Annelated Semibullvalenes: A Theoretical Study of How They "Cope" with Strain

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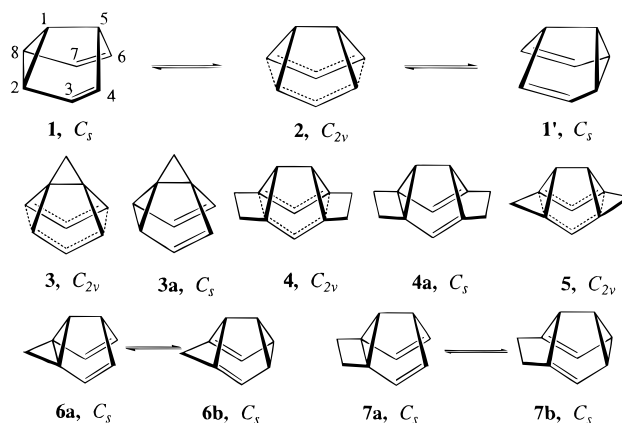
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Abstract: High levels of ab initio (MP2, CASSCF, CASPT2N) and density functional (Becke3LYP) theory have been used to assess the homoaromatic character of some strained semibullvalenes. Based on geometric, energetic, and magnetic criteria (magnetic susceptibility exaltations and the nucleus independent chemical shifts, NICS), C_s semibullvalene itself is not aromatic, but the C_{2v} transition state for its Cope rearrangement is highly bishomoaromatic. Appropriate annelations destabilize the C_s geometries, and the bishomoaromatic structures are the only minima for several semibullvalenes: 1,5-methano; 2,8:4,6-bisethano and -bismethano; and 2,8-monoethano. In contrast, the 4,6-ethanosemibullvalene is predicted to be localized and not homoaromatic. Inclusion of dynamic electron correlation is very important for computing the geometries and relative energies of the delocalized structures. To aid experimental investigations, the UV and ^{13}C NMR spectra of some of the semibullvalenes have been predicted. Long-wavelength UV absorptions and down-field ^{13}C NMR chemical shifts for $C_{2,8,4,6}$ are characteristic.

Introduction

Semibullvalene (**1**) has intrigued chemists since it was first prepared by Zimmerman *et al.*[1] in 1966. The barrier to the degenerate Cope rearrangement in semibullvalene (4.8 kcal/mol)[2] is much smaller than that in 1,5-hexadiene (33.5 kcal/mol)[3] and in bullvalene (10.9 kcal/mol).[4] The small barrier in **1** raises the possibility that appropriate substituents might stabilize the delocalized bishomoaromatic transition state (**2**) to such an extent that it becomes an energy minimum.[5−7] Dannenberg,[5] Hoffmann,[6] and Dewar[7] suggested that electron-withdrawing groups at $C_{2,8}$, $C_{3,7}$, and $C_{4,6}$ might stabilize **2** preferentially and eliminate the barrier. However, despite numerous attempts, no experimental realization of a homoaromatic semibullvalene ground state has been achieved.[8] Taking a different approach, Jiao and Schleyer[9] recently predicted

computationally that **2** is stabilized, relative to **1**, by Li$^+$ complexation. The upfield Li chemical shift computed for the **2**-Li$^+$ complex provided good evidence for the aromaticity of the complex.

1, C_s **2**, C_{2v} **1'**, C_s

3, C_{2v} **3a**, C_s **4**, C_{2v} **4a**, C_s **5**, C_{2v}

6a, C_s **6b**, C_s **7a**, C_s **7b**, C_s

Annelation strategies, which employ strain to destabilize the C_s localized geometry and thus to favor the delocalized C_{2v} geometry, also have been proposed.[10] MNDO (2×2 CI) semiempirical calculations by Dannenberg *et al.* predicted the C_{2v} structure of 1,5-methanosemibullvalene (**3**)[5] to be 9.1 kcal/mol lower in energy than the C_s localized form **3a**. This preference for **3** over **3a** was ascribed to the strain reduction

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when the $C_2-C_1-C_8$ angle is opened and also to the electronic interaction of the symmetric combination of the allyl nonbonding orbitals with a cyclopropane orbital of appropriate symmetry. Williams and Kurtz's MNDO and AM1 (2×2 CI) semiempirical calculations indicated that 2,8:4,6-bisethano annelation results in a delocalized C_{2v} (**4**) energy minimum, 10.4 kcal/mol lower in energy (MNDO) than the localized form (**4a**).[11]

We have now used ab initio and density functional theory (DFT) calculations to compare the geometries, energies, and magnetic properties of the annelated semibullvalenes **3** and **4** with those of the parent **1**. Other strained semibullvalenes, with bismethano (**5**), monomethano (**6**), and monoethano (**7**) annelations,[12] also have been examined. We have computed the UV and ^{13}C NMR spectra of the C_{2v} geometries of **3** and **4** to aid experimental investigations.

Computational Methodology

Geometries were optimized at the HF, MP2(fc), Becke3LYP, and (6,6)CASSCF levels by using the 6-31G* basis set with the Gaussian 94 suite of programs.[13] Vibrational frequencies (at HF/6-31G*, Becke3LYP/6-31G*, and CASSCF/3-21G) were used to characterized the nature of stationary points.[14] Single-point CASSCF and CASPT2N energies were computed at the CASSCF/6-31G* geometries with the 6-31G* and 6-311G** basis sets, using the MOLCAS program.[15] Magnetic susceptibilities and ^{13}C NMR chemical shifts were computed at the Becke3LYP/6-31G* geometries, with Kutzelnigg's IGLO (individual gauge for localized orbitals) method and the standard DZ basis set.[16] Nucleus independent chemical shifts (NICS)[17] were computed at GIAO-SCF /6-31G* with Gaussian 94.

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Table 1. Calculated Relative Electronic Energies (E_{rel}, kcal/mol) and Activation Enthalpies ($\Delta H^{\ddagger}_a$, kcal/mol) of Semibullvalene in C_s (**1**) and C_{2v} (**2**)

level	$E_{rel}{}^a$	$\Delta H^{\ddagger}{}^b$
HF/3-21G	13.4	12.3
HF/6-31G*	18.0	16.9
MP2(fu)/6-31G*	5.2	4.1
Becke3LYP/6-31G*	5.6	4.5
Becke3LYP/6-311G*	5.2	4.1^c
Becke3LYP/6-311+G*	4.9	3.8^c
Becke3LYP/6-311+G(2d,p)	4.4	3.3^c
(6,6)CASSCF/3-21G	6.8	5.7
(6,6)CASSCF/6-31G*	10.4	9.3^d
CASPT2N/6-31G*	8.0	6.9^d
(6,6)CASSCF/6-31G*	10.7	9.6
CASPT2N/6-31G*	9.3	8.2^e
CASPT2N/6-31G*	7.1	6.0^f
expt		4.8 ± 0.1^g

^{a} Energy difference between the C_{2v} (**2**) and C_s (**1**) semibullvalene. ^{b} $\Delta H^{\ddagger} = E_{rel} + \Delta$ZPE [Becke3LYP/6-31G*, 83.3 kcal/mol (C_{2v}, **1**) and 84.4 kcal/mol (C_s, **2**) at 0 K]. ^{c} Using Becke3LYP/6-31G* geometries. ^{d} Using (6,6)CASSCF/3-21G geometries. ^{e} Using (6,6)CASSCF/6-31G* geometries. ^{f} Minimum energy geometry predicted using three CASPT2N energies fitted to a quadratic equation (see text), and the CASPT2N/6-31G*//(6,6)CASSCF/6-31G* C_s energy was used for the E_{rel} calculation. ^{g} Reference 2.

