

Are 1,5-Disubstituted Semibullvalenes that Have C_{2v} Equilibrium Geometries Necessarily Bishomoaromatic?

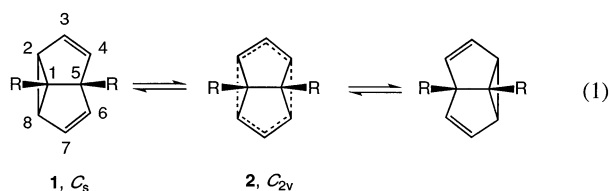
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Received June 20, 2002

Abstract: Unrestricted density functional theory (UB3LYP), CASSCF, and CASPT2 calculations have been employed to compute the relative energies of the C_s and C_{2v} geometries of several 1,5-disubstituted semibullvalenes. Substitution at these positions with $R = F$, $-\text{CH}_2-$, or $-\text{O}-$ affords semibullvalenes that are predicted to have C_{2v} equilibrium geometries. Calculated singlet–triplet energy splittings and the energies of isodesmic reactions are used to assess the amount of bishomoaromatic character at these geometries. The results of these calculations show that employing strain to destabilize the C_s geometries of semibullvalenes can lead to a significant decrease in the amount of bishomoaromatic stabilization of the C_{2v} geometries, due to reduced through-space interaction between the two allyl groups. However, the C_{2v} equilibrium geometries of the 1,5-disubstituted semibullvalenes with $R = F$ and $-\text{RR}- = -\text{O}-$ do benefit from stabilizing through-bond interactions between the two allyl groups. These interactions involve mixing of the bisallyl HOMO with the low-lying C–F or C–O σ^* orbital combinations of the same symmetry. In contrast, for $-\text{RR}- = -\text{CH}_2-$, through-bond interactions destabilize the bisallyl HOMO and are predicted to make the ground state of this semibullvalene a triplet.

Semibullvalene (**1a**) possesses an enthalpic barrier to degenerate Cope rearrangement (eq 1) of only 4.8–5.2 kcal/mol.^{1,2} This low barrier makes semibullvalene an obvious template for selective derivatization, such that a C_{2v} form (**2**) becomes the energy minimum. Because at such a C_{2v} geometry six electrons are cyclically delocalized, **2** is often described as being bishomoaromatic.^{3,4}



(a) $R = \text{H}$ (b) $R = \text{F}$ (c) $-\text{RR}- = -\text{CH}_2-$ (d) $-\text{RR}- = -\text{O}-$

On the basis of qualitative molecular orbital theory arguments⁵ and a variety of semiempirical calculations,^{6–9} several substitu-

tion patterns have been proposed that should lower the energy of the C_{2v} geometry (**2**) relative to that of the C_s form (**1**). Hoffmann and Stohrer suggested that placing π radical stabilizing groups at the C_2 , C_4 , C_6 , and C_8 positions of **1** should selectively stabilize **2**.⁵ Indeed, it has been found experimentally that substitution of the C_2 , C_4 , C_6 , and C_8 positions of **1** with groups such as phenyl¹⁰ and cyano¹¹ lowers the barrier to Cope rearrangement to nearly zero. Recently, density functional theory calculations have predicted that 2,6-dicyano-4,8-diphenyl-semibullvalene should, in fact, have a C_{2v} equilibrium geometry.¹²

Another result of the qualitative molecular orbital theory analysis of Hoffmann and Stohrer is that placement of σ electron-withdrawing groups at the C_1 and C_5 positions should destabilize the cyclopropane ring in **1**. In fact, Hoffmann and Stohrer's extended Hückel (EH)MO calculations indicated that placement of fluorines at the C_1 and C_5 positions of **1b** should result in **2b** being the equilibrium geometry.⁵ Although AM1 calculations by Dewar and Jie found that **2b** lies 6 kcal/mol higher in energy than **1b**,⁷ MP4 calculations by Szabo and Cremer predict that **2b** actually is the equilibrium geometry.¹³

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Another strategy for making **2** the equilibrium geometry of a substituted semibullvalene is to destabilize the cyclopropane ring in **1** by adding short chains of one or two atoms.^{8,9,14–16} For example, annelation of the C₁/C₅ positions of **1** with –CH₂– affords 1,5-methanosemibullvalene (**1c**), which contains a [2.2]spiropentane moiety. The semiempirical calculations of Dannenberg et al. predict that the resulting strain destabilizes **1c** sufficiently to make **2c** the equilibrium geometry.⁸ Schleyer, Borden, and co-workers have reported the results of ab initio and density functional theory calculations on **2c** that support this semiempirical finding.¹⁵

