Semibullvalenes and Related Molecules: Ever Closer Approaches to Neutral Homoaromaticity

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Dedicated to Professor Helmut Quast

Keywords: Fluxionality / Aromaticity / Rearrangements / Semibullvalenes / Thermochromism

Since the first synthesis of semibullvalene by Zimmerman et al. more than three decades ago, this molecular system has been the focus of extensive study. A major factor in the continuing fascination with semibullvalenes is the potential for realizing a neutral homoaromatic ground state species. Dewar-Hoffmann electronic stabilization of the transition state of barbaralanes and semibullvalenes has been very successfully applied, principally by Quast, to yield negligible barriers to their Cope rearrangement. In our work we are attempting to "eliminate" the barrier to the Cope rearrangement of semibullvalenes through strain mediated destabilization of the localized forms. We predict, from the results of high level quantum mechanical calculations, that small ring annelation of the semibullvalene nucleus will result in homoaromatic ground state species. Experimentally, our small series of bisannelated semibullvalenes have proved to be localized Cope systems with exceptionally low activation barriers to the Cope rearrangement in the *condensed phases.*

Introduction

The Cope rearrangement has proved to be a source of fascination since its discovery by Cope more than fifty years ago.[1,2a] An early frustration with this ubiquitous reaction was the failure of scrupulous studies to elucidate its mechanism. Principally, because of its lack of conventional intermediates, of solvent sensitivity and of sensitivity to catalysts, Doering termed the Cope rearrangement, and other reactions now classed as pericyclic reactions,[3] a "no-mechanism" reaction.[2c] His insightful mechanistic investigations led him to studies aimed at lowering the activation barrier of the Cope rearrangement.[2a,2b,4] These studies were eminently successful resulting in a full report on the first fluxional molecule homotropilidine (**1**), mention of the even more facile degenerate Cope rearrangement in barbaralone (**2**) and speculation about bullvalene (**3**).[4] Doering proposed that the hypothetical molecule bullvalene should be fluxional and, by a succession of Cope rearrangements, every carbon and every hydrogen would be equivalent. He pointed out that there are more than 1.2 million combinations of the 10 CH groups each forming bullvalene and each interconvertible by Cope rearrangement.[4] Shortly after Doering made these predictions, Schröder prepared bullvalene and demonstrated that in the NMR fast-exchange limit all of the protons are equivalent.[5] Later, Doering et al. detailed their syntheses and studies of bullvalene, bullvalone (**4**), barbaralone, and barbaralane (**5**).[6] At this point, the only member missing from the defining structures comprising the bullvalene family is semibullvalene (**6**) the focus of this microreview.[7] Zimmerman et al. were the first to prepare and study semibullvalene.[8] Unlike with the previously studied barbaralanes and bullvalenes,[4–6] Zimmerman et al. were unable to "freeze out" the degenerate Cope rearrangement in semibullvalene. Even at 163 K, the limit of slow-exchange for semibullvalene could not be reached

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MICROREVIEWS: This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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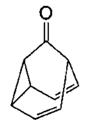
with a 60 MHz (^{1}H) NMR spectrometer. This inability to observe the quenching of the Cope rearrangement not only demonstrated that semibullvalene had the lowest activation barrier to the Cope rearrangement of any compound studied to that time, but also led Zimmerman to speculate that semibullvalene might exist as the delocalized (homoaromatic) species (**6c**). Zimmerman rapidly dismissed this notion on the basis of the similarity of its NMR and UV spectra to those of the bullvalenes. Several years later Meinwald and Anet et al., using a 251 MHz (^{1}H) NMR spectrometer, reached the slow-exchange limit for semibullvalene and determined the activation barrier for its Cope rearrangement ($\Delta G^{\ddagger}$ = 5.5 kcal/mol at 130 K).[9] More recently, this value was refined using ^{13}C NMR spectroscopic data ($\Delta G^{\ddagger}$ = 5.8 and 6.2 kcal/mol at 173 and 298 K, respectively).[10] Although semibullvalene is not a ground state homoaromatic, it is generally recognized that the semibullvalene nucleus is the species most closely approaching the holy grail of neutral homoaromaticity.[7,11,12] The low-lying transition state for the Cope rearrangement of semibullvalene has the bishomoaromatic C_{2v} symmetric structure **6c**.[13]


1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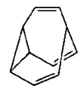
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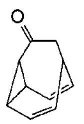
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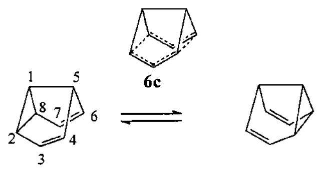
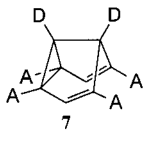