Results and Discussion

Semibullvalene 1. The relative energies between C_s (**1**) and C_{2v} (**2**) semibullvalene are summarized in Table 1. At all levels **1** is computed to be the energy minimum and **2** is found to be the transition state for a boat-like Cope rearrangement. However, HF, CASSCF, and CASPT2N//CASSCF activation enthalpies are significantly (>3 kcal/mol) higher than the experimental value of 4.8 ± 0.1 kcal/mol.[2] Computational studies of the Cope rearrangement of 1,5-hexadiene have shown that (6,6)-CASSCF calculations do not give correct transition state geometries or energies.[18] Because dynamic electron correlation is not included, the (6,6)CASSCF tends to overestimate the diradical character of the wave function for the active electrons in the transition states for pericyclic reactions.[19] The C_{2v} geometry of semibullvalene (**2**) was refined at CASPT2N, which includes dynamic electron correlation.

Since it was not possible to optimize the geometry of **2** fully at the CASPT2N level, the same strategy used in the calculations of the Cope rearrangement of 1,5-hexadiene[18] was employed. Single-point CASPT2N calculations were performed at various C_{2v} geometries. These were optimized at the CASSCF level with fixed values of the $C_2-C_1-C_8$ ($C_4-C_5-C_6$) angle which controls the interallylic distance, R, at each C_{2v} geometry (Figure 1). The CASPT2N energies were fitted to a quadratic potential; these gave an optimized $C_2-C_1-C_8$ angle for the C_{2v} geometry (**2**) of semibullvalene.

The smaller CASPT2N interallylic distance, R, in **2** results in stronger interaction between the two allylic fragments. The resulting decrease in the diradical character of **2** is reflected in the increase in the ratio in the CASSCF wave function (Table 2) of the squares of the coefficients of the two most important configurations, $|...a_1^2 b_2^2 b_1^2\rangle$ and $|...a_1^2 b_2^2 a_2^2\rangle$. After CASPT2N geometry optimization, the CASSCF wave function is dominated by the first configuration, which corresponds to the orbital occupancy of a fully delocalized, aromatic species.

As shown in Table 1, the CASPT2N//CASPT2N value of $\Delta H^{\ddagger}$ is closer to experiment than the CASPT2N//CASSCF for

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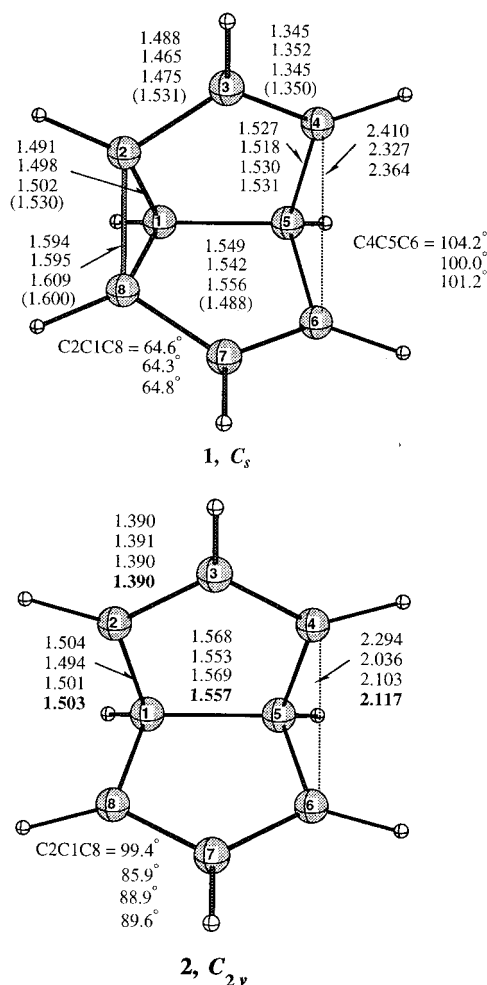
Figure 1. Optimized C_s (**1**) and C_{2v} (**2**) geometries (angstroms and degrees) for semibullvalene at (6,6)CASSCF/6-31G*, MP2(fc)/6-31G*, Becke3LYP/6-31G*, and CASPT2N/6-31G* (in bold). Values in parentheses were obtained by gas-phase electron diffraction.[20]

Table 2. Calculated Interallylic Bond Lengths, R (Å), and Ratios of the Weights (c_1^2/c_2^2) of the Two Most Important CASSCF Configurations at (6,6)CASSCF/6-31G* and CASPT2N/6-31G* Geometries of Semibullvalene (**2**), Methanosemibullvalene (**3**), and Bis(ethano)semibullvalene (**4**)

molecule	geometry	R (Å)	ratio $(c_1^2/c_2^2)^a$
2 (C_{2v})	(6,6)CASSCF/6-31G*	2.294	6.9
	CASPT2N/6-31G*	2.117	15.6
3 (C_{2v})	(6,6)CASSCF/6-31G*	2.615	1.7
	CASPT2N/6-31G*	2.477	3.3
4 (C_{2v})	(6,6)CASSCF/6-31G*	2.168	6.4
	CASPT2N/6-31G*	2.075	10.4

^{a} c_1 is the coefficient of the configuration $|...a_1^2 b_2^2 b_1^2\rangle$, and c_2 is the coefficient of $|...a_1^2 b_2^2 a_2^2\rangle$.

2, while Becke3LYP/6-31G* gives the best agreement with the measured activation enthalpy. However, the correspondence between the Becke3LYP/6-31G* (4.5 kcal/mol) and the experimental (4.8±0.1 kcal/mol)[2] values is fortuitous, since Becke3LYP calculations with larger basis sets give $\Delta H^{\ddagger}$ values which deviate significantly from experiment.

As shown in Figure 1, the MP2(fc)/6-31G*, Becke3LYP/6-31G*, and (6,6)CASSCF/6-31G* geometries for C_s semibullvalene (**1**) correspond well with one another. They also agree with the gas-phase electron diffraction structure of **1**,[20] except for the large discrepancies in the C_1-C_5 and C_2-C_4 bond lengths. The experimental C_1-C_5 (1.488 Å) distance is too short and the C_2-C_3 bond length (1.531 Å) is too long (compare,

e.g., 1.499 Å in cyclopentadiene and 1.498 Å in 1,3-pentadiene[21]). Evidently, the lengths assigned to the C_1-C_5 and C_2-C_3 bonds from the electron diffraction data need to be interchanged; this would result in good agreement with the computed bond lengths.

The distance between vinyl carbons C_4 and C_6 in **1** is 2.410 ((6,6)(CASSCF), 2.327 (MP2(fc)), and 2.364 Å (Becke3LYP/6-31G*). Does a long-range interaction between C_4 and C_6 at such large distances result in some degree of homoaromaticity in **1**?

In order to asses the homoaromaticity of semibullvalene **1**, we calculated its magnetic susceptibility exaltation (Λ), which is associated uniquely with aromaticity.[22,23] Generally, Λ is defined as the difference between the bulk magnetic susceptibility (χ_M) of a compound and the susceptibility (χ_M') estimated from an additivity scheme for the same structure, assuming no cyclic delocalization ($\Lambda = \chi_M - \chi_M'$).[22] Since magnetic susceptibilities of non-aromatic organic molecules show additive behavior of their constituent groups, values of χ_M' can be estimated within an accuracy of a few ppm cgs by increment methods based on group (e.g., CH_3, CH_2, CH, and C) contributions. Due to ring current effects, aromatic compounds show diamagnetic susceptibility exaltations (more negative values of χ_M than those expected from the group additivity). The magnetic susceptibilities reported in this paper are derived from IGLO computations.

In addition to magnetic susceptibility exaltations, nucleus independent chemical shifts (NICS) are also simple and efficient probes for aromaticity.[17] NICS, the negative of the absolute magnetic shielding, can be computed at the ring center (nonweighted mean of the heavy atom coordinates on the ring perimeter) with the Gaussian 94 program. Negative NICS values denote aromaticity (-11.5 for benzene) and positive NICS values antiaromaticity (28.8 for cyclobutadiene). Nonaromatics have negligible NICS (-2.1 for cyclohexane).

NICS as an indicator of aromaticity agrees well with magnetic susceptibility exaltation and has the advantage of being less dependent on ring size and can be used for individual rings in polycyclic systems. For example, the NICS values for the five- (-21.5) and seven-membered (-8.3) rings of azulene resemble cyclopentadienyl anion (-19.4) and tropylium ion (-8.2). The calculated NICS values for benzocyclobutadiene show that the aromaticity of the six-membered ring (-4.2) is reduced from

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Table 3. IGLO/DZ//MP2(fc)/6-31G* Computed and Experimental[a] (given in parentheses for comparison) Magnetic Susceptibilities (χ_{tot}), Magnetic Susceptibility Exaltations (Λ_{tot}, in ppm cgs), and Nucleus Independent Chemical Shifts (NICS, ppm) for Cyclopropane and Its Methyl Derivatives at GIAO-SCF/6-31G*//MP2(fc)/6-31G* as Well as Reference Molecules

molecules and group increments	χ_{tot}	Λ_{tot}	NICS
CH_3^-	-17.8^b		
$>CH_2$	-14.8^c		
$-CH<$	-11.5^d		
$>C<$	-7.6^e		
$-CH=CH-$	-20.0^f		
$>C=C<$	-13.8^g		
cyclopropane	-48.6 (-39.9)	-4.2 $(-4.5)^h$	-43.3 $(-7.7)^i$
bicyclopropyl	-90.8	-8.6	-43.2
methylcyclopropane	-63.3	-4.4	-44.0
cis-1,2-dimethylcyclopropane	-78.1	-4.7	-43.5
trans-1,2-dimethylcyclopropane	-77.8	-4.4	-44.6
cis,cis-1,2,3-trimethylcyclopropane	-93.6	-5.7	-42.6
spiropentane	-77.9	-11.1	
benzene	-74.5 (-54.7)	-14.5 $(-14.8)^h$	
ethane	-35.6 (-26.8)		
propane	-50.4 (-38.6)		
isobutane	-64.9 (-50.5)		
neopentane	-78.8 (-63.1)		
ethylene	-23.7 (-18.8)		
1,3-butadiene	-43.7 (-32.1)		
2,3-dimethyl-2-butene	-85.0 (-65.9)		

[a] Experimental data are taken from ref 16e. [b] From C_2H_6. [c] From propane − ethane. [d] From isobutane − $3CH_3$. [e] From neopentane − $4CH_3$. [f] From 1,3-*trans*-butadiene − ethylene. [g] From 2,3-dimethyl-2-butene − $4CH_3$. [h] The exaltation from Dauben (ref 22) increment systems is -5.1 for cyclopropane and -13.7 for benzene, see also ref 16c. [i] At a point 1.1 Å above the three-ring center.

Table 4. IGLO/DZ//Becke3LYP/6-31G* Computed Magnetic Susceptibilities (χ_{tot}), Magnetic Susceptibility Exaltations (Λ_{tot}, ppm cgs), and δLi^+ for Some Lithium Cation Complexes as Well as Nucleus Independent Chemical Shifts (NICS, ppm) at GIAO-SCF/6-31G*//Becke3LYP/6-31G* for **1**–**7**

compd	symmetry	χ_{tot}	Λ_{tot}	NICS	δLi^+
1	C_s	-92.9	-6.9	-10.3	
2	C_{2v}	-114.8	-28.8	-22.7	-10.8
3a[a]	C_s	-102.9	-9.9	-7.5	
3	C_{2v}	-126.6	-33.6	-22.5	
4a[a]	C_s	-137.9	-6.7	-14.9	
4	C_{2v}	-148.7	-17.5	-22.6	-9.1
5	C_{2v}	-125.9	-24.3	-23.6	-7.9
6a	C_s	-111.0	-18.0	-15.2	
7a	C_s	-131.0	-23.2	-22.5	
7b	C_s	-116.9	-7.5	-12.7	

[a] The localized HF/6-31G* geometries are used, since both **3a** and **4a** do not exist at the Becke3LYP/6-31G*.

that in benzene and the antiaromaticity of the four-membered ring (21.5) is reduced from that in cyclobutadiene.[17a]

In order to analyze C_s semibullvalene (**1**), the abnormal magnetic properties of the cyclopropane ring need to be taken into account.[24] Table 3 summarizes the calculated magnetic susceptibilities of group increments and their reference molecules, as well as magnetic properties for the parent and methyl-substituted cyclopropanes. Cyclopropane is computed to have a magnetic susceptibility exaltation of $\Lambda = -4.2$ ($\Lambda = -5.1$ experimentally[22]) and a NICS of -43.3. However, this large NICS is due in part to the local shielding of the C−C bonds, since the ring center in cyclopropane is only 0.44 Å away from the midpoints of these bonds. For comparison, we calculate that the NICS value for planar cyclohexane (D_{6h}) is only -1.7 at the ring center, but about -30 at a distance of 0.4 Å from a C−C bond. The average contribution of the exalted magnetic susceptibility of three-membered rings is ca. -4.5 ppm cgs.

The IGLO/DZ//Becke3LYP/6-31G* magnetic susceptibility exaltation for **1** is only -6.9 ppm cgs (Table 4), which is much smaller than that of -13.4 ppm cgs for benzene.[25] When the

contribution of the three-membered ring (-5.7 ppm cgs for trimethylcyclopropane, Table 3) is deleted, the susceptibility of **1** is found not to be exalted. Hence, C_s semibullvalene is not aromatic.

The same conclusion is reached from the NICS value for **1**, which is computed to be -10.3 ppm at the geometric center of the six "active" atoms ($C_{2,3,4,6,7,8}$). However, this geometric center is only *ca.* 1.1 Å above the three-membered ring. The face of a cyclopropane ring is known to result in shielding, as discussed by Jackman and Sternhell.[26] To demonstrate this, we calculated a set of NICS values at points above the center of the ring plane in cyclopropane. At distances of 1.0 and 1.1 Å, the calculated NICS values of -9.4 and -7.7 ppm are close to the value of -10.3 in C_s semibullvalene. This indicates that the cyclopropane unit in semibullvalene is largely responsible for the NICS value and that there is no significant contribution from homoconjugation.

In contrast to **1**, the C_{2v} semibullvalene transition state **2** is delocalized. The optimized geometries at the Becke3LYP and CASPT2N levels agree well (Figure 1). The C−C bond lengths of 1.390 Å are close to those in benzene as well as those in other pericyclic transition state structures.[23] The interallylic distance, $R \approx 2.1$ Å, is in the same range as the forming/breaking C−C bond lengths in the aromatic transition structure of the parent Cope rearrangement of 1,5-hexadiene[18,27] and in many other pericyclic reactions. Thus, the geometry of **2** suggests that it is bishomoaromatic.

The magnetic susceptibility exaltation of -28.8 ppm cgs is larger in magnitude than that in semibullvalene (Table 4), and the large upfield Li^+ chemical shift of -10.8 ppm in the C_{2v} Li^+ complex provides independent evidence of the bishomoaromatic character of **2**.[9] The calculated NICS value of -22.7 at

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(25) Jiao, H.; Schleyer, P. v. R. Antiaromaticity: Evidence from Magnetic Criteria. In *Proceedings of the First European Conference on Computational Chemistry*; Bernardi, F., Rivail, J.-L., Eds.; American Institite of Physics: Woodbury, NY, 1995; p 107.

(26) Jackman, L. M.; Sternhell, S. *Applications of Nuclear Magnetic Resonance spectroscopy in Organic Chemistry*, 2nd ed.; Pergamon Press: Oxford, 1969; Vol. 5.

(27) Jiao, H.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 334 and cited references

Table 5. Calculated Relative Electronic Energies (E_{rel}, kcal/mol) of 1,5-Methanosemibullvalene in C_s (**3a**) and C_{2v} (**3**)

level	$E_{rel}{}^a$
HF/6-31G*	12.1
Becke3LYP/6-31G*	-3.3^b
(6,6)/CASSCF/3-21G	-10.3
(6,6)/CASSCF/6-31G*	-8.1^c
CASPT2N/6-31G*	-4.3^c
(6,6)/CASSCF/6-31G*	-7.1
(6,6)/CASSCF/6-311G**	-7.4^d
CASPT2N/6-31G*	-3.3^d
CASPT2N/6-31G*	-3.9^e
MNDO	$(-9.1)^f$

^{a} Energy difference between C_{2v} (**3**) and C_s (**3a**) 1,5-methanosemibullvalene. ^{b} Becke3LYP/6-31G* single-point calculations using the HF/6-31G* geometry, since the C_s form collapses to the C_{2v} form at Becke3LYP/6-31G*. ^{c} Using (6,6)CASSCF/3-21G geometries. ^{d} Using (6,6)CASSCF/6-31G* geometries. ^{e} Minimum energy geometry predicted using three CASPT2N energies fitted to a quadratic equation (see text), and the CASPT2N/6-31G*//(6,6)CASSCF/6-31G* C_s energy was used for the E_{rel} calculation. ^{f} Reference 5 (the MNDO (2×2 CI) activation energy is the difference between the calculated heats of formation for the localized (**3a**) and homoconjugated (**3**) forms).

the geometric center of the active atoms ($C_{2,3,4,6,7,8}$) is the same as found in the aromatic transition state of the boat Cope rearrangement of 1,5-hexadiene. (The NICS value of the chair-like transition state is -24.9 ppm.[28])

1,5-Methanosemibullvalene (3). The methano bridge in 1,5-methanosemibullvalene results in a strained spiropentane moiety in the C_s structure (**3a**), which is absent in the C_{2v} alternative. Based on MNDO (2×2 CI), Dannenberg *et al.*[5] predicated 1,5-methanosemibullvalene to have a C_{2v} equilibrium geometry (**3**), which was computed to be 9.1 kcal/mol lower in energy than the C_s form (**3a**). At HF/6-31G*, **3** is the transition state for the Cope rearrangement, 12.1 kcal/mol higher in energy than the C_s ground state equilibrium geometry. However, electron-correlated Becke3LYP/6-31G* and MP2(fc)/6-31G* optimizations lead the C_s form to the bishomoaromatic **3** (C_{2v}). Frequency calculations at Becke3LYP/6-31G* show that **3** is an energy minimum. The energy difference between **3** and **3a** is only 3.3 (Becke3LYP/6-31G*, using the HF geometry for **3a**) and 3.9 kcal/mol (CASPT2N) (Table 5).

As shown in Figure 2, the Becke3LYP/6-31G* and MP2-(fc)/6-31G* geometries are similar with interallylic distances of $R = 2.279$ and 2.243 Å, respectively. The (6,6)CASSCF/6-31G* value of $R = 2.615$ Å is much larger, and the CASPT2N/6-31G* distance ($R = 2.477$ Å) is intermediate. The large interallylic distances in **3** result in considerable diradical character in the wave functions. This is reflected in the relatively small $c_1{}^2/c_2{}^2$ ratios of 3.3 and 1.7 at the CASPT2N and CASSCF geometries, respectively (Table 2). As discussed above for **2**, CASSCF probably overestimates the diradical character of the wave function and, hence, the interallylic distance. On the other hand, because of the importance of the second configuration in the wave function for **3**, computational methods, such as MP2 and DFT, which are based on a single determinantal wave function, may underestimate the diradical character of the wave function and, hence, the interallylic distance. CASPT2N is most likely to give the most accurate value of R in **3**.

The magnetic properties calculated for **3** show it to be a neutral bishomoaromatic. At IGLO/DZ//MP2(fc)/6-31G*, **3** is computed to have a very large magnetic susceptibility exaltation of -33.6 ppm cgs. After deleting the estimated cyclopropyl

(28) Jiao, H.; Schleyer, P. v. R. Unpublished results. The NICS are computed at the GIAO-SCF-6-31G* level with the CISD/6-31G* geometries taken from ref 27.
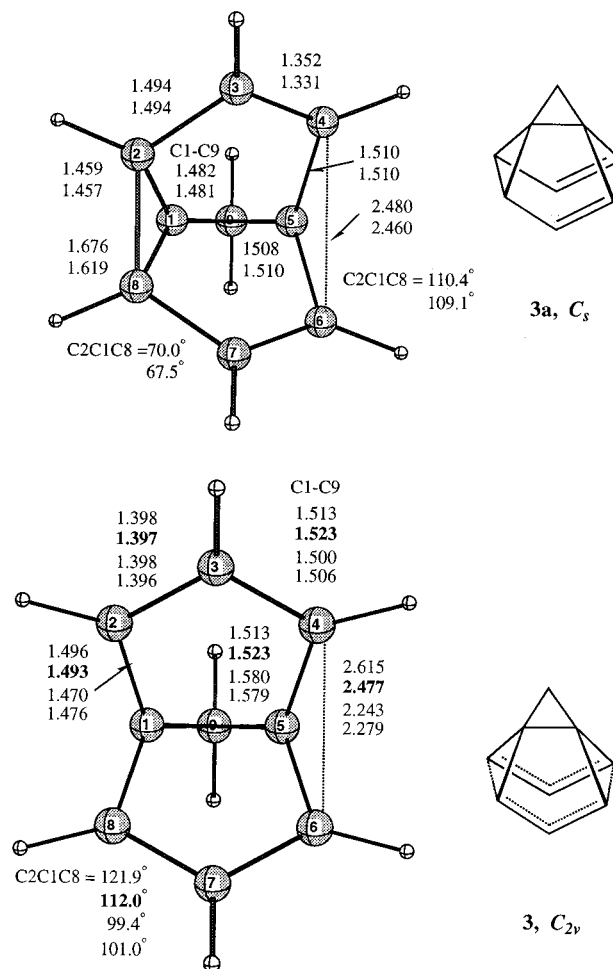