Combining the strategies of destabilizing **1** by placing σ electron-withdrawing substituents at C₁ and C₅ and by adding a one-atom bridge across these two carbons suggests that the epoxide **1d** should display an even greater preference for a C_{2v} equilibrium geometry (**2d**) than either **1b** or **1c**. In this paper, we report the results of ab initio and DFT calculations that were performed to test this conjecture.

We also carried out calculations aimed at assessing the degree of bishomoaromatic character of **2a–d**. Specifically, we computed the energies of isodesmic reactions that allow us to separate the effects of strain on destabilization of the C_s geometries of **1a–d** from the effects of bishomoaromaticity on stabilization of the C_{2v} geometries of **2a–d**. The results of our calculations, which are described in this paper, predict that **1d** does have a much larger preference than **1a–c** for a C_{2v} equilibrium geometry; yet our calculations find that **2c** and **2d** are both much less stabilized by bishomoaromaticity than either **2a** and **2b**.

Computational Methodology

All calculations were performed with the 6-31+G(d) basis set.¹⁷ Calculations based on density functional theory were carried out with the three-parameter functional of Becke and the correlation functional of Lee, Yang, and Parr (B3LYP).¹⁸ Geometries were optimized at the unrestricted (U)B3LYP level of theory by the standard methods implemented in the *Gaussian 98* suite of programs.¹⁹ For all but **2c** and **2d**, the UB3LYP wave function converged to a restricted (R)B3LYP wave function with $\langle S^2 \rangle = 0.00$.

(U)B3LYP vibrational analyses were performed at each stationary point, to confirm its identity as a minimum or a transition state. The vibrational frequencies were used, without scaling, to convert energy differences into enthalpy differences at 298 K.

CASSCF and CASPT2^{20,21} calculations were performed with the *MOLCAS 5.0* suite of programs.²² In the (6/6)CASSCF and (6/6)CASPT2 calculations on **1**, the six active electrons were distributed among the π and π^* orbitals of the two double bonds and the σ and σ^* orbitals of the unique cyclopropane ring bond. For the (6/6)CASSCF and (6/6)CASPT2 calculations on **2**, the orbitals in the active space were the three filled and three empty benzene-like MOs, formed from the orbitals of the two allylic π systems. For the (4/4)CASSCF and (4/4)CASPT2 calculations on bicyclo[3.3.0]octa-2,6-diene, the active space was comprised of four electrons, distributed among the π and π^* orbitals of the two double bonds.

Because analytical gradients of CASPT2 energies with respect to nuclear displacements are not yet available, full CASPT2 geometry optimizations are impractical for molecules of the size of **1** and **2**. As was done previously,¹⁵ partial CASPT2 geometry optimizations were performed on the lowest singlet state of **2** by fixing the C₂–C₈ and C₄–C₆ bond distances (d) at different values and using UB3LYP calculations to optimize the geometry of the remainder of the molecule at each value of d . (6/6)CASPT2 calculations were then performed at each of the partially optimized geometries, to determine which value of d gave the lowest (6/6)CASPT2 energy.

Geometries for the triplet states of **2** were optimized with UB3LYP calculations. Single-point (6/6)CASPT2 calculations were carried out at the UB3LYP optimized triplet geometries.

CASPT2 calculations on **1a–c** were performed at geometries optimized with restricted (R)B3LYP calculations. However, RB3LYP geometry optimizations did not locate a C_s minimum corresponding to **1d**; only a C_{2v} geometry (**2d**) was found. Nevertheless, it was possible to optimize a C_s geometry for **1d** by performing RHF calculations, because RHF calculations do not include the electron correlation that is necessary to describe the wave function for **2d** properly. Single-point (U)B3LYP and (6/6)CASPT2 calculations were then carried out at the optimized RHF geometry of **1d**.

To obtain a partially optimized (6/6)CASPT2 C_{2v} geometry for **2d**, geometry optimizations at different values of d were carried out with both UB3LYP and RHF calculations. Thus, two (6/6)CASPT2 geometries were obtained for **2d**, one that had been partially optimized with UB3LYP calculations and the other with RHF calculations. The former was found to have the lower (6/6)CASPT2 energy.