6c

6a **6b**

Dewar and Hoffmann predicted that the energy of the Cope transition state for semibullvalene would be lowered by electron-withdrawing substituents (A) at the 2,4,6 and 8 positions and electron donating groups (D) at the 1 and 5 positions (**7**).[14,15] Numerous Dewar-Hoffmann semibullvalenes have been prepared and, although their activation barriers are significantly lower than the parent **6**, none have a homoaromatic ground state.[7] Recently, Quast et al. presented evidence for the experimental observation, under ordinary conditions, of homoaromatic vibrationally excited states of some Dewar-Hoffmann systems, and even concluded that in highly dipolar solvents the delocalized (homoaromatic) species were of lower energy than the localized tautomers.[16,17]



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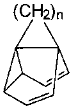
Annelated Semibullvalenes

In contrast to the electronic stabilization of the transition state advanced by Dewar and Hoffmann, we favor an approach to homoaromatic semibullvalenes through strain-induced destabilization of the localized forms (**6a**,**b**). Such destabilization may be mediated through small ring annelation of the semibullvalene nucleus. Variously substituted 1,5- and 2,8(4,6)-monoannelated semibullvalenes (**8**) and (**9**) have been prepared. Unfortunately, only medium ring compounds (n ≥ 3) were obtained and, although the Cope equilibrium is skewed in the unsymmetrical examples and the activation parameters are changed with respect to semibullvalene itself, none were demonstrated to be homoaromatic.



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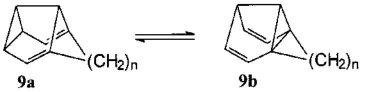
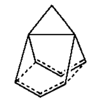


9a **9b**

Theoretical studies [semiempirical, ab initio and density functional theory (DFT)][13a,18] all predict that 1,5-methanosemibullvalene (**10**) has a homoaromatic ground state while semiempirical calculations suggest that 1,5-ethanosemibullvalene (**11**) does not.[18] Paquette and Chamot proposed that in the semibullvalene (**12**) the bisannelation would inhibit the "breathing motion" associated with the Cope rearrangement and thus perhaps favor the delocalized form.[19] Extended Hückel calculations on the bisetheno-annelated semibullvalene **13** led Hoffmann and Stohrer to predict that its Cope rearrangement would be inhibited and would proceed through the highly strained cyclodecapentaene transition state **14**.[15]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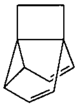
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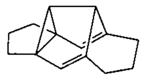
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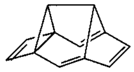
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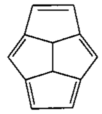
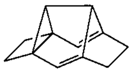

14

Our first excursion into the area of homoaromaticity in general, and semibullvalene chemistry in particular, came with the recognition that 2,8:4,6-bisethanosemibullvalene (**15**) is an ideal candidate for neutral homoaromaticity. The left-hand side of structure **15a** is destabilized by a high energy bicyclo[2.1.0]pentane moiety in addition to two spirocyclic features. Similarly, the right-hand side of **15a** is destabilized by two double bonds to bridgeheads (doubly anti-Bredt). These unfavorable interactions, which are mirrored in **15b**, are considerably reduced in the delocalized **15c**. In agreement with intuition, we concluded from semiempirical calculations (MNDO CI2 and AM1 CI2) that **15** should have a homoaromatic ground state (**15c**).[20] In these semiempirical calculations electron correlation was incorporated through a simple 2 × 2 configuration interaction (CI2) involving the highest occupied and lowest unoccupied molecular orbitals. The MNDO CI2 calculations resulted in a C_{2v} symmetric ground state (**15c**) 10.4 kcal/mol lower in energy than the localized forms (**15a**,**b**), while at AM1 CI2 the localized forms are not even stationary points on the potential energy surface. It can, of course, be argued that possession of high-symmetry by a semibullvalene (or other potential homoaromatic) does not guarantee homoaromaticity.[7,11] We developed a set of semiempirical discriminators, based on favorable two-center energy partitioning terms between the nuclei completing the homoaromatic interaction and on a significant decrease in the calculated heats of formation between the SCF and CI2 levels, for detecting homoaromatic interactions.[21] These discriminators have proved to be extremely reliable in assessing homoaromatic interactions in semibullvalenes and various other systems and provide results in complete agreement with other discriminators for homoaromaticity.[7,13a,21] Using these discriminators, we gained further support for the designation of **15** as a homoaromatic. We have shown that semiempirical methods *incorporating electron correlation* are capable of modeling compounds possessing extended conjugation.[7,13a,21,22] However, despite our confidence in these methods, there is always a concern that their parameterization is perhaps inadequate for such finely balanced systems as the semibullvalenes. Due to improvements in both hardware and software, it is now feasible to routinely study molecules even larger than **15** by electron correlated ab initio and DFT procedures. Such higher-order methods provided additional confirmation for the homoaromaticity of **15c** through the calculated geometry, build up of electron density between both C(2,8) and C(4,6) and magnetic properties.[13a,23]



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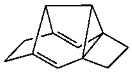

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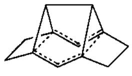
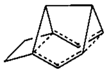


15c

Schleyer asserts that the magnetic properties of a potential aromatic molecule are the only observable properties directly correlated with aromaticity.[24] He proposed a definition of aromaticity based upon magnetic susceptibility exaltation, a feature long-recognized as an indicator of aromaticity.[24] More recently Schleyer introduced nucleus-independent chemical shifts (NICS), the negative of the absolute magnetic shieldings usually computed at the ring centroids of the B3LYP/6−31G* geometry, as another gauge of aromaticity.[25] At DFT and correlated ab initio levels of theory, the only stationary point found is **15c** which is calculated to have a magnetic susceptibility exaltation greater than benzene (−17.5 cf. benzene −13.4 ppm cgs) and similarly a greater NICS value than that of benzene (−22.6 cf. benzene −11.5 ppm).[13a] These calculations on **15** clearly confirm the homoaromatic nature of its ground state.

Our semiempirical studies of a series of 2,8(4,6)-monoannelated semibullvalenes led to the intriguing prediction that the 2,8(4,6)-ethanosemibullvalene (**16**) would have a homoaromatic ground state.[26] Later ab initio, DFT, magnetic susceptibility exaltation and NICS calculations all supported the homoaromaticity of **16** and suggested that the mono- and bis-annelated **17** and **18** are also homoaromatic.[13a] It is noteworthy that our correlated semiempirical results are in excellent agreement with the correlated ab initio and DFT results.



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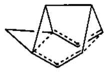

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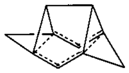
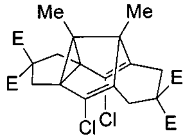


18

The first experimental realization of a bisannelated semibullvalene was due to Müllen et al. They prepared **19** which they concluded to be a classical Cope system with a very low activation barrier to rearrangement.[27] Compound **19** is not an ideal candidate for homoaromaticity as doubtless the 3,7-dichloro substitution inhibits the Cope rearrangement.[7,28] Müllen and Düll also attempted to prepare **20** (Scheme 1) which spontaneously rearranged and could not be observed.[29]



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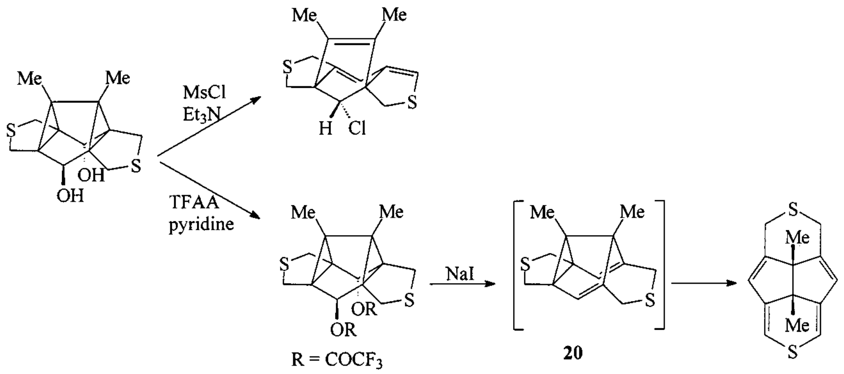
E = CO_2Me

Selected Experimental Probes for Homoaromaticity

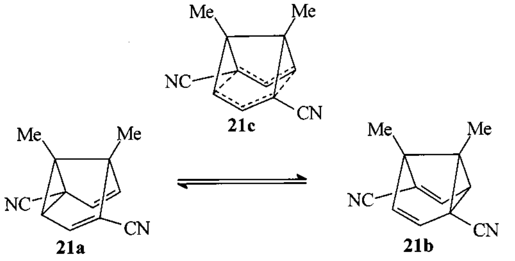
It is not a trivial matter to prove that a candidate molecule exhibits the desired property of homoaromaticity.[7] Although dynamic NMR spectroscopy potentially yields the most information about the Cope rearrangement in the bullvalene family,[30] it is only useful for processes that are relatively slow on the NMR time scale. Many barbaralanes and semibullvalenes show little or no change in their NMR spectra down to the lowest temperature achievable with the most sophisticated of modern instruments.[7] In these systems other methods must be used to decide upon the nature of the ground state (localized Cope or delocalized homoaromatic).

