 1995; Vol. 2, p 411.
(15) For example, see refs 16−20.
(16) Garratt, P. J. In *Comprehensive Organic Chemistry*; Barton, D. H. R., Ollis, W. D., Eds.; Pergamon Press: Oxford, 1979; Vol. 1, p 361.
(17) Garratt, P. J. *Aromaticity*; J. Wiley & Sons: New York, 1986.
(18) Stevenson, G. R. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH Publishers: Deerfield Beach, 1986; Vol. 3, p 57.
(19) Balaban, A. R.; Banciu, M.; Ciorba, V. *Annulenes, Benzo-, Hetero-, Homo-Derivatives and their Valence Isomers*; CRC Press: Boca Raton, 1987.
(20) Minkin, V. I.; Glukhovtsev, N.; Simkin, B. Y. *Aromaticity and Antiaromaticity: Electronic and Structural Aspects*; John Wiley & Sons: New York, 1994.
(21) For example, see refs 16, 17, 19, 20, and 22−26 and references therein.
(22) *Aromaticity Pseudo-Aromaticity, Anti-Aromaticity*. Proceedings of an International Symposium held in Jerusalem, 31 March−3April 1970; Bergmann, E. D., Pullman, B., Eds.; Academic Press: New York, 1971.
(23) Schleyer, P. v. R.; Jiao, H. *Pure Appl. Chem.* **1996**, *68*, 209.
(24) Lloyd, D. *J. Chem. Inf. Comput. Sci.* **1996**, *36*, 442.
(25) Glukhovtsev, M. *J. Chem. Educ.* **1997**, *74*, 132.
(26) Krygowski, T. M.; Cyrañski, M. K.; Czarnocki, Z.; Häfelinger, G.; Katritzky, A. R. *Tetrahedron* **2000**, *56*, 1783.
(27) Hückel, E. Z. *Phys.* **1931**, *70*, 204.
(28) Dewar, M. J. S.; Gleicher, G. J. *J. Am. Chem. Soc.* **1965**, *87*, 685.
(29) The arguments for σ- versus π-enforcement of bond equalization are summarized in the following articles and references therein: refs 24−26 and 30−31.
(30) Glendening, E. D.; Faust, R.; Streitwieser, A.; Vollhardt, K. P. C.; Weinhold, F. *J. Am. Chem. Soc.* **1993**, 115, 10952.
(31) Shaik, S.; Zilberg, S.; Haas, Y. *Acc. Chem. Res.* **1996**, *29*, 211.
(32) Sondheimer, F.; Calder, I. C.; Elix, J. A.; Gaoni, Y.; Garratt, P. J.; Grohmann, K.; di Maio, G.; Mayer, J.; Sargent, M. V.; Wolovsky, R. *Chem. Soc. Spec. Publ.* **1967**, *21*, 75. Sondheimer, F. *Acc. Chem. Res.* **1972**, *5*, 81.
(33) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.
(34) King, R. A.; Crawford, T. D.; Stanton, J. F.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1999**, *121*, 10788.
(35) Nendel, M.; Houk, K. N.; Tolbert, L. M.; Vogel, E.; Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 748.
(36) Nyulászi, L.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1999**, *121*, 6872.
(37) Winstein, S.; Adams, R. *J. Am. Chem. Soc.* **1948**, *70*, 838.
(38) Simonetta, M.; Winstein, S. *J. Am. Chem. Soc.* **1954**, *76*, 18.
(39) Shoppee, C. W. *J. Chem. Soc.* **1946**, 1147.
(40) Maier, G. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 402.
(41) Vogel, E. *Pure Appl. Chem.* **1969**, *20*, 237.
(42) Vogel, E. *Chem. Soc. Spec. Publ.* **1967**, *21*, 113.
(43) Massamune, S.; Brooks, D. W.; Morio, K.; Sobezak, R. L. *J. Am. Chem. Soc.* **1976**, *98*, 8277. Massamune, S.; Brooks, D. W. *Tetrahedron Lett. 1977*, 3239.
(44) Dewey, H. J.; Deger, H. Frölich, W.; Dick, B.; Klingensmith, K. A.; Hohlneicher, G.; Vogel, E.; Michl, J. *J. Am. Chem. Soc.* **1980**, *102*, 6412.
(45) Scott, L. T.*Pure Appl. Chem.* **1986**, *58*, 105.
(46) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9. Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, 1990.
(47) See refs 13 and 14 and references therein.
(48) Williams, R. V.; Kurtz, H. A.; Farley, B. *Tetrahedron* **1988**, *44*, 7455.
(49) Williams, R. V. *Adv. Theor. Interesting Mol.* **1998**, *4*, 157.
(50) Jiao, H.; Nagelkerke, R.; Kurtz, H. A.; Williams, R. V.; Borden, W. T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 5921.
(51) Sawicka, D.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1999**, *121*, 664.
(52) Haddon, R. C.; *Tetrahedron Lett.* **1974**, *33*, 2797. Haddon, R. C.; *Tetrahedron Lett.* **1974**, 4303.
(53) Jorgensen, W. L. *J. Am. Chem. Soc.* **1976**, *98*, 6784.
(54) For example, see Childs, R. F.; Faggiani, R.; Lock, J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1986**, *108*, 3613.
(55) Sieber, S.; Schleyer, P. v. R.; Otto, A. H.; Gauss, J.; Reichel, F.; Cremer, D. *J. Phys. Org. Chem.* **1993**, *6*, 445.
(56) Cunje, A.; Rodriquez, C. F.; Hopkinson, A. C. *J. Org. Chem.* **1996**, *61*, 5212.
(57) Notario, R.; Elguero, J. *J. Chem. Soc., Chem. Commun.* **1995**, 1543.

(58) Maksić, Z. B.; Kovaćević, B.; Lesar, A. *Chem. Phys.* **2000**, *253*, 59.

(59) (a) Milburn, R. K.; Hopkinson, A. C.; Sun, J.; Bohme, D. K. *J. Phys. Chem. A* **1999**, *103*, 7528. (b) Milburn, R. K.; Bohme, D. K.; Hopkinson, A. C. *Int. J. Mass Spectrom.* **2000**, *195/196*, 393.

(60) (a) Minkin, V. I.; Dorogan, I. V.; Minyaev, R. M. *J. Phys. Org. Chem.* **2000**, *13*, 3. (b) Minkin, V. I.; Dorogan, I. V.; Minyaev, R. M. *Russ. J. Org. Chem.* **1998**, *34*, 1532. (c) Minkin, V. I.; Dorogan, I. V.; Minyaev, R. M. The Mechanism and Stereochemistry of Circumambulatory Rearrangement of the 4-Hydroxycyclobutenyl Cation. In *Atual. Fis.-Quim. Org.* [*Latin American Conference on Physical Organic Chemistry*], 4th ed.; Humeres, E., Yunes, R., Eds.; Universidade Federal de Santa Catarina: Florianopolis, Brazil, 1999; p 258.

(61) Szabo, K. J.; Kraka, E.; Cremer, D. *J. Org. Chem.* **1996**, *61*, 2783.

(62) Laube, T. *Acc. Chem. Res.* **1995**, *28*, 399. Laube, T. *J. Am. Chem. Soc.* **1989**, *111*, 9224. Laube, T.; Lohse, C. *J. Am. Chem. Soc.* **1994**, *116*, 9001.

(63) Evans, W. J.; Forrestal, K. J.; Ziller, J. W. *J. Am. Chem. Soc.* **1995**, *117*, 12635.

(64) Prakash, G. K. S.; Rasul, G.; Yudin, A. K.; Olah, G. A. *Gazz. Chim. Ital.* **1996**, *126*, 1.

(65) Prakash, G. K. S.; Farnia, M.; Keyanian, S.; Olah, G. A.; Kuhn, H. J.; Schaffner, K. *J. Am. Chem. Soc.* **1987**, *109*, 911.

(66) Prakash, G. K. S.; Rasul, G.; Olah, G. A. *J. Phys. Chem. A* **1998**, *102*, 2579.

(67) Prinzbach, H.; Gescheidt, G.; Martin, H.-D.; Herges, R.; Heinze, J.; Prakash, G. K. S.; Olah, G. A. *Pure Appl. Chem.* **1995**, *67*, 673.

(68) Wever, K.; Lutz, G.; Knothe, L.; Mortensen, J.; Heinze, J.; Prinzbach, H. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1991.

(69) Etzkorn, M.; Wahl, F.; Keller, M.; Prinzbach, H.; Barbosa, F.; Person, V.; Gescheidt, G.; Heinze, J.; Herges, R. *J. Org. Chem.* **1998**, *63*, 6080.

(70) Prakash, G. K. S.; Weber, K.; Olah, G. A.; Prinzbach, H.; Wollenweber, M.; Etzkorn, M.; Voss, T.; Herges, R. *Chem. Commun.* **1999**, 1029.

(71) Exner, K.; Prinzbach, H.; Gescheidt, G.; Grossman, B.; Heinze, J. *J. Am. Chem. Soc.* **1999**, *121*, 1964.

(72) Reindl, B.; Clark, T.; Schleyer, P. v. R. *J. Phys. Chem. A* **1998**, *102*, 8953.

(73) Haumann, T.; Benet-Buchholz, J.; Klärner, F.-G.; Boese, R. *Leibigs Ann./Recl.* **1997**, 1429.

(74) Paquette, L. A.; Watson, T. J.; Friedrich, D.; Bishop, R.; Bacqué, E. *J. Org. Chem.* **1994**, *59*, 5700.

(75) Bremer, M.; Schleyer, P. v. R.; Schötz, K.; Kausch, M.; Schindler, M. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 761.

(76) Chan, M. S. W.; Arnold, D. R. *Can J. Chem.* **1997**, *75*, 192.

(77) Dai, S.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1990**, *112*, 2837.

(78) Dai, S.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1990**, *112*, 2835.

(79) Roth, H. D.; Lakkaraju, P. S. *J. Phys. Chem.* **1993**, *97*, 13403.

(80) Williams, F. *J. Phys. Chem.* **1994**, *98*, 8258. Williams, F. *J. Chem. Soc., Faraday Trans.* **1994**, *90*, 1681. Bally, T.; Truttmann, L.; Dai, S.; Williams, F. *J. Am. Chem. Soc.* **1995**, *117*, 7916. Bally, T. Truttmann, L.; Williams, F. *J. Mol. Struct. (THEOCHEM)* **1997**, *398*−*399*, 255.

(81) Roth, H. D. *Adv. Theor. Interesting Mol.* **1995**, *3*, 261.

(82) Jiao, H.; Schleyer, P. v. R. In *AIP Conference Proceedings 330: E.C.C.C. 1, Computational Chemistry*; Bernardi, F., Rivail, J.-L., Eds.; American Institute of Physics: Woodbury, NY, 1995; p 107.

(83) Houk, K. N.; Gandour, R. W.; Strozier, R. W.; Rondan, N. G.; Paquette, L. A. *J. Am. Chem. Soc.* **1979**, *101*, 6797.

(84) Wagenseller, P. E.; Birney, D. M.; Roy, D. *J. Org. Chem.* **1995**, *60*, 2853.

(85) Jiao, H.; Schleyer, P. v. R. *J. Phys. Org. Chem.* **1998**, *11*, 655.

(86) Morao, I.; Cossío, F. P. *J. Org. Chem.* **1999**, *64*, 1868.

(87) For example, see: Wehrmann, R.; Klusik, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 369. Cremer, D.; Gauss, J.; Schleyer, P. v. R.; Budzelaar, P. H. M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 370.

(88) Williams, R. V.; Kurtz, H. A. *J. Org. Chem.* **1988**, *53*, 3626.

(89) Seefelder, M.; Quast, H. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1068.

(90) Roth, W. R.; Klärner, F.-G.; Siepert, G.; Lennartz, H.-W. *Chem. Ber.* **1992**, *125*, 217.

(91) Rogers, D. W.; Podosenin, A.; Liebman, J. F. *J. Org. Chem.* **1993**, *58*, 2589.

(92) Schleyer, P. v. R. Personal communication at the 8th International Sympossium on Novel Aromatic Compounds, Braunschweig, Germany, July 30−August 4, 1995.

(93) Roth, W. R.; Adamczak, O.; Breukman, R.; Lennartz, H.-W.; Boese, R. *Chem. Ber.* **1991**, *124*, 2499.

(94) Lew, C. S. Q.; Capon, B. *J. Org. Chem.* **1997**, *62*, 5344.

(95) Nishinaga, T.; Izukawa, Y.; Komatsu, K. *J. Phys. Org. Chem.* **1998**, *11*, 475.

(96) See also this earlier study in which the structures of cycloheptatriene and some methoxy derivatives were optimized using semiempirical, DFT, and ab initio methods: Donovan, W. H.; White, W. E. *J. Org. Chem.* **1996**, *61*, 969.

(97) Jiao, H.; Schleyer, P. v. R.; Mo, Y.; McAllister, M. A.; Tidwell, T. T. *J. Am. Chem. Soc.* **1997**, *119*, 7075.

(98) Doering, W. v. E. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1990**, *34*, 334.

(99) For a summary of earlier work on the mechanism of the Cope rearrangement, see ref 49 and, for example, more recent refs 100−106 and references therein.

(100) Black, K. A.; Wilsey, S.; Houk, K. N. *J. Am. Chem. Soc.* **1998**, *120*, 5622.

(101) Roth, W. R.; Gleiter, R.; Paschmann, V.; Hackler, U. E.; Fritzsche, G.; Lange, H. *Eur. J. Org. Chem.* **1998**, 961.

(102) Hrovat, D. A.; Duncan, J. A.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 169.

(103) Hrovat, D. A.; Beno, B. R.; Lange, H.; Yoo, N.-Y.; Houk, K. N.; Borden, W. T. *J. Am. Chem. Soc.* **1999**, *121*, 10529.

(104) Doering, W. v. E.; Wang, Y. *J. Am. Chem. Soc.* **1999**, *121*, 10967.

(105) Oliva, J. M. *Theor. Chem. Acc.* **1999**, *103*, 1.

(106) Staroverov, V. N.; Davidson, E. R. *J. Am. Chem. Soc.* **2000**, *122*, 186.

(107) Gajewski, J. J. *Hydrocarbon Thermal Isomerizations*; Academic Press: New York, 1981. Gajewski, J. J. *Acc. Chem. Res.* **1980**, *13*, 142.

(108) Zimmerman, H. E.; Grunewald, G. L. *J. Am. Chem. Soc.* **1966**, *88*, 183. Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunewald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3316.

(109) Cheng, A. K.; Anet, F. A. L.; Mioduski, J.; Meinwald, J. *J. Am. Chem. Soc.* **1974**, *96*, 2887.

(110) Moskau, D.; Aydin, R.; Leber, W.; Günther, H.; Quast, H.; Martin, H.-D.; Hassenrück, K.; Miller, L. S.; Grohmann, K. *Chem. Ber.* **1989**, *122*, 925.

(111) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1760.

(112) Paquette, L. A.; Liao, C. C.; Burson, R. L.; Wingard, R. W., Jr.; Shih, C. N.; Fayos, J.; Clardy, J. *J. Am. Chem. Soc.* **1977**, *99*, 6935.

(113) Dewar, M. J. S.; Lo, D.-H. *J. Am. Chem. Soc.* **1971**, *93*, 7201.

(114) Hoffmann, R.; Stohrer, W.-D. *J. Am. Chem. Soc.* **1971**, *93*, 6941.

(115) Jackman, L. M.; Fernandes, E.; Heubes, M.; Quast, H. *Eur. J. Org. Chem.* **1998**, 2209.

(116) Williams, R. V. *Eur. J. Org. Chem.* **2001**, 227.

(117) Miller, L. S.; Grohmann, K.; Dannenberg, J. J. *J. Am. Chem. Soc.* **1983**, *105*, 6862.

(118) Dewar, M. J. S.; Jie, C. *Tetrahedron*, **1988**, *44*, 1351.

(119) Williams, R. V.; Kurtz, H. A. *J. Chem. Soc., Perkin Trans. 2* **1994**, 147.

(120) Williams, R. V.; Gadgil, V. R.; Chauhan, K.; Jackman, L. M.; Fernandes, E. *J. Org. Chem.* **1998**, *63*, 3302.

(121) Williams, R. V.; Gadgil, V. R.; Chauhan, K.; van der Helm, D.; Hossain, M. B.; Jackman, L. M.; Fernandes, E. *J. Am. Chem. Soc.* **1996**, *118*, 4208.

(122) Williams, R. V.; Gadgil, V. R.; Luger, P.; Koritsanszky, T.; Weber, M. *J. Org. Chem.* **1999**, *64*, 1180.

(123) Benesi, A.; Jackman, L. M.; Mayer, A.; Quast, H.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *J. Am. Chem. Soc.* **1989**, *111*, 1512.

(124) Quast, H.; Carlsen, J.; Janiak, R.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1992**, *125*, 955.

(125) Benesi, A.; Bertermann, R.; Förster, H.; Heubes, M.; Jackman, L. M.; Koritsanszky, T.; Luger, P.; Mayer, A.; Quast, H.; Seefelder, M.; Zobel, D. *J. Am. Chem. Soc.* **2000**, *122*, 4455.

(126) Siehl, H.-U. *Adv. Phys. Org. Chem.* **1987**, *23*, 63.

(127) Gompper, R.; Schwarzensteiner, M.-L.; Wagner, H.-U. *Tetrahedron Lett.* **1985**, *26*, 611.

(128) For example, see: Wiberg, K. B.; Keith, T. A.; Frisch, M. J.; Murcko, M. J. *J. Phys. Chem.* **1995**, *99*, 9027 and references therein.

(129) Quast, H.; Herkert, T.; Witzel, A.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1994**, *127*, 921.

(130) Quast, H.; Seefelder, M. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 1064.

(131) Zilberg, S.; Haas, Y.; Danovich, D.; Shaik, S. *Angew. Chem., Int. Ed.* **1998**, *37*, 1394.

(132) Quast, H.; Seefelder, M.; Becker, C.; Heubes, M.; Peters, E.-M.; Peters, K. *Eur. J. Org. Chem.* **1999**, 2763.

(133) Quast, H.; Knoll, K.; Peters, E.-M.; Peters, K.; von Schnering, H. G. *Chem. Ber.* **1993**, *126*, 1047. Quast, H.; Seefelder, M.; Peters, E.-M.; Peters, K. *Eur. J. Org. Chem.* **1999**, 1811.

(134) Woodward, R. B.; Fukunaga, T.; Kelly, R. C. *J. Am. Chem. Soc.* **1964**, *86*, 3162.

(135) Leibman, J. F.; Paquette, L. A.; Peterson, J. R.; Rogers, D. W. *J. Am. Chem. Soc.* **1986**, *108*, 8267.

(136) Rogers, D. W.; Logins, S. A., Samuel, S. D.; Finnerty, M. A.; Liebman, J. F. *Struct. Chem.* **1990**, *1*, 481.

(137) Verevkin, S. P.; Beckhaus, H.-D.; Rüchardt, C.; Haag, R.; Kozhushkov, S. I.; Zywietz, T.; de Meijere, A.; Jiao, H.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1998**, *120*, 11130.

(138) McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Duyne, G. V.; Gleiter, R.; Schäfer, W.; White, D. H. *J. Am. Chem. Soc.* **1984**, *106*, 5018. McMurry, J. E.; Haley, G. J.; Matz, J. R.; Clardy, J. C.; Duyne, G. V.; Gleiter, R.; Schäfer, W.; White, D. H. *J. Am. Chem. Soc.* **1986**, *108*, 2932.

(139) Scott, L. T.; Cooney, M. J.; Rogers, D. W.; Dejroongruang, K. *J. Am. Chem. Soc.* **1988**, *110*, 7244.

(140) Scott, L. T.; Cooney, M. J. in*Modern Acetylene Chemistry*; Stang, P. J., Diederich, F., Eds.; VCH: Weinheim, 1995; p 321.

(141) de Meijere, A.; Kozhushkov, S. I. *Top. Curr. Chem*. **1999**, *201*, 1.

(142) Jiao, H.; van Eikema Hommes, N. J. R.; Schleyer, P. v. R.; de Meijere, A. *J. Org. Chem*. **1996**, *61*, 2826.

(143) Golz, T.; Hammes, S.; Klärner, F.-G. *Chem. Ber*. **1993**, *126*, 485.

(144) Klärner, F.-G.; Golz, T.; Uhländer, C.; Yaslak, S. *Tetrahedron Lett*. **1996**, *37*, 1385.

(145) Person, G.; Keller, M.; Prinzbach, H. *Liebigs. Ann*. **1996**, 507

(146) Rücker, C.; Müller-Bötticher, H.; Braschwitz, W.-D.; Prinzbach, H.; Reifenstahl, U.; Irngartinger, H. *Liebigs. Ann./Recl*. **1997**, 967.

(147) Mohler, D. L.; Vollhardt, K. P. C.; Wolff, S. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 563.

(148) Wudl, F. *Acc. Chem. Res*. **1992**, 25, 157.

(149) Haddon, R. C.; Raghavachari, K. *Tetrahedron* **1996**, *52*, 5207.

(150) Kiely, A. F.; Haddon, R. C.; Meier, M. S.; Selegue, J. P.; Brock, C. P.; Patrick, B. O.; Wang, G.-W.; Chen, Y. *J. Am. Chem. Soc.* **1999**, *121*, 7971.

(151) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* **1991**, *254*, 1186.

(152) Freeman, P. K. *J. Am. Chem. Soc*. **1998**, *120*, 1619.

(153) Freeman, P. K.; Pugh, J. K. *J. Org. Chem*. **2000**, *65*, 6107.

(154) Steiner, D.; Balzereit, C.; Winkler, H.-J.; Stamatis, N.; Hofmann, M.; Schleyer, P. v. R.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl*. **1994**, *33*, 2303.

(155) Steiner, D.; Winkler, H.-J.; Balzereit, C.; Happel, T.; Hofmann, M.; Subramanian, G.; Schleyer, P. v. R.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl*. **1996**, *35*, 1990.

(156) Unverzagt, M.; Subramanian, G.; Hofmann, M.; Schleyer, P. v. R.; Berger, S.; Harms, K.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed. Engl*. **1997**, *36*, 1469. Berndt, A.; Steiner, D.; Schweikart, D.; Balzereit, C.; Menzel, M.; Winkler, H. J.; Mehle, S.; Unverzagt, M.; Happel, T.; Schleyer, P. v. R.; Subramanian, G.; Hofmann, M. In *Advances in Boron Chemistry*; Siebert, W., Ed.; The Royal society of Chemistry: Cambridge, 1997; p 61.

(157) Schleyer, P. v. R.; Jiao, H.; Glukhovtsev, M. N.; Chandrasekhar, J.; Kraka, E. *J. Am. Chem. Soc.* **1994**, *116*, 10129. Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. *Tetrahedron Lett*. **1979**, 3707.

(158) Scheschkewitz, D.; Ghaffari, A.; Amseis, P.; Unverzagt, M.; Subramanian, G.; Hofmann, M.; Schleyer, P. v. R.; Schaefer, H. F., III; Geisler, G.; Massa, W.; Berndt, A. *Angew. Chem., Int. Ed*. **2000**, *39*, 1272.

(159) Lö*β*lein, W.; Pritzkow, H.; Schleyer, P. v. R.; Schmitz, R.; Siebert, W. *Angew. Chem., Int. Ed*. **2000**, *39*, 1276.

(160) Werstiuk, N. H.; Ma, J. *Can. J. Chem*. **1999**, *77*, 752.

(161) Werstiuk, N. H.; Ma, J. *Can. J. Chem*. **1996**, *74*, 875.

(162) Exner, K.; Hunkler, D.; Gescheidt, G.; Prinzbach, H. *Angew. Chem., Int. Ed*. **1998**, *37*, 1910.

(163) Sauers, R. S. *Tetrahedron* **1998**, *54*, 5143.

CR9903149