Optimized RB3LYP geometries for **1a–c** and the optimized RHF geometry for **1d** are available as Supporting Information, as are the optimized (U)B3LYP geometries for **2a–d**. The (6/6)CASSCF and CASPT2 energies for **1a–d** and **2a–d**, computed at partially optimized (U)B3LYP geometries at different values of d , are also provided.

Results and Discussion

Energy Differences between 2 and 1. For each substituent, the B3LYP and CASPT2 energy differences between delocalized C_{2v} structure **2** and localized C_s semibullvalene **1** are given in Table 1. The optimized C₂–C₈ and C₄–C₆ bond distances (d) in **2** are also listed in Table 1. The geometries of **1a/2a** and **1c/2c** have previously been optimized at the B3LYP and CASPT2 levels of theory with the 6-31G(d) basis set by Schleyer, Borden, and co-workers.¹⁵ Although we chose to augment this basis set with diffuse functions, our optimized

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Table 1. Energy and Enthalpy Differences between C_s (**1**) and C_{2v} (**2**) Semibullvalenes, and C_2-C_8 ($=C_4-C_6$) Bond Distances (d), $\langle S^2 \rangle$, and Adiabatic Singlet–Triplet Energy Differences (ΔE_{ST}) in **2^a**

substituents at C_1 and C_5	$\Delta E(2-1)$ (kcal/mol)	$\Delta H^{298}(2-1)$ (kcal/mol)	d (Å)	$\langle S^2 \rangle$ (au)	ΔE_{ST} (kcal/mol)
R = H	5.0 <i>6.1</i>	3.9 ^b	2.117 <i>2.122</i>	0.00	12.3 <i>15.7</i>
R = F	−0.8 <i>−0.9</i>	−1.7	2.216 <i>2.243</i>	0.00	19.3 <i>21.4</i>
RR = −CH ₂ −	−5.9 <i>−5.6</i>	−7.4	2.654 <i>2.472</i>	1.03	−1.5 <i>−1.3</i>
RR = −O−	−20.3 <i>−22.1^d</i> <i>−19.9^e</i>	−19.5 ^c	2.661 <i>2.574</i> <i>2.585</i>	0.87	1.8 <i>3.3</i>

^a (6/6)CASPT2/6-31+G(d) values are given in italics below the UB3LYP/6-31+G(d) values. ^b ΔH^\ddagger . ^c Based on scaling the RHF vibrational frequencies for **1d** by 0.8929. ^d CASPT2//RHF energy for **1d** and CASPT2//CASPT2-UB3LYP energy for **2d**. ^e CASPT2//RHF energy for **1d** and CASPT2//CASPT2-RHF energy for **2d**.

B3LYP and CASPT2 geometries for these molecules are very close to those that have previously been published.

As shown in Table 1, unlike the case for the parent hydrocarbon, the C_{2v} geometry for 1,5-difluorosemibullvalene (**2b**) is predicted by both B3LYP and CASPT2 to be ca. 1 kcal/mol lower in energy than the C_s geometry (**1b**). However, the possible errors in these calculations are at least this large, so that the prediction of a C_{2v} equilibrium geometry for **1b** should be regarded as equivocal. Nevertheless, the B3LYP and CASPT2 finding that **2b** is lower in energy than **1b** is consistent with the MP4 results of Szabo and Cremer.¹³

At both the B3LYP and the CASPT2 levels, the optimized interallylic distance (d) in **2b** is ca. 0.1 Å longer than d in **2a**. As noted previously,¹⁵ the fact that the CASPT2 optimized value of d is slightly larger than the RB3LYP value probably reflects the greater ability of CASPT2 to represent a wave function that has diradical character.

The results of our UB3LYP calculations on **1c** and **2c** are in qualitative agreement with the previously reported RB3LYP results of Schleyer, Borden, and co-workers – the energy of the C_{2v} geometry is lower in energy than that of the C_s form.¹⁵ However, our calculations find the energy of the UB3LYP optimized geometry of **2c** to be 3.6 kcal/mol lower than that of the geometry optimized with RB3LYP. In addition, the UB3LYP value of $d = 2.654$ in **2c** is 0.356 Å longer than the RB3LYP value of $d = 2.298$ Å.