X-ray structure determination would appear to be the ideal means to probe the nature of the ground state in crystalline semibullvalenes. The homoaromatic species should have high-symmetry with an equalization of bond/interatomic distances which would be readily apparent from the crystal structure. The β-form of the dinitrile **21** displays apparent C_2 symmetry in its X-ray structure which, at first sight, suggests that it is homoaromatic (**21c**).[31] However, variable temperature solid ^{13}C CP-MAS studies revealed that **21** is a localized Cope system with **21a** in dynamic equilibrium with its nondegenerate tautomer **21b**. At ambient temperature there is accidental degeneracy of the equilibrating and otherwise nondegenerate tautomers of **21** which results in the apparent C_2 symmetry at this temperature.[31] These results explain the observed variation of internuclear distances [particularly C(2,8) and C(4,6)] with temperature in the X-ray structures of some semibullval-



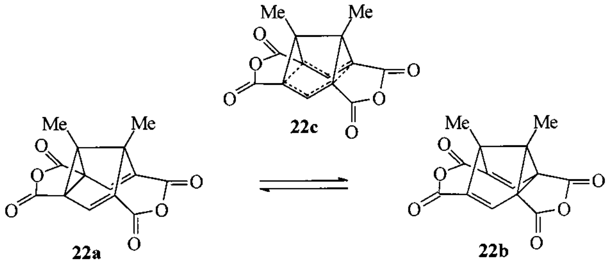
Scheme 1. The attempted synthesis of bisannelated semibullvalene **20**

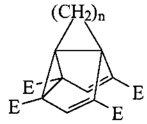
enes. Changing the acquisition temperature for structure determination will change the population distribution between equilibrating nondegenerate tautomers and, in response, the internuclear distances.[32,33] Similarly, population changes induced by varying the acquisition temperature in solids NMR studies will cause the time and population averaged chemical shifts to vary with temperature. In contrast, delocalized (homoaromatic ground state) systems will maintain high-symmetry at all temperatures and will only exhibit minor variations in structure (and chemical shift) with temperature. This lifting of the degeneracy of semibullvalenes in the solid state is, of course, a result of the crystal environment. A similar lifting of degeneracy can be achieved in the solution phase by means of the Saunders' isotopic perturbation method, in which an unsymmetrical species is produced by isotopic substitution of a symmetrical precursor.[34] In this case the changes in population with temperature for equilibrating isotopically perturbed systems are monitored by NMR spectroscopy. A tracking of chemical shift with temperature will be observed in equilibrating systems, whereas in delocalized (homoaromatic) semibullvalenes the chemical shifts will be essentially temperature independent.[7]



1,5-Dimethyl-2,4,6,8-semibullvalenetetracarboxylic Acid Dianhydride

From AM1 CI2 calculations in conjunction with our semiempirical discriminators we predicted a C_{2v} symmetric bishomoaromatic ground state **22c** for the bisannelated 1,5-dimethyl-2,4,6,8-semibullvalenetetracarboxylic dianhydride **22**.[35] The known[36] semibullvalene tetraester **23** (Scheme 2) appeared to be an ideal starting material for the synthesis of the dianhydride **22**. Grohmann and his coworkers devised an ingenious synthesis of this tetraester **23**[36] beginning with the Weiss-Cook reaction.[37] Using the same basic route, they were also able to prepare the 1,5-annelated semibullvalenes **24** and the barbaralanes **25** and **26**.[38,39]





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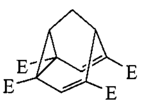
n = 3-6



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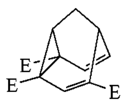

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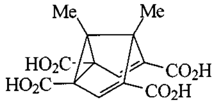
E = CO_2Me

Employing Grohmann's synthesis, we prepared **23** in 24% overall yield from 2,3-butanedione (Scheme 2A). In an effort to improve the yield of **23** and to avoid the use of the pyrophoric triisobutylaluminum, we developed a modified and operationally simpler procedure which gave the desired tetraester **23** in 32% overall yield from 2,3-butanedione (Scheme 2B).[35] The tetraacid **27**, which was easily obtained upon hydrolysis of **23**, was subjected to several methods of dehydration. Eventually we discovered conditions, using trifluoroacetic anhydride, to effect the clean dehydration of **27** to give the dianhydride **22**.



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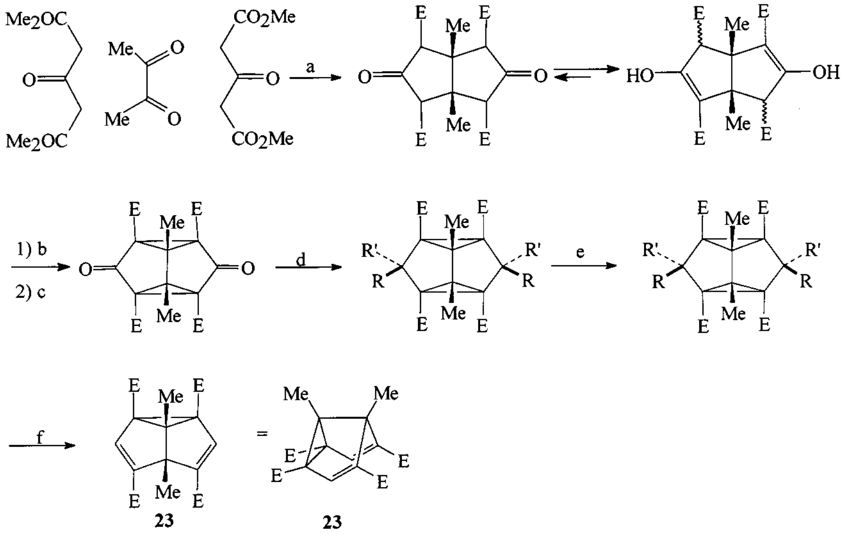
In contrast with many other semibullvalenes that tend to readily react with oxygen and to undergo facile thermolysis to cyclooctatetraenes,[7] the dianhydride **22** proved to be remarkably stable. Our usual method of purification of **22**, by atmospheric pressure sublimation at 200 °C, provides convincing evidence of its enhanced stability. Initial studies of the properties of **22** led to much excitement as all of our

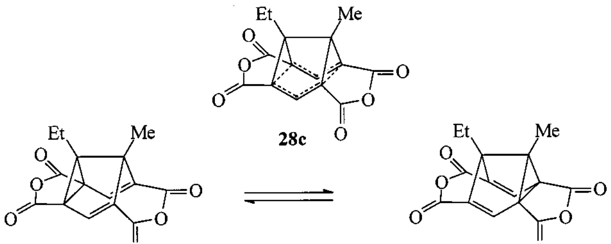


Scheme 2. The synthesis of tetraester **23**

Scheme 2A:	a: $NaHCO_3$, H_2O (82%) b: Br_2, $CHCl_3$ (88%) c: Et_3N, $CHCl_3$ (78%) d: *i*Bu_3Al, toluene, ambient temperature, 4 h, R = OH, R′ = H (76%) e: MsCl, Et_3N, CH_2Cl_2, 5 °C→ambient, 40 h, R = OMs, R′ = H, (83%) f: NaI, acetone, reflux, 3.5 h. (63%)
Scheme 2B:	a: $NaHCO_3$, H_2O (82%) b: Br_2, $CHCl_3$ (88%) c: Et_3N, $CHCl_3$ (78%) d: $NaBH_4$, THF, H_2O, <0 °C, 8 h, R = H, R′ = OH (82%) e: PBr_3, benzene, H_2O, 45°C, 48 h, R = Br, R′ = H (81%) f: NaI, acetone, reflux, 5 h (85%)

early results indicated a homoaromatic ground state **22c** for the dianhydride.[35] Not surprisingly, using solution phase ^{13}C NMR spectroscopy (75 or 125 MHz) at temperatures down to 183 K we were unable to freeze out any Cope rearrangement that might be occurring (vide supra). In addition, we were not even able to detect any line broadening of the key C(2,4,6,8) signal in the resulting ^{13}C spectra. X-ray structure determinations at temperatures between 293 and 163 K revealed C_2 symmetric structures for **22** with the C(2,8) and C(4,6) distances equal (≈1.96 Å). The variable temperature solid state ^{13}C CP-MAS NMR spectra of **22** were temperature invariant in the range 293−223 K. These solid state results are strongly suggestive of a homoaromatic ground state for **22**. Similar studies on other semibullvalenes revealed a temperature dependence of internuclear distances and ^{13}C chemical shifts indicating Cope equilibrium between nondegenerate (induced by the crystal environment) tautomers (vide supra). Unfortunately, in subsequent X-ray structures determined at 148 and 123 K, **22** was no longer C_2 symmetric [C(2,8) = 1.679(4) and C(4,6) = 2.197(4) Å at 123 K]. Closer examination of the higher temperature X-ray data revealed a dynamic disorder consistent with an equilibrium **22a**$\rightleftarrows$**22b**. These X-ray results proved that **22** is not homoaromatic in the *solid state.* We extended our studies of the solid state properties of **22** by determining its X-ray structures at temperatures from 123 to 15 K and its charge density distribution at 15 K.[40] As previously determined, the C_2 symmetry observed at higher temperatures is broken by 148 K and there is a change in space group from *C2*/*c* to *Cc*. [35] Between 123 and 40 K there were minor changes in structure and, from these data, we were able to estimate the difference in free energy (in the solid state) of **22a** and **22b** ($\Delta G^\circ \approx 0.162$ kcal/mol). Below 40 K, we concluded that the tautomeric equilibrium (**22a**$\rightleftarrows$**22b**) was frozen out. At 15 K there is no evidence of any disorder in the structure, which must represent that of a single localized tautomer. The charge density distribution at 15 K confirmed the localized nature of the ground state in the solid phase. There is remarkable agreement between the calculated Hartree−Fock (HF/6−311G**) structure and charge density and the corresponding experimental properties determined at 15 K. At higher levels of theory (which include electron correlation) the predicted ground state for **22** is the homoaromatic C_{2v} symmetric **22c**.[41] Using ab initio, second order Möller-Plesset perturbation theory with frozen core electrons (MP2/6−31G*), and DFT (DFT with the B3LYP functional and a 6−31G* basis set) methods we were unable to locate stationary points corresponding to **22a**,**b** on the potential energy surface.

In such a finely balanced system as **22a**,**b**,**c**, crystal packing forces could easily become of paramount importance and effectively alter the nature of the ground state. It was therefore important to further probe the solution phase properties of **22**. To this end we used a modification of the Saunders' isotopic perturbation method pioneered by Gompper et al.[42] In Gompper's method the symmetry of a semibullvalene is broken by substitution with mildly perturbing inequivalent alkyl groups at C(1) and C(5) and, as a consequence, the degeneracy of the localized forms is lifted. We prepared the 1,5-(ethylmethyl) dianhydride **28** and examined its ^{13}C NMR spectra at a range of temperatures. The C(2,8) and C(4,6) signals in particular showed an equilibrium-driven variation of chemical shift with temperature, clearly demonstrating that **28**, and by analogy **22**, is not homoaromatic in the solution phase.[35] We were unable to freeze out the Cope rearrangement of **22** or **28** in solution and, from ^{13}C NMR spectra at 125 MHz, we estimated the *upper* limit for the activation barrier of the Cope rearrangement **22a**$\rightleftarrows$**22b** to be 3.3 kcal/mol.[35] In a recent collaboration with Quast, we studied a series of unsymmetrically substituted semibullvalenes, including **28**, by solution phase ^{13}C variable temperature NMR spectroscopy.[43] The ^{13}C spectra were obtained at 151 MHz and very precisely determined temperatures down to as low as 104 K. Again we were unable to freeze out the Cope equilibrium **28a**$\rightleftarrows$**28b** (^{13}C NMR spetroscopy at 151 MHz down to 185 K).



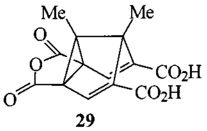
28c

28a

28b

1,5-Dimethyl-2,4,6,8-semibullvalenetetracarboxylic Acid Diimide

Despite the stability of dianhydride **22** to both oxygen and elevated temperatures, our studies of its properties were hampered by its relatively easy hydrolysis to the monoanhydride diacid **29** and by its low solubility.[35] It appeared to us that both of these problems would be circumvented in the diimides **30** while retaining the advantageous thermal stability and resistance to oxidation of **22**. We anticipated that the diimides would be difficult to hydrolyze and would have solubilities that could be modulated by manipulation of the substituents R on the nitrogens. Although the diphenyldiimide **31** was not expected to exhibit the desired enhanced solubility, its postulated ease of synthesis made it an attractive first target and model compound for further studies. Reaction of dianhydride **22** with aniline gave a mixture of isomeric diacid diamides which were not isolated but directly dehydrated with acetic anhydride to give the diimide **31** in 60% overall yield from **22**. As predicted, **31** is stable to thermolysis, to oxygen and to hydrolysis. We were unsuccessful in obtaining crystals of **31** suitable for X-ray structure determination. Similarly to the dianhydride **22**, we could not reach the slow-exchange limit for **31** at 75 MHz (^{13}C) nor, in a later experiment on the unsymmetrical **32**,[43] at 151 MHz (^{13}C) and 185 K. To determine the nature, delocalized homoaromatic or localized Cope system, of the diimide in the solution phase we again resorted to Gompper's modification of the Saunders' isotopic perturbation method.[42] We prepared the diimide **32** and examined its variable temperature ^{13}C NMR spectra. Just as in the case of the unsymmetrical dianhydride **28**, the ^{13}C spectra of diimide **32** showed a clear equilibrium-driven tracking of chemical shifts with temperature. These results demonstrate that **32** and, by analogy, **31** have localized Cope ground states in solution.



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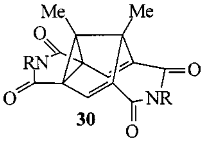

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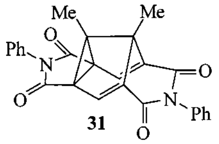

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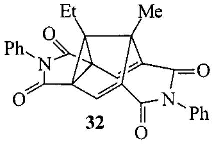
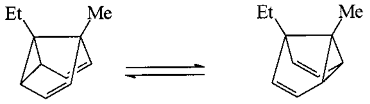


32

In neither unsymmetrical semibullvalene, diimide **32** nor dianhydride **28**, could the Cope rearrangement be frozen out. Consequently, it was not possible to identify directly the low-energy tautomer. However, for the parent 1,5-(ethylmethyl)semibullvalene (**33**) the slow-exchange limit ^{13}C NMR spectra was obtained, and it was established that in the low-energy tautomer (**33a**) the ethyl group is on the cyclopropane ring.[43] We assumed a similar preference for the ethyl group to be on the cyclopropane ring in **28** and **32**.[43] We extended the Saunders' treatment of isotopic perturbation[44] to allow the estimation of the population difference and the perturbation thermodynamic parameters (ΔH^{p}, ΔS^{p} and ΔG^{p}) for equilibria skewed by substituents other than isotopes. In these new protocols the effects of the substituents upon the chemical shifts are specifically accounted for.



33a

33b

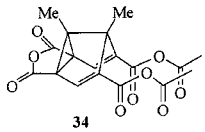
Thermochromism

The most fluxional barbaralanes and semibullvalenes tend to be thermochromic.[7,16,45] Quast considers such thermochromism to result from a very flat potential energy surface with an exceptionally low barrier to the Cope rearrangement.[16,45] Zilberg et al., using the valence-bond derived "twin-state" concept, have provided evidence in support of this hypothesis.[46] Quast further reports that the colored, high temperature, species are in a vibrationally excited state above the Cope barrier and are homoaromatic.[16]

The dianhydride **22**, tetraester **23**, and diimide **31** are all thermochromic.[35,41] To gain further insight into this thermochromism, we wished to calculate the relative energies and intensities of the UV/Vis spectra of **22** using the INDO/S (ZINDO) program.[47] In order to do this we required good structural parameters for **22a**,**b** and **22c**. The HF calculated geometry for **22a**,**b** is in excellent agreement with the X-ray structure of **22a**,**b** determined at 15 K.[40,41] We therefore assumed that our HF geometry for the transition state (**22c**) also provided a reasonable representation of the condensed phase structure of **22c**. Using higher levels of theory incorporating electron correlation (B3LYP/6−31G* and MP2/6−31G*) to calculate structures for **22** resulted in a single minimum surface with a symmetric homoaromatic ground state species (**22c**).[41] In addition to the experimental X-ray (at 15 K) and HF structures of **22a**,**b**, we used the HF, B3LYP and MP2 structures of **22c** to calculate the UV/Vis spectra of **22a**,**b** and **22c**.[41] In each case, no matter which was the source of the structure used in our UV/Vis calculations, the results were qualitatively the same and furnish strong support for Quast's model. The localized species **22a**,**b** were calculated to give only short wavelength absorptions (<276 nm) while the delocalized homoaromatic **22c** gave absorptions at longer wavelength.

Miscellany

We prepared the anhydrides **29** and **34** by treatment of the tetraacid **27** with oxalyl chloride[35b] and acetic anhydride, respectively. These anhydrides are potentially useful for the synthesis of unsymmetrical bisannelated semibullvalenes such as **35**.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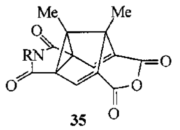
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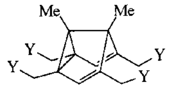
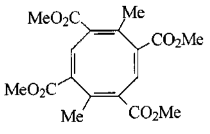

36

We are attempting to elaborate the tetraester **23**, tetraacid **27**, dianhydride **22**, and diimide **31** to functionalized semibullvalenes **36** that may serve as precursors to other novel bisannelated semibullvalenes. As already noted, the dianhydride **22** and diimide **31** are remarkably stable to thermolysis. However, the tetraester and tetraacid are much more readily thermolyzed. Grohmann et al. reported that the tetraester **23** slowly rearranges to the cyclooctatetraene **37** in refluxing acetone and similarly rearranges even upon prolonged storage in solution at temperatures as low as 5 °C.[36,48] Recently Quast et al. determined the kinetics for the relatively facile thermolysis of four of their semibullvalenes to the corresponding cyclooctatatetraenes.[49] We found that, qualitatively, the tetraacid **27** appears to be much more rapidly thermolyzed to **38** than is **23** to **37**.[50] We were unable to determine the kinetics for this thermolysis as the reaction is not completely clean and some interfering contaminants are also produced. This ease of thermolysis limits the range of synthetic possibilities and mandates that all attempted transformations must be carried out under mild conditions.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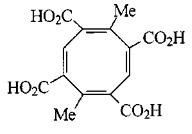
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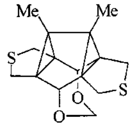
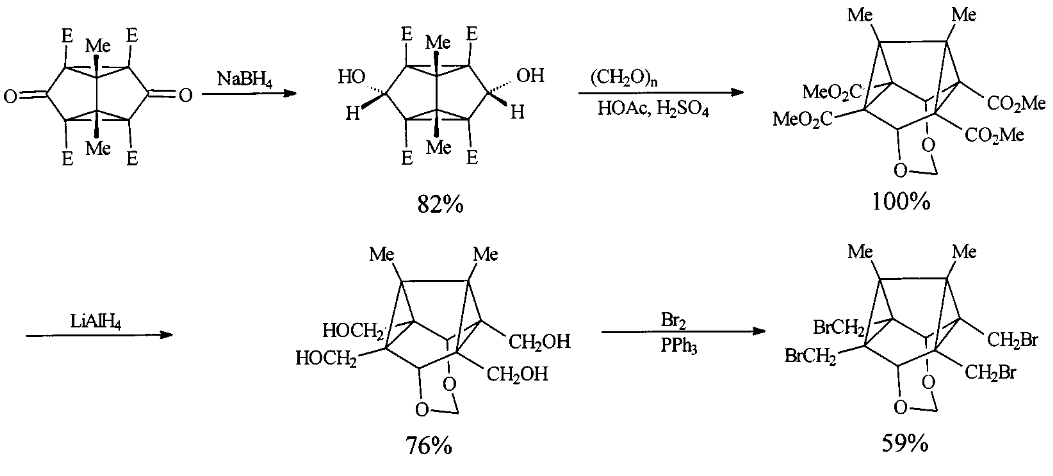

39

In a different approach to bisannelated semibullvalenes, we are also exploring the possibility of completing the annelations prior to formation of the semibullvalene nucleus (Scheme 3). Similarly to Müllen and Düll,[29] we were unable to isolate any semibullvalene products from the sulfide **39**.[51]

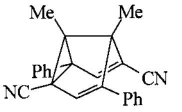
Conclusion

Our explorations in the area of annelated semibullvalenes, particularly the very detailed study of dianhydride **22**, lead to a fascinating dichotomy. Experimental evidence gathered in the condensed phases unequivocally establishes that dianhydrides **22** and **28** and diimides **31** and **32** are not homoaromatic in their ground states. Solution phase variable temperature ^{13}C NMR and UV/Vis studies demonstrate that these bisannelated semibullvalenes have exceptionally low barriers to the Cope rearrangement (e.g. ^{13}C NMR spectroscopy at 125 MHz reveals a *maximum* barrier height of 3.3 kcal/mol for **22a**$\rightleftarrows$**22b**). However, electron correlated calculations at all levels of theory that we used (semiempirical, ab initio and DFT) clearly predict homoaromatic ground states for a range of small-ring mono- and bisannelated semibullvalenes. There are two possible explanations for the origin of this dichotomy: Either the level

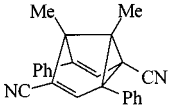


Scheme 3. The synthesis of a potential precursor to bisannelated semibullvalenes

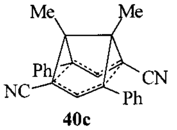
of theory used is not appropriate for the complexity of the problem or the fact that our experimental data is all from the condensed phases while, of course, our calculations apply to the isolated molecule in the gas phase. In an ideal gas phase calculation the Schrödinger equation would be solved exactly through the use of a complete basis set and full configuration interaction.[52] In practice this ideal cannot (presently) be achieved especially for quantum mechanically large molecules such as **22**. A compromise between accuracy and feasibility must be reached. In general, for molecules of this size calculations using a 6−31G* basis set and incorporating electron correlation through MP2 treatment or through the use of DFT are considered to be adequate. We have shown that there are essentially no changes between the 6−311G** and 6−31G* HF levels for calculations on **22** supporting our continuing use of the more economical 6−31G* basis set.[41] Recently, however, Schaefer et al. demonstrated, using coupled cluster theory [CCSD(T)], that the MP2 and DFT methods result in incorrect relative energy ordering of the various conformers of [10]annulene.[53] Noteworthy in these and other studies is the fact that the geometries of the various stationary points do not change greatly between the lower and higher levels of theory. It is still common, where the energy of the system is of greatest concern, to carry out geometry optimizations at a lower level and then determine single point energies at the highest practical level.[52] Indeed, Schaefer et al. used this method in their initial CCSD(T) reinvestigation of [10]annulene.[53b] Our correlated calculations reveal a single minimum potential energy surface for **22** corresponding with the delocalized structure **22c**, the localized forms **22a,b** are not stationary points on the B3LYP or MP2 surfaces. We therefore believe that the level of theory we have used is appropriate for the gas phase modeling of these annelated semibullvalenes. In systems such as these, in which there is a very fine energy balance between the homoaromatic and localized states, it is not unreasonable to postulate that matrix forces can alter the nature of the ground state.[54] In further support of this contention, Quast et al. found that in the highly dipolar solvent, *N*,*N′*-dimethylpropylene urea, the delocalized homoaromatic forms (**40c** and **41c**) of the semibullvalene **40** and barbaralane **41** are more stable than the localized forms **40a**,**b** and **41a**,**b**, while in less dipolar solvents the localized forms are the low energy species.[16b,17] These observations led Quast to conclude that the homoaromatic species will in fact be less favored in the gas phase! Clearly, much work remains to be done in this fascinating area. Although modeling studies in the solution phase can be problematic,[55] we are beginning work in this area. Another high priority in our continuing efforts is the experimental scrutiny of annelated semibullvalenes in the gas phase.



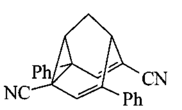
40a



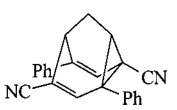
40b



40c



41a



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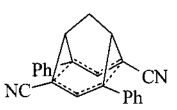

41c

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