Figure 2. Optimized C_s (**3a**, CASSCF/6-31G* and HF/6-31G*) and C_{2v} (**3**, CASSCF/6-31G*, CASPT2N/6-31G* (in bold), MP2(fc)/6-31G*, and Becke3LYP/6-31G*) geometries (angstroms and degrees) for 1,5-methanosemibullvalene.

contribution of ca. -4.5 ppm cgs, **3** still has a large magnetic susceptibility exaltation, comparable to the Λ of -28.8 for C_{2v} semibullvalene (**2**). The calculated NICS of -22.5 is also nearly the same as that of **2** (-22.7). Although 1,5-methanosemibullvalene (**3**) is bishomoaromatic, the localized HF/6-31G* C_s structure (**3a**) is not. It is computed to have $\Lambda = -9.9$ ppm cgs, less than spiropentane itself, $\Lambda = -11.1$ ppm cgs. The NICS value of -7.5 ppm for this localized C_s structure (**3a**) is, as in semibullvalene, largely due to the effect of the three-membered ring (Table 4).

2,8:4,6-Bis(ethano)semibullvalene (4). The ethano bridges in **4a** result in a highly strained bicyclo[2.1.0]pentane moiety in the C_s but not in the C_{2v} geometry (**4**). At HF/6-31G*, both the localized C_s (**4a**) minimum and the delocalized C_{2v} (**4**) transition state are stationary points. However, at all correlated levels of theory **4** is lower in energy and **4a** is not a stationary point (Table 6). Thus, MP2(fc)/6-31G* and Becke3LYP/6-31G* geometry optimizations of the C_s form (**4a**) lead to the C_{2v} geometry (**4**), which is an energy minimum at the latter level. Single-point energy calculations, using the HF/6-31G* geometry of **4a**, show **4** to be 7.1 (Becke3LYP/6-31G*) and 9.1 kcal/mol (MP2(fc)/6-31G*) lower in energy than **4a**. Similar results were obtained with both CASSCF(6,6)/6-31G* and CASPT2N/6-31G*. The MNDO energy difference between **4a** and **4** is 10.4 kcal/mol.[11a]

As shown in Figure 3, the geometries optimized at various levels of theory generally agree well with one another.

Table 6. Calculated Relative Energies (kcal/mol) of
2,8:4,6-Bis(ethano)semibullvalene in C_{2v} (**4**) and C_s (**4a**)

level	$E_{rel}{}^a$
HF/3-21G	1.2
HF/6-31G*	3.3
MP2(fc)/6-31G*	-9.1^b
Becke3LYP/6-31G*	-7.1^b
(6,6)CASSCF/6-31G*	-3.7
CASPT2N/6-31G*	-4.3^c
CASPT2N/6-31G*	-5.9^d
MNDO	-10.4^e

^{a} Energy difference between C_{2v} (**4**) and C_s (**4a**) 2,8:4,6-bis(etha-no)semibullvalene. ^{b} Using the C_s symmetric HF/6-31G* geometry for single-point energy calculations, since the C_s form does not exist at MP2 and Becke3LYP. ^{c} Using the CASSCF(6,6)/6-31G* geometry. ^{d} Minimum energy geometry predicted using three CASPT2N energies fitted to a quadratic equation (see text), and the CASPT2N/6-31G*// (6,6)CASSCF/6-31G* C_s energy was used for the E_{rel} calculation. ^{e} See ref 11a (the MNDO (2×2 CI) relative energy is the difference of the calculated heats of formation between **4** and **4a**).

However, for **4**, as for **2** and **3**, CASSCF gives a significantly longer interallylic distance, R, than MP2, Becke3LYP, and CASPT2N. The values of R in **4** of *ca.* 2.0 Å are slightly smaller than those in the C_{2v} transition structure (**2**) for the parent semibullvalene. The allylic 1.396−1.398 Å C−C bond lengths in **4** are close to the benzene value (1.397 Å).

Despite the smaller R value at both the CASSCF and CASPT2N optimized geometries, bis(ethano)semibullvalene (**4**) has a smaller $c_1{}^2/c_2{}^2$ ratio and more diradical character than **2** (Table 2). This is due to the greater pyramidalization of the terminal allylic carbons in **4** away from the concave face (Figure 3). The deviation of the angle, ϕ, between the C_2-C_3 bond and the $C_1-C_2-C_{10}$ plane from 0° describes the degree of pyramidalization at C_2, $\phi = 24.9°$ at the CASSCF optimized geometry and $\phi = 29.4°$ at the CASPT2N optimized geometry. The large degree of pyramidalization of the four equivalent, terminal allylic carbons results in a smaller amount of interallylic bonding in **4** than in C_{2v} semibullvalene (**2**), for which $\phi = 1.0°$ (CASSCF) and 4.3° (CASPT2N).

As shown in Table 4, the magnetic susceptibility exaltation of $\Lambda = -17.5$ ppm cgs in **4**, computed at IGLO/DZ//MP2(fc)/6-31G*, is larger than the benzene value ($\Lambda = -13.4$ (IGLO)[23] and -13.7 (expt)[22]). The bishomoaromatic character of **4** is also shown by the calculated NICS of -22.6 ppm. Another demonstration of aromaticity is the upfield Li chemical shift in the lithium cation complex of **4**. In the complex **4**-Li$^+$, the calculated δLi$^+ = -9.1$ may be compared with -6.9 (CpLi), -10.8 (Cp$_2$Li$^-$),[29] and -7.4 (benzene-Li$^+$)[23] as well as -10.8 for the C_{2v} complex of Li$^+$ with semibullvalene.[9] In contrast, the magnetic susceptibility exaltation and the NICS of the localized C_s HF/6-31G* **4a** structure do not show any significant indication of aromaticity, after correction for the three-membered ring contribution (Table 4).

There are no significant geometric changes in **4**-Li$^+$ relative to **4**. The Li−C$_2$ and Li−C$_3$ distances, 2.108 and 2.431 Å, are comparable to those in the Li$^+$ complexed semibullvalene transition structure.[9] The calculated complexation energy for **4**-Li$^+$ is 46.4 kcal/mol at Becke3LYP/6-31G*. On the basis of geometric, energetic, and magnetic criteria, **4** is a neutral bishomoaromatic molecule.

2,8:4,6-Bis(methano)semibullvalene (5). In contrast to the bisethano annelated **4**, only the C_{2v} 2,8:4,6-bis(methano)-

(29) Paquette, L. A.; Bauer, W.; Sivik, M. R.; Bühl, M.; Feigel, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1990**, *112*, 8776. For a review, see: Bauer, W. *Lithium Chemistry, A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; John Wiley & Sons, Inc.: New York, 1995; Chapter 5, pp 125−172.
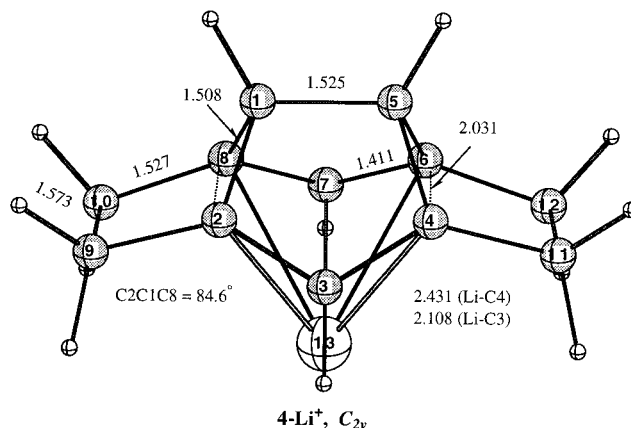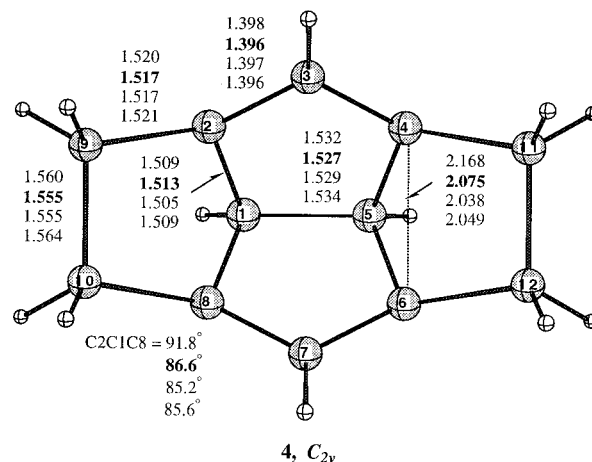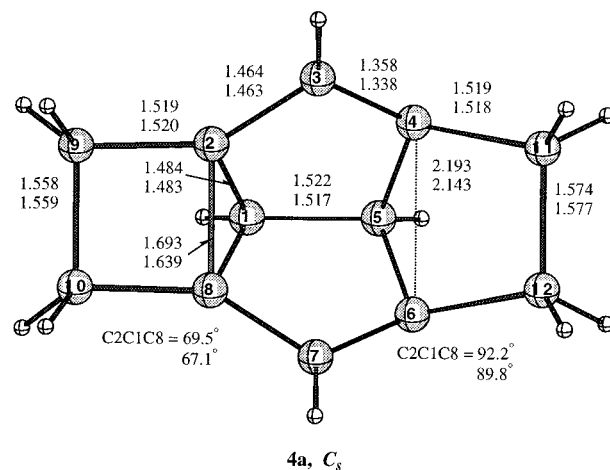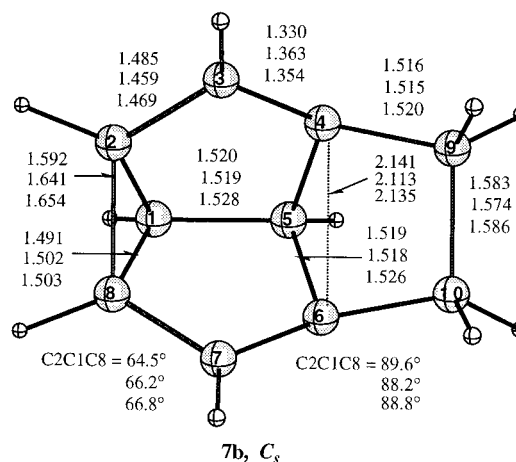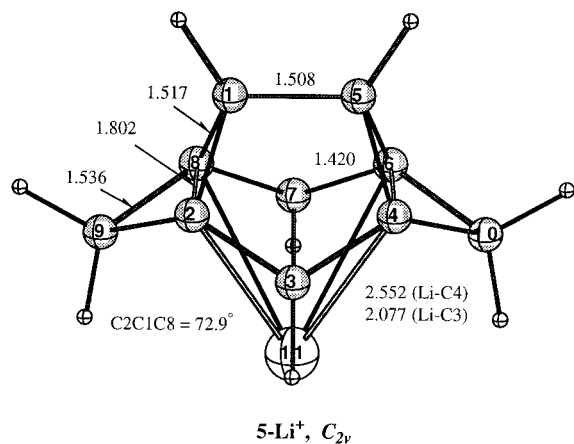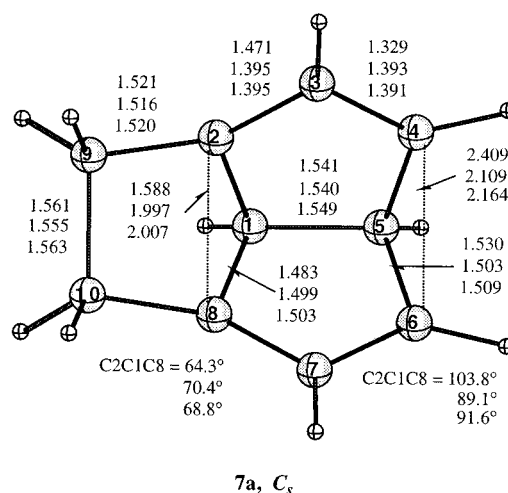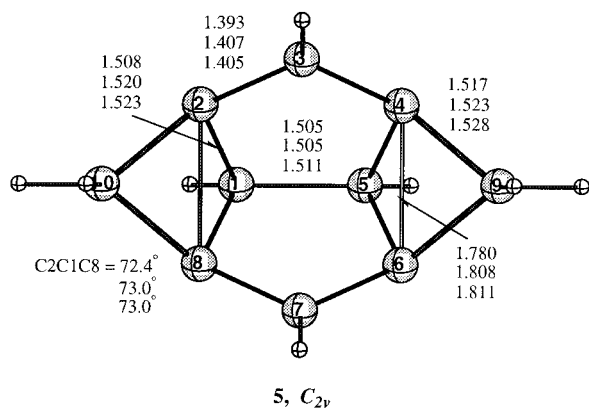

Figure 3. Optimized C_s (**4a**, CASSCF/6-31G* and HF/6-31G*) and C_{2v} (**4**, CASSCF/6-31G*, CASPT2N/6-31G* (in bold), MP2(fc)/6-31G*, and Becke3LYP/6-31G*) geometries (angstroms and degrees) for 2,8:4,6-bis(ethano)semibullvalene and for **4**-Li$^+$ (Becke3LYP/6-31G*).

semibullvalene (**5**) was optimized at HF/6-31G*, MP2(fc)/6-31G*, and Becke3LYP/6-31G*. Frequency analyses (HF and Becke3LYP) show **5** to be an energy minimum. The allylic CC bond lengths (about 1.41 Å) are close to the benzene value, and the relatively short interallylic separation of $R = 1.808-1.811$ Å indicates a pronounced neutral homoconjugative interaction in **5** (Figure 4). The computed magnetic susceptibility exaltation of -24.3 ppm cgs (Table 4) in **5** is very large, and the calculated upfield Li$^+$ chemical shift of -7.9 ppm for the **5**-Li$^+$ complex (Figure 4) as well as the NICS (-23.6 ppm) support the conclusion that **5** is bishomoaromatic.

Figure 4. Optimized C_{2v} (HF/6-31G*, MP2/6-31G*, and Becke3LYP/6-31G*) geometries (angstroms and degrees) for 2,8:4,6-bis(methano)-semibullvalene (**5**) and for **5**-Li$^+$ (Becke3LYP/6-31G*).
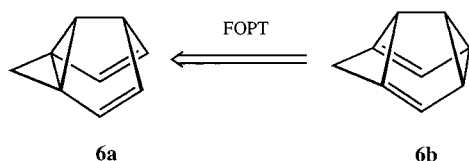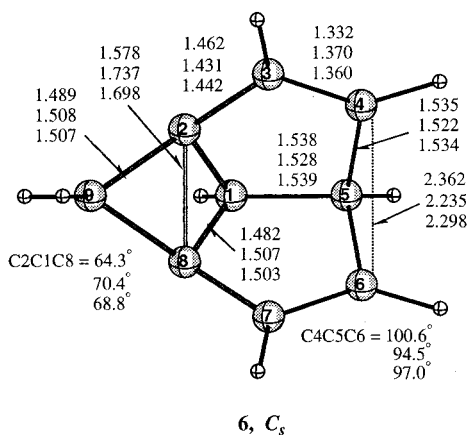

Figure 5. Optimized C_s (HF/6-31G*, MP2(fc)/6-31G* and Becke3LYP/6-31G*) geometries (angstroms and degrees) for 2,8-methanosemi-bullvalene (**6**).

Figure 6. Optimized C_s (HF/6-31G*, MP2(fc)/6-31G*, and Becke3LYP/6-31G*) geometries (angstroms and degrees) for 2,8- and 4,6-ethanosemibullvalene (**7**).

MP2(fc) and Becke3LYP. Do these structural features result in partial homoconjugation?

At IGLO//Becke3LYP/6-31G*, **6a** is computed to have a magnetic susceptibility exaltation of −18.0 ppm cgs. However, **6a** has a bicyclobutane unit; and 1,3-dimethylbicyclobutane is computed to have an exaltation of −8.2 ppm cgs. After deleting this contribution, the net exaltation of −9.8 for **6a** indicates some aromatic character. In addition, the calculated NICS of −15.2 ppm is larger than the contribution of the three-membered rings, and also supports a modest degree of homoaromaticity of **6a** (Table 4).

2,8- (and 4,6-) Ethanosemibullvalenes (7a and 7b). In contrast to methanosemibullvalene **6**, but in agreement with earlier semiempirical results,[12] two ethanosemibullvalene isomers (**7a** and **7b**) are found at HF, MP2(fc), and Becke3LYP. One isomer is C_2−C_8 annelated (**7a**), and the other is C_4−C_6 annelated (**7b**). Both are minima at HF/6-31G* and Becke3LYP/6-31G*. However, **7a** is 0.6 (MP2(fc)/6-31G*) or 1.0 kcal/mol (Becke3LYP/6-31G*) less stable than **7b** after ZPE correction.

At HF/6-31G*, **7a** has a localized structure; the C_2−C_8 and C_4−C_6 distances are 1.588 and 2.409 Å, respectively. At MP2-(fc)/6-31G* and at Becke3LYP/6-31G*, C_2−C_8 elongates to 1.997 Å and the C_4−C_6 shortens to 2.109 Å. The C_2−C_3 and C_3−C_4 bond lengths, which are typical localized values at HF, are delocalized (1.395 and 1.393 Å) at MP2, i.e., nearly the same as in **4**. Accordingly, **7a** should be considered as homoaromatic based on its geometry. Indeed, the large

Table 7. CASPT2N/6-31G* Vertical UV Absorptions λ (nm) for (6,6)CASSCF/6-31G* and CASPT2N/6-31G* Optimized Geometries of Semibullvalene, Methanosemibullvalene, and Bis(ethano)semibullvalene

compd excitation	λ (nm)	
	CASSCF	CASPT2N
1 (C_s)		
$1(^1A') \rightarrow 1(^1A'')$	207	
$1(^1A') \rightarrow 2(^1A')$	201	
3a (C_s)		
$1(^1A') \rightarrow 1(^1A'')$	229	
$1(^1A') \rightarrow 2(^1A')$	224	
2 (C_{2v})	($R = 2.294$ Å)	($R = 2.117$ Å)
$1(^1A_1) \rightarrow 1(^1B_1)$	336	284
$1(^1A_1) \rightarrow 1(^1B_2)$	374	310
$1(^1A_1) \rightarrow 1(^1A_2)$	275	218
$1(^1A_1) \rightarrow 2(^1A_1)$	261	169
3 (C_{2v})	($R = 2.615$ Å)	($R = 2.477$ Å)
$1(^1A_1) \rightarrow 1(^1B_1)$	389	377
$1(^1A_1) \rightarrow 1(^1B_2)$	634	531
$1(^1A_1) \rightarrow 1(^1A_2)$	396	352
$1(^1A_1) \rightarrow 2(^1A_1)$	516	383
4 (C_{2v})	($R = 2.168$ Å)	($R = 2.075$ Å)
$1(^1A_1) \rightarrow 1(^1B_1)$	369	346
$1(^1A_1) \rightarrow 1(^1B_2)$	488	408
$1(^1A_1) \rightarrow 1(^1A_2)$	309	270
$1(^1A_1) \rightarrow 2(^1A_1)$	213	194

Table 8. IGLO/DZ//Becke3LYP/6-31G* Computed ^{13}C Chemical Shifts (ppm, using TMS as standard) for Semibullvalenes **1** and **2** Compared with the Observed Values at -95 and -160 °C

assignment[a]	IGLO on **1**[b]	IGLO on **2**	obsd	
			at -160 °C[b,c]	at -95 °C[c]
C_1	51.2		48.0	
C_5	52.7		53.1	
$C_{2,8}$	44.5		42.2	
$C_{3,7}$	119.0		121.7	
$C_{4,6}$	126.6		131.8	
$C_{1,5}$	(52.0)	50.2	(50.6)	50.7
$C_{2,8,4,6}$	(85.6)	96.7	(87.0)	87.2
$C_{3,7}$	(119.0)	125.4	(121.7)	121.7

[a] The numbering system is shown in Figure 1. [b] The average chemical shift values are given in parentheses. [c] Taken from ref 2a. [d] Calculations performed on **1**. [e] Calculations performed on **2**.

Table 9. IGLO/DZ//Becke3LYP/6-31G* Computed ^{13}C Chemical Shifts for **2**−**7** using TMS as Standard (in ppm)[a]

Nr.	$C_{1;5}$	$C_{2,8;4,6}$	$C_{3,7}$	others
3a (C_s)[b]	37.9; 45.9	38.3; 144.6	141.0	15.4 (C_9)
3 (C_{2v})	41.3	106.7	137.7	5.5 (C_9)
4a (C_s)[b]	40.6; 52.5	48.1; 129.0	129.8	23.0 (C_9); 23.8 (C_{11})
4 (C_{2v})	54.0	103.9	133.5	23.4 (C_9)
5 (C_{2v})	68.6	86.5	165.2	53.9 (C_9)
6a (C_s)	77.1; 48.3	51.8; 134.9	140.8	51.6 (C_9)
7a (C_s)[b]	65.4; 45.7	47.0; 134.5	134.1	23.3 (C_9)
7a (C_s)	56.2; 43.6	106.4; 92.0	128.3	21.6 (C_9)
7b (C_s)	33.7; 54.6	40.4; 145.6	134.2	24.5 (C_9)

[a] The numbering system is shown in Figures 2−6. [b] Using HF/6-31G* geometries.

magnetic susceptibility exaltation (-23.2 ppm cgs) and NICS (-22.5 ppm) for **7a** confirm its homoaromatic character (Table 4). This agrees with the conclusions of Williams and Kurtz (based on energetic analyses of semiempirical configuration interaction calculations) that **7a** is "another example of a neutral homoaromatic ground state hydrocarbon".[12]

In contrast, **7b** has a more localized structure than **7a** at HF, MP2, and Becke3LYP/6-31G*. The C_2−C_8 bond length is 1.641 Å (1.592 Å at HF) and the C_4−C_6 separation is 2.133 Å. Thus, homoconjugation must be less in **7b** than in **7a**. The magnetic susceptibility exaltation in **7b** is only -7.5 and the NICS is -12.7. Both these values are only slightly outside the range for cyclopropanes (Table 3). When the three-ring contributions are removed, no pronounced magnetic susceptibility exaltation of **7b** and its NICS provides evidence for homoconjugation.

Predicted UV and ^{13}C NMR Spectra. As an aid to experimentalists, the UV spectra of the semibullvalenes were calculated to help distinguish between the C_{2v} (open) and C_s (closed) geometries. Table 7 lists the wavelengths predicted for different geometries. The C_{2v} geometries are all expected to absorb at much longer wavelengths that their C_s counterparts. However, the very strong dependence of the wavelengths on the interallylic distance, R, indicates that accurate prediction of the UV spectra for these molecules would require very accurate values of R.

Both strongly allowed excitations for the C_{2v} species, $^1A_1 \rightarrow$ $^1B_1$ and $^1A_1 \rightarrow$ $^1B_2$, are computed to shift to the red as the interallylic interactions decrease. In fact, Quast[8b] and Williams[30] have observed reversible thermochroism in semibullvalenes and barbaralanes that are close to being bishomoaromatic. Quast has correlated this phenomenon with a very flat double minimum potential energy surface and an exceptionally low activation barrier to the Cope rearrangement.[8b]

Although bis(ethano)semibullvalene (**4**) has a smaller interallylic distance, R, than C_{2v} semibullvalene (**2**), the UV absorptions are calculated to occur at longer wavelengths in **4**

than in **2**. This apparent anomaly is due to the high degree of pyramidalization of the terminal allylic carbons in **4** away from the concave face. The reduced orbital overlap between the terminal allylic carbons in **4** results in the calculated red shift of the strongly allowed excitations.

We have computed the ^{13}C NMR chemical shifts for semibullvalene at both the C_s equilibrium (**1**) and C_{2v} transition state (**2**) geometries. In Table 8 the computed chemical shifts are compared with the experimental values at $-95°$ and $-160°$. The IGLO/DZ calculated values for **1** agree well with those observed at $-160°$. The largest difference between the calculated and observed values is -5.2 ppm for $C_{4,6}$. As indicated in Table 8, only three signals are observed in the ^{13}C NMR spectrum of **1** at -95 °C. At this temperature the $C_{3,7}$ chemical shift is the same as at -160 °C; and the chemical shifts of $C_{2,8,4,6}$ and of $C_{1,5}$ at -95 °C are very close to the averages of respectively $C_{2,8}$ and $C_{4,6}$ as well as C_1 and C_5 at -160 °C. This averaging results from the rapid equivalent C_s equilibrium geometries (**1** and **1′**) at -95 °C.

In contrast, the computed ^{13}C NMR chemical shifts using the homoaromatic C_{2v} geometry of **2** do not agree satisfactorily overall with the -95 °C experimental data. The largest deviation is found for the calculated $C_{2,8,4,6}$ chemical shifts in **2** (96.7 ppm); these are 11.1 ppm downfield from the average computed for $C_{2,8}$ and $C_{4,6}$ in **1** (85.6 ppm) and 9.5 ppm downfield from the shifts observed for these four carbons at $-95°$. The calculated chemical shift for $C_{3,7}$ in **2** is 6.4 ppm downfield from that calculated for $C_{3,7}$ in **1** but only 3.7 ppm from that observed at $-95°$.

Although a small downfield shift also is computed for $C_{3,7}$ from the C_s (**4a**) to the C_{2v} geometry of bis(ethano)semibullvalene (**4**), an upfield shift for $C_{3,7}$ is calculated from the C_s (**3a**) to the C_{2v} geometry for methanosemibullvalene (**3**) (Table 9). However, the computed chemical shifts of $C_{2,8,4,6}$ at the C_{2v} geometry in both of these annelated semibullvalenes

(30) 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.

are 15 ppm downfield from the average of the chemical shifts for the same carbons in the C_s geometry. Similarly, the $C_{2,8}$ and $C_{4,6}$ chemical shift average is computed to be at significantly lower field in the Becke3LYP geometry for **7a** (99.2 ppm) than in the HF geometry both for **7a** (90.8 ppm) and for **7b** (93.0 ppm). The ^{13}C chemical shifts for $C_{2,8}$ and $C_{4,6}$ in semi-bullvalenes (**1**−**4** and **7**) are sensitive to the geometry and can be used as a structural probe. ^{13}C NMR chemical shifts for $C_{2,8,4,6}$ in delocalized semibullvalenes are at significantly lower fields than those expected for these carbons in localized semibullvalenes. This should be a useful diagnostic tool.

Conclusions

On the basis of geometric, energetic, and more importantly magnetic criteria of aromaticity, the C_{2v} symmetric transition structure (**2**) for the Cope rearrangement in the parent semi-bullvalene is bishomoaromatic. In annelated semibullvalenes, such as 1,5-methano (**3**), 2,8:4,6-bisethano (**4**), and 2,8:4,6-bismethano (**5**), as well as in the 2,8-ethanosemibullvalene, the bishomoaromatic form is predicted to be lower in energy than the localized structures. The delocalized structures have exalted magnetic susceptibilities and significantly negative values of the nucleus independent chemical shift (NICS). On the basis of these magnetic criteria, 2,8-methanosemibullvalene has partial aromatic character, and 4,6-ethanosemibullvalene is predicted not to be aromatic. The predicted long-wavelength UV absorptions and down field ^{13}C NMR chemical shifts for $C_{2,8,4,6}$ are characteristic for the homoaromatic semibullvalenes.

Supporting Information Available: Computed total ener-gies (hartrees) for compounds **1**−**7** at various computational levels are summarized in Tables 1−5 (5 pages). See any current masthead page for ordering and Internet access instructions.

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