In contrast to the value of $\langle S^2 \rangle = 0.00$ found for the UB3LYP wave function at the optimized geometries of both **2a** and **2b**, $\langle S^2 \rangle = 1.03$ at the optimized geometry of **2c**. Thus, the “singlet” wave function for **2c** is an approximately 1:1 mixture of pure singlet ($\langle S^2 \rangle = 0$) and triplet ($\langle S^2 \rangle = 2$) states. The large amount of spin contamination in this wave function suggests that, in agreement with previous calculations,¹⁵ **2c** has a large amount of diradical character.

At the CASPT2 level of theory, our calculations with the 6-31+G(d) basis set essentially reproduce the energy difference between **2c** and **1c** found by Schleyer et al. with the 6-31G(d) basis set. The 0.2 Å smaller interallylic distance, d , at the CASPT2 than at the UB3LYP level indicates that UB3LYP underestimates the interallylic bonding in **2c**. This is not surprising, because the UB3LYP wave function has 50% triplet character, whereas CASPT2 gives a pure singlet wave function.

As predicted, annelation of the C_1 and C_5 positions with O, rather than CH₂, is calculated to further lower the energy of **2**

relative to **1**. We find that ΔE (**2d** – **1d**) = −20.3 and −22.1 kcal/mol at the UB3LYP and CASPT2 levels of theory, respectively.

Like the UB3LYP wave function for **2c**, the UB3LYP wave function for **2d** contains a great deal of triplet character. However, despite the slightly longer UB3LYP interallylic bond distance (d) in **2d** than in **2c**, $\langle S^2 \rangle = 0.87$ for **2d** is smaller than $\langle S^2 \rangle = 1.03$ for **2c**. Apparently, d is not the only factor that determines the amount of triplet character in the “singlet” UB3LYP wave function for **2** (vide infra).

Bonding between the Allylic Fragments in 2 As Assessed by ΔE_{ST} . Table 1 shows that as the energy of the C_{2v} geometry (**2**) is lowered relative to the C_s geometry (**1**), the interallylic distances (d) in **2** increase. This finding suggests that interallylic bonding decreases on moving from **2a** to **2d**.

One way to assess the amount of interallylic bonding in **2** is to compute the adiabatic singlet–triplet energy difference, ΔE_{ST} . As the interallylic distance increases, one would expect that the two allyl fragments would interact less. Because there should be little or no interallylic interaction at the optimized geometry of the triplet state, ΔE_{ST} would be expected to decrease with increasing values of d in the singlet state.

For **2c** and **2d**, the large $\langle S^2 \rangle$ values for the UB3LYP “singlets” make the absolute UB3LYP values for ΔE_{ST} highly suspect. Nevertheless, as shown in Table 1, the UB3LYP values of ΔE_{ST} do show the same trend as the much more reliable CASPT2 values – **2b** > **2a** >> **2d** > **2c**. In fact, unlike the case in **2a**, **b**, and **d**, the ground state of **2c** is predicted to be a triplet by both UB3LYP and CASPT2 calculations. The possibility of a triplet ground state for **2c** was not considered previously.^{15,23}

It is surprising to find that the ground state of **2c** is predicted to be a triplet when, despite the larger interallylic distance in **2d** than in **2c**, the ground state of **2d** is predicted to be a singlet. However, this finding parallels the same type of inversion, already noted, in the amount of triplet character in the “singlet” UB3LYP wave functions for **2c** and **2d**.

Both ΔE_{ST} and $\langle S^2 \rangle$ in **2** are expected to depend on the difference in orbital energies between the HOMO and LUMO. Therefore, it is reasonable to seek the origin of the seemingly anomalous results for **2c** and **2d** by examining the changes that occur in the energies of these frontier orbitals upon substitution of −CH₂− by −O−. Because the amount of interallylic bonding through space is apparently small at the large d values in both of these C_{2v} semibullvalenes, one must consider whether the difference between the through-bond interallylic interactions in the HOMO and/or the LUMO of **2c** and **2d** could be larger than the difference between the interallylic interactions through space.

As shown in Figure 1, the orbitals of the three-membered ring all lie in a nodal plane of the a_2 LUMO of the bisallylic fragment. Consequently, the ring orbitals do not affect the energy of this orbital in **2c** or **2d**. In contrast, the b_1 combinations of bonding and antibonding orbitals of the three-membered rings in **2c** and **2d** have the same symmetry as the HOMO of the bisallylic fragment. Interaction with the b_1 bonding orbital of the three-membered ring raises the energy of the bisallyl

(23) We have investigated the possibility that 2,6-dicyano-4,8-diphenylsemibullvalene¹² also possesses a low-lying triplet state. Indeed, $\Delta E_{ST} = 2.1$ kcal/mol at the UB3LYP/6-31G* level, with $\langle S^2 \rangle = 0.67$ for the “singlet”. Clearly the intraallylic electron delocalization in this semibullvalene reduces the interallylic bonding interactions, relative to those in **2a**.

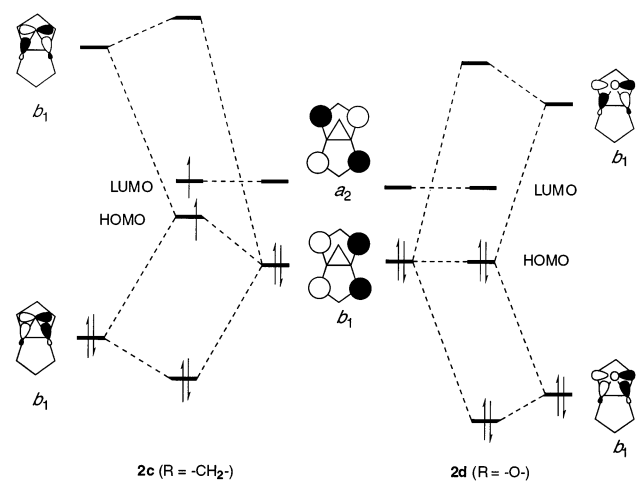


Figure 1. Schematic representation of the interactions of the out-of-phase combinations of the σ and σ^* orbitals between the bridgehead carbons and the bridging group (CH_2 in **2c** and O in **2d**) with the HOMO and LUMO, formed by through-space interactions between the π orbitals of the two allyl groups.

HOMO, whereas interaction with the b_1 antibonding ring orbital lowers the energy of the bisallyl HOMO.

In **2c**, the interaction of the HOMO of the bisallylic fragment with the high-lying, b_1 , bonding orbital of the cyclopropane ring orbitals is strong enough to raise the energy of the HOMO, relative to that of the LUMO, so that these orbitals are very close in energy in **2c**. This is shown schematically on the left side of Figure 1. The energy difference between the HOMO and LUMO of **2c** ($\Delta E_{\text{HL}} = 23.3$ kcal/mol) is apparently small enough that, as depicted in Figure 1, the ground state of **2c** is, in fact, predicted to be a triplet, by both UB3LYP and CASPT2 (Table 1).

Substitution of the oxygen atom in **2d** for the $-\text{CH}_2-$ group in **2c** affects the interactions between the HOMO of the bisallylic fragment and the b_1 ring orbitals in two ways. First, the electronegative oxygen lowers the energy of both the bonding and the antibonding b_1 orbitals of the three-membered ring in **2d**, relative to the energies of these b_1 orbitals in **2c**. Second, the oxygen polarizes the bonding b_1 ring MO toward oxygen and away from C_1 and C_5 , whereas the oxygen has the opposite effect on the antibonding b_1 ring MO.

The effects of the electronegativity of oxygen on the energies of the b_1 bonding and antibonding orbitals of the three-membered ring and on the contribution of C_1 and C_5 to these orbitals serve to decrease the interaction of the b_1 bonding orbital with the bisallyl HOMO and to increase the interaction of the b_1 antibonding orbital with the bisallyl HOMO.²⁴ Consequently, as shown schematically in Figure 1, substitution of $-\text{O}-$ in **2d** for $-\text{CH}_2-$ in **2c** serves to lower the energy of the HOMO, relative to the LUMO.²⁵

Thus, despite the effect of the large value of d on the strength of the interallylic bonding through space in **2d**, through-bond interactions serve to make the HOMO–LUMO gap large enough that a singlet ground state is predicted for **2d**. This

(24) The latter interaction provides net stabilization of **2d**, relative to **2c**. Similarly, replacement of the CH_2 group in norcaradiene by the oxygen atom in benzene oxide should selectively stabilize for the latter molecule by enhancing the interaction between the HOMO of butadiene and the LUMO of the three-membered ring. This interaction probably provides at least some of the enthalpic stabilization that has been measured for benzene oxide.⁴

Table 2. Bishomoaromatic Stabilization Energies and Enthalpies (BHASEs) for the C_{2v} Semibullvalenes (**2**) and Strain Energies and Enthalpies (SEs) for the C_s Semibullvalenes (**1**)^a

R	BHASEs ^b		SEs ^c	
	ΔE	ΔH^{298}	ΔE	ΔH^{298}
H	10.9 <i>15.4</i>	10.0	38.9 40.1	35.7
F	16.9 <i>19.3</i>	15.5	38.7 43.2	35.8
RR = $-\text{CH}_2-$	-2.0 <i>-1.7</i>	-1.8	62.7 68.9	58.8
RR = $-\text{O}-$	1.3 2.9	1.2	73.8 80.8	67.9 ^d

^a CASPT2 values are given in italics below the UB3LYP values.

^b Computed from the energy/enthalpy of the isodesmic reaction in eq 2.

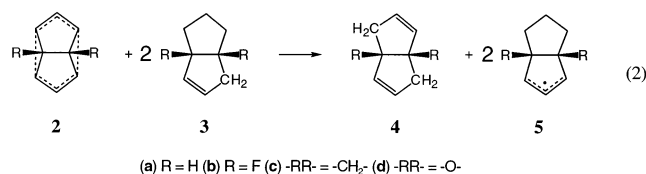
^c Computed from the energy/enthalpy of the isodesmic reaction in eq 3.

^d Based on scaling the RHF vibrational frequencies in **1d** by 0.8929.

prediction contrasts with that of a triplet ground state for **2c**, where through-bond interactions result in a smaller HOMO–LUMO gap than that in **2d**.

The through-bond interactions in **2b**, involving the low-lying $\text{C}-\text{F}$ σ^* orbitals,²⁶ are qualitatively similar to those in **2d**. Thus, despite the stronger interallylic interactions through space in **2a**, through-bond interactions in **2b** make the HOMO–LUMO energy difference in **2b** much larger than that in **2a**.²⁵ This explains why **2b** has a 6–7 kcal/mol larger value of ΔE_{ST} than **2a**, even though d is ca. 0.1 Å longer in **2b** than it is in **2a**.

Assessment of the Bishomoaromatic Stabilization Energies (BHASEs) in 2 by Hydrogenation. Another way to assess the strengths of the interallylic interactions in **2a–d** is to compute the hydrogenation energy of each of these C_{2v} species, relative to the hydrogenation energy of two isolated allyl radicals in appropriate reference compounds. We chose **5a–d** as the reference compounds. The relative hydrogenation energies are given by the isodesmic reaction in eq 2, and the energies computed for this reaction are shown in Table 2.



These energies represent the sum of the bonding interactions (both through space and through bonds) between the two allyl fragments in **2a–d**, minus any strain that is required to achieve these interactions. Although the net interallylic interaction energies, defined by eq 2, include through-bond contributions,

(25) The energy of the bisallyl HOMO is also lowered upon decreasing the interallylic distance, d , in **2**, and the energy of the bisallyl LUMO is raised. Because d is different at the equilibrium geometries of **2a–d**, calculating the HOMO–LUMO energy difference (ΔE_{HL}) at the equilibrium geometry of each C_{2v} semibullvalene does not provide a straightforward assessment of how substitution of H in **2a** by F in **2b** and the CH_2 group in **2c** by O in **2d** affects the through-bond interactions in these semibullvalenes. The most straightforward way to compare the effect of through-bond interactions on the values of ΔE_{HL} in two different C_{2v} semibullvalenes is to perform calculations on both at the equilibrium geometry of just one of them. For example, using the Kohn–Sham orbital energies from B3LYP calculations on the triplet states, $\Delta E_{\text{HL}}(\mathbf{2a}) = 75.3$ kcal/mol and $\Delta E_{\text{HL}}(\mathbf{2b}) = 85.7$ kcal/mol at $d = 2.122$ Å, the CASPT2-optimized interallylic distance in **2a**. Similarly, at $d = 2.472$ Å, the CASPT2-optimized interallylic distance of **2c**, $\Delta E_{\text{HL}}(\mathbf{2c}) = 23.3$ kcal/mol and $\Delta E_{\text{HL}}(\mathbf{2d}) = 35.8$ kcal/mