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The Search for Bishomoaromatic Semibullvalenes and Barbaralanes: Computational Evidence of Their Identification by UV/Vis and IR Spectroscopy and Prediction of the Existence of a *Blue* Bishomoaromatic Semibullvalene

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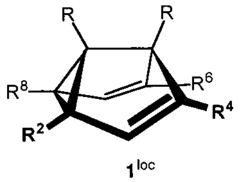
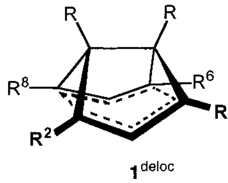
Abstract: Time-dependent B3LYP/6-31G* calculations have been performed at the optimized C_2 or C_{2v} geometries of several substituted semibullvalenes ($\mathbf{1}^{\text{deloc}}$) and barbaralanes ($\mathbf{2}^{\text{deloc}}$), to compare the computed vertical electronic excitation energies with the temperature-dependent, long-wavelength absorptions that have been observed in the UV/vis spectra of some of these compounds by Quast and co-workers. The excellent agreement between the calculated vertical excitation energies and the observed values of λ_{max} provides strong support for the identification of the bishomoaromatic species $\mathbf{1}^{\text{deloc}}$ and $\mathbf{2}^{\text{deloc}}$ as the source of these absorptions. Furthermore, the CN stretching frequencies, computed for the C_2 geometry of 1,5-dimethyl-2,6-dicyano-4,8-diphenylsemibullvalene ($\mathbf{1f}^{\text{deloc}}$), fit the low-frequency absorptions seen in the IR spectrum of **1f**, thus furnishing independent evidence that bishomoaromatic geometries of semibullvalenes have, in fact, been observed spectroscopically. B3LYP/6-31G* calculations predict that 2,6-dicyano-4,8-diphenylsemibullvalene **1c** has a C_2 equilibrium geometry ($\mathbf{1c}^{\text{deloc}}$) and that the long-wavelength UV/vis absorption ($\lambda_{\text{max}} = 585$ nm) and CN stretching frequencies (2192 and 2194 cm^{-1}) computed for $\mathbf{1c}^{\text{deloc}}$ should serve to identify this bishomoaromatic semibullvalene when it is synthesized.

Introduction

Following the serendipitous synthesis of semibullvalene (**1a**) and the discovery that it is a fluxional molecule which undergoes a very rapid, degenerate Cope rearrangement,[1] dynamic NMR studies measured $\Delta H^{\ddagger} = 4.8-5.2$ kcal/mol for this process.[2,3] With such a small enthalpy difference between the C_s, localized structure ($\mathbf{1a}^{\text{loc}}$) and the C_{2v}, bishomoaromatic transition structure ($\mathbf{1a}^{\text{deloc}}$), both theoreticians and experimentalists accepted the challenge of finding a derivative of **1** in which $\mathbf{1}^{\text{deloc}}$ is the global energy minimum.[4] Calculations have been used to investigate both the electronic stabilization of $\mathbf{1}^{\text{deloc}}$, relative to $\mathbf{1}^{\text{loc}}$, by substituents[5−10] and the destabilization of $\mathbf{1}^{\text{loc}}$, relative to $\mathbf{1}^{\text{deloc}}$, by the strain introduced by annelation.[7,11,12] Both strategies have also been investigated experimentally, and promising results have been obtained; but there is as yet no definitive evidence that a derivative of **1** has been prepared in which $\mathbf{1}^{\text{deloc}}$ is the equilibrium geometry.[4]



$\mathbf{1}^{\text{loc}}$



$\mathbf{1}^{\text{deloc}}$

(a) R = H, $R^{2,4,6,8}$ = H
(b) R = H, $R^{2,6}$ = Ph, $R^{4,8}$ = H
(c) R = H, $R^{2,6}$ = CN, $R^{4,8}$ = Ph
(d) R = Me, $R^{2,6}$ = Ph, $R^{4,8}$ = H
(e) R = Me, $R^{2,6}$ = CN, $R^{4,8}$ = H
(f) R = Me, $R^{2,6}$ = CN, $R^{4,8}$ = Ph

Dynamic NMR studies cannot distinguish between the existence of a barrier below 2−3 kcal/mol to passage through

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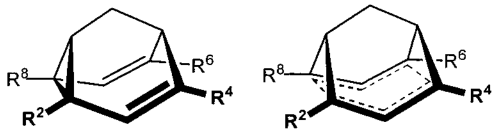
1$^{\text{deloc}}$ and the possibility that **1**$^{\text{deloc}}$ is the global energy minimum.[13] Saunders' isotopic perturbation method[14,15] and its extension to equilibrating localized and bishomoaromatic structures[16] provides, in principle, an answer to the question of how it would be possible to recognize a semibullvalene derivative that has a bishomoaromatic equilibrium geometry. However, another serendipitous observation has provided a possible criterion that does not require the synthesis of labeled derivatives.

Quast and co-workers found that crystals and solutions of **1e** are yellow,[17] even though **1e**$^{\text{loc}}$ lacks a chromophore that would be expected to produce a long-wavelength absorption. Even more surprising, the UV/vis spectrum of **1e** is temperature-dependent, with the amount of the yellow-colored species increasing with temperature. The observed thermochromism was interpreted in terms of an equilibrium between the (colorless) semibullvalene **1e**$^{\text{loc}}$ and the (yellow) bishomoaromatic structure **1e**$^{\text{deloc}}$.[18, 19]

Subsequently, additional thermochromic semibullvalenes[20] (e.g., **1d**[21] and **1f**[22]) and barbaralanes (**2b**,[23] **2d**,[24] and **2f**[25]) have been discovered, leading to the hypothesis that thermochromism is generally associated with extremely low Cope barriers. Deconvolution of the temperature-dependent UV/vis spectra of these molecules into contributions from the localized and the bishomoaromatic structures has permitted the estimation of the enthalpy differences, ΔH, between these two species[26] and the measurement of the dependence of the enthalpy differences on solvent dipolarity.[27]



2$^{\text{loc}}$ **2**$^{\text{deloc}}$

(a) $R^{2,4,6,8} = H$
(b) $R^{2,6} = Ph,\ R^{4,8} = H$
(c) $R^{2,6} = CN,\ R^{4,8} = H$
(d) $R^{2,6} = CN,\ R^{4,8} = Ph$
(e) $R^{2,4,6,8} = CN$
(f) $R^{2,4,6,8} = Ph$

Although temperature-dependent population of geometries that correspond to those of **1**$^{\text{deloc}}$ and **2**$^{\text{deloc}}$ represents a possible explanation of the thermochromism, there is currently a lacuna of independent evidence to support this hypothesis. In an attempt to fill this void, we have used time-dependent density functional theory[28] to compute the vertical excitation energies of derivatives of **1**$^{\text{deloc}}$ and **2**$^{\text{deloc}}$. In this paper we report the results of these calculations, which provide strong support for the hypothesis that these bishomoaromatic structures are, indeed, responsible for the long-wavelength absorptions that have been observed.

In addition, the computed CN stretching frequencies for **1f**$^{\text{deloc}}$ are in excellent agreement with the frequency of a mysterious band, observed below the CN stretching region in the IR spectrum of **1f**.[22] This agreement provides independent evidence that bishomoaromatic structures, such as **1f**$^{\text{deloc}}$, can be observed spectroscopically.

Finally, we have computed the UV/vis vertical excitation energy and CN stretching frequencies in **1c**$^{\text{deloc}}$, for comparison with those that will be observed when semibullvalene **1c** is synthesized. This comparison can be used to test the prediction that the equilibrium geometry of this species will prove to be that of **1c**$^{\text{deloc}}$, not **1c**$^{\text{loc}}$.[10]

Computational Methodology

All the calculations for this study were carried out with the 6-31G* basis set,[29] using Becke's hybrid, three-parameter functional[30] and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP).[31] An integration grid consisting of 99 radial points and 974 angular points was employed. A B3LYP/6-31G* vibrational analysis was performed at each stationary point found. Optimized geometries, energies, and thermal corrections for all the molecules discussed in this paper have either already been published[10] or are available as Supporting Information.

Excitation energies were computed using time-dependent density functional theory.[28] Excellent agreement with experimental values has previously been found for excitation energies computed by this method, when it is coupled with the B3LYP hybrid functional.[28,32] All of the calculations were carried out with the Gaussian 98 suite of programs.[33]

Results and Discussion

Given in Table 1 are the results of our calculations of the vertical UV/vis excitation energies of the bishomoaromatic geometries (**1**$^{\text{deloc}}$ and **2**$^{\text{deloc}}$) of the semibullvalenes (**1**) and

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(19) At least in principle, **1**$^{\text{deloc}}$ could be a local minimum, separated by a transition structure from the global minima (**1**$^{\text{loc}}$ and the product formed by its Cope rearrangement). Alternatively, **1**$^{\text{deloc}}$ could be a transition structure connecting the global minima. In the latter case the observed thermochromism would be attributed to population of energy levels of the vibration, connecting **1**$^{\text{deloc}}$ to **1**$^{\text{loc}}$, that are at or above the energy of **1**$^{\text{deloc}}$. For **1e** the value of $\Delta H^{\ddagger} = 2.2$ kcal/mol, obtained by dynamic NMR measurements,[13] is lower than, but well within experimental error of $\Delta H = 2.6$ kcal/mol,[18, 26] the enthalpy difference between **1e**$^{\text{loc}}$ and **1e**$^{\text{deloc}}$ that was obtained by variable-temperature UV/vis measurements. Therefore, if **1e**$^{\text{deloc}}$ does reside in an energy well, the well cannot be very deep.

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Table 1. B3LYP/6-31G* Vertical Electronic Excitation Energies, Expressed as Wavelengths [nm], Calculated Oscillator Strengths [*f*], and Experimental Values of λ_{max} and log ϵ for Bishomoaromatic Geometries of Semibullvalenes (**1**^{deloc}) and Barbaralanes (**2**^{deloc})

compd	λ_{calcd}	f	λ_{max}[a]	log ϵ[a,b]
1a^{deloc}	269	0.1636		
1b^{deloc}	462	0.7112		
1c^{deloc}	585	0.3327		
1d^{deloc}	388	0.5729		
1e^{deloc}	358	0.2623	360	4.08
1f^{deloc}	468	0.2919	450	4.21
2a^{deloc}	251	0.1623		
2b^{deloc}	384	0.7250	350[b]	5.27
2c^{deloc}	337	0.2889		
2d^{deloc}	473	0.3891	460	3.74
2e^{deloc}	429	0.2207		
2f^{deloc}	482	0.3612	465	3.95

[a] Solvent butyronitrile.[26] [b] This work.

barbaralanes (**2**).[34] Shown for comparison are the λ_{max} values of the temperature-dependent, long-wavelength absorptions actually seen in the UV/vis spectra of those derivatives of **1** and **2** that are thermochromic. The agreement between the computed, gas-phase and the observed, solution-phase wavelengths is very good. Even the 15 nm difference between the experimental λ_{max} values for **1f**^{deloc} and **2f**^{deloc} is mirrored by our calculations. We believe that this agreement provides convincing evidence that the thermochromism seen in **1e**, **1f**, **2b**, **2d**, and **2f** really is due to a temperature-dependent contribution to the UV/vis absorption spectra from the bishomoaromatic species, **1e**^{deloc}, **1f**^{deloc}, **2b**^{deloc}, **2d**^{deloc}, and **2f**^{deloc}.

Further evidence that bishomoaromatic structures, such as these, can be observed spectroscopically comes from comparison of the calculated, gas-phase CN stretching frequencies for **1f**^{loc} and **1f**^{deloc} with the CN stretching frequencies observed for **1f** in different media. The relevant portion of each of the experimental spectra is shown in Figure 1, and the calculated and observed frequencies are compared in Table 2.

After scaling the calculated frequencies by 0.9505 (Table 2), the CN stretching frequencies, computed for the nonequivalent cyano groups in **1f**^{loc} and the equivalent cyano groups in **1f**^{deloc}, are all higher than their experimental counterparts, recorded for solution, by ca. 5 cm^{-1}. However, the calculations predict an average difference of 27 cm^{-1} between the CN stretching frequencies in **1f**^{loc} and **1f**^{deloc}, which is almost exactly the average difference (26 cm^{-1}) between the pair of higher-frequency CN stretches and the lower-frequency CN stretch in the experimental spectrum. This agreement provides strong evidence that the lower-frequency CN stretches in the experimental IR spectra do, indeed, belong to **1f**^{deloc}.

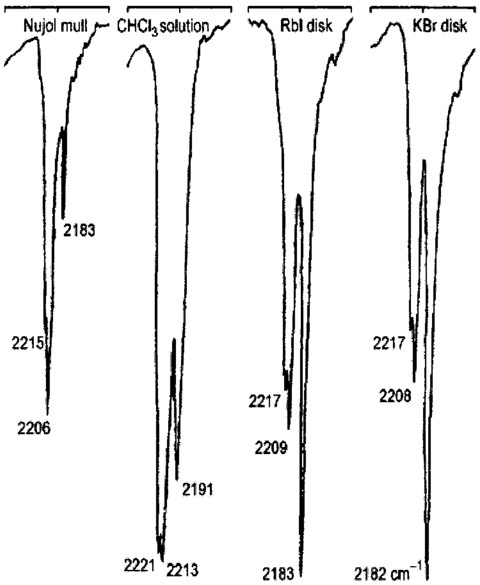

Figure 1. IR spectra recorded for **1f** in the range 2000−2200 cm^{-1}. The lowest frequencies are assigned to the bishomoaromatic structure **1f**^{deloc}.

Table 2. Comparison of B3LYP/6-31G* CN Stretching Frequencies [cm^{-1}], Computed for Localized and Bishomoaromatic Semibullvalene- (**1**^{loc}/**1**^{deloc}) and Barbaralanedicarbonitriles (**2**^{loc}/**2**^{deloc}), with the CN Stretching Frequencies Actually Found in the IR Spectra

	cyclopropyl-CN		C=C−CN			antisym. CN	sym. CN	
cmpd	calcd[a]	exptl	calcd[a]	exptl	cmpd	calcd[a]	calcd[a]	exptl[b]
1e^{loc}	2231	2230.5[c]	2217.5	2218.0[c]	**1e**^{deloc}	2202	2202	
1f^{loc}	2228	2221[d]	2217.5	2213[d]	**1f**^{deloc}	2196	2195	2191[d]
		2217[e]		2208[e]				2182[e]
		2217[f]		2209[f]				2183[f]
		2215[g]		2206[g]				2183[g]
		2215[h]		2206[h]				2182[h]
2c^{loc}	2237	2239.7[i]	2220	2216.8[i]	**2c**^{deloc}	2207	2205	
		2238.8[j]		2216.6[j]				
2d^{loc}	2235	2229[k]	2219	2209[k]	**2d**^{deloc}	2200	2200	

[a] A scaling factor for the calculated frequencies of 0.9505 was used. It is the average of the scaling factors that are necessary to fit the B3LYP/6-31G* CN stretching frequencies for **1e**^{loc} and **2c**^{loc}, which are given in the Table. [b] The CN frequency below the usual CN range[22] (Figure 1) is assigned to the antisymmetrical and symmetrical CN vibrations of **1f**^{deloc}. [c] Solution in tetrachloroethene.[17] [d] Solution in chloroform.[22] [e] KBr pellet.[22] [f] RbI pellet.[22] [g] Nujol mull.[22] [h] Fluorolube mull.[22] [i] Solution in tetrachloroethene.[35] [j] Solution in chloroform.[35] [k] Solution in dichloromethane.[24]

Why do the IR spectra of the other semibullvalenes and barbaralanes listed in Table 2 not show the predicted bands for the CN stretches in the corresponding bishomoaromatic species? We believe that these bands are probably present in the IR spectra but are too weak to be seen. Previous measurements have found that the enthalpy difference between the bishomoaromatic species and the localized semibullvalene or barbaralane is significantly larger for all the other molecules in Table 2 than for **1f**^{deloc} and **1f**^{loc}.[26, 27, 36]

Table 3 shows that, in agreement with experiment, B3LYP/6-31G* calculations predict **1f** is the most likely of the known semibullvalenes and barbaralanes to be bishomoaromatic.

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(34) The vertical excitation energies of the localized semibullvalenes **1**^{loc} and barbaralanes **2**^{loc} were also computed and are given in the Supporting Information. Unlike the case for the bishomoaromatic geometries **1**^{deloc} and **2**^{deloc}, long-wavelength absorptions are not predicted for either **1**^{loc} or **2**^{loc} by the calculations.

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(36) The enthalpy differences are solvent dependent, with dipolar solvents generally providing the smallest enthalpy differences.[27] It is significant, therefore, that the relative intensities of the lower-frequency CN stretches in Figure 1 increase with the polarity of the medium in which each IR spectrum was obtained.

Table 3. B3LYP/6-31G* Enthalpies at 298 K [ΔH_{Rel} (kcal/mol)] of the Delocalized, Bishomoaromatic Geometries, Relative to the Localized Geometries, of Semibullvalenes (**1**) and Barbaralanes (**2**), Experimental Enthalpies of Activation for the Cope Rearrangements ($\Delta H^{\ddagger}$) and Enthalpy Differences (ΔH) between the Localized and Bishomoaromatic Structures, as Estimated from Variable-Temperature UV/Vis Spectra

cmpd	ΔH_{rel}	$\Delta H^{\ddagger a}$	ΔH
1a	4.5[b]	4.8[c], 5.2[d]	
1b	−0.9[e]		
1c	−6.2[f]		
1d	3.9		
1e	0.7[e]	2.2	2.6[g,h]
1f	−2.0,[e] −1.9[i]		1.0[j]
2a	6.5	7.6	
2b	3.2	4.7	4.4[g,k]
2c	2.9	5.7	
2d	−1.5		1.6[l]
2e	−0.7		
2f	−1.3		1.8[l]

[a] Reference 13. [b] Reference 12. [c] Reference 2. [d] Reference 3. [e] Reference 10. [f] Difference between the B3LYP/6-31G*//RHF/6-31G* energies, since no stationary point was found for the localized geometry (**1c**^{loc}) by B3LYP/6-31G*.[10] [g] In butyronitrile.[26] [h] See p 34 of the Supporting Information for details. [i] Difference between B3LYP/6-31G*//RHF-6-31G* energies.[10] [j] Estimated for saturated hydrocarbon solvents from the value for butyronitrile and the difference (0.8 kcal/mol) between ΔH for this solvent and for saturated hydrocarbon solvents from measurements on **2d**.[27] [k] See p 35 of the Supporting Information for details. [l] In saturated hydrocarbon solvents.[27]

However, the calculations find that the methyl groups at the bridgehead carbons, C-1 and C-5, prevent maximal stabilization of **1f**$^{\mathrm{deloc}}$ by the phenyl groups at C-4 and C-8 by forcing the phenyls to twist out of conjugation (by 42°) with the 2p-π AOs at these carbons.[10] Replacing the methyls with hydrogens reduces the computed phenyl twist angles by 30°, so that the phenyl groups are predicted to provide considerably more stabilization for **1c**$^{\mathrm{deloc}}$ than for **1f**$^{\mathrm{deloc}}$.[37]

In fact, B3LYP/6-31G* calculations find that semibullvalene **1c**$^{\mathrm{loc}}$ is not a potential energy minimum; and comparisons of B3LYP/6-31G* energies at RHF optimized geometries place the delocalized, homoaromatic geometry (**1c**$^{\mathrm{deloc}}$) 6.2 kcal/mol lower in energy than the localized geometry (**1c**$^{\mathrm{loc}}$).[10] However, as is apparent in Table 3, B3LYP/6-31G* calculations tend to overestimate the stability of the delocalized geometries of **1** and **2**, relative to the localized geometries, by up to 3 kcal/mol. Nevertheless, even after correcting for this error, our calculations unequivocally predict that **1c** should be bishomoaromatic.

The phenyl groups in **1c**$^{\mathrm{deloc}}$, which are more highly conjugated than those in **1f** $^{\mathrm{deloc}}$, are computed to shift the vertical electronic transition of lowest energy from 468 nm in **1f** $^{\mathrm{deloc}}$ to 585 nm in **1c**$^{\mathrm{deloc}}$. Thus, **1c**$^{\mathrm{deloc}}$ should be blue; and since it is predicted to be an energy minimum, its UV/vis spectrum should not be highly temperature-dependent.[38]

The IR spectrum of **1c** is also expected to be very different from the IR spectra of all the other dinitriles in Table 1. A pair of high-frequency CN stretches, due to the presence of **1c**$^{\mathrm{loc}}$, is not expected to be observed. Only closely spaced bands at 2192 and 2194 cm^{-1}, corresponding to, respectively, the antisymmetric and symmetric combinations of CN stretches in bishomoaromatic species **1c**$^{\mathrm{deloc}}$, are predicted to be seen.

Conclusions

We hope the unequivocal prediction that semibullvalene **1c** will turn out to be bishomoaromatic,[10] combined with the predicted UV/vis and IR spectroscopic signatures of **1c**$^{\mathrm{deloc}}$ in this paper, will stimulate the synthesis of the first molecule that will be found to display neutral bishomoaromaticity at its equilibrium geometry.[19] Since **1f** has been synthesized,[22] and a promising precursor to **1c** is readily available,[40] the preparation of **1c**, which differs from **1f** only by the absence of the methyl groups at C-1 and C-5, seems well within the realm of possibility.

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Supporting Information Available: Optimized geometries, energies, and thermal corrections for **1b**$^{\mathrm{loc}}$/**1b**$^{\mathrm{deloc}}$, **1f**$^{\mathrm{loc}}$/**1f**$^{\mathrm{deloc}}$, and **2a**$^{\mathrm{loc}}$/**2a**$^{\mathrm{deloc}}$ − **2f**$^{\mathrm{loc}}$/**2f**$^{\mathrm{deloc}}$, electronic excitation energies and oscillator strengths for **1a**$^{\mathrm{loc}}$/**1a**$^{\mathrm{deloc}}$ − **1f**$^{\mathrm{loc}}$ /**1f**$^{\mathrm{deloc}}$**,** and **2a**$^{\mathrm{loc}}$ /**2a**$^{\mathrm{deloc}}$ − **2f**$^{\mathrm{loc}}$ /**2f**$^{\mathrm{deloc}}$, and experimental details for how the UV/vis spectra of **1e** and **2b** were obtained and analyzed (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(37) Similarly, as shown in Table 3, phenyl groups at C-2 and C-6 are predicted to provide considerably more stabilization ofr **1b**$^{\mathrm{deloc}}$ than **1d**$^{\mathrm{deloc}}$.

(38) The vibration that distorts **1c**$^{\mathrm{deloc}}$ toward the geometry of **1c**$^{\mathrm{loc}}$ is computed to have $\bar{\nu} = 355$ cm^{-1}, resulting in predicted populations of the $n = 1$ level of 1, 7, 15, and 22% at temperatures of 100, 200, 300, and 400 K, respectively. Due to the expected difference between the spacing of energy levels for this vibration in the ground and excited electronic states of **1c**$^{\mathrm{deloc}}$,[39] $\lambda_{\max}$ for the long-wavelength absorption in the vis spectrum of **1c**$^{\mathrm{deloc}}$ might appear to shift slightly to the blue as the temperature is raised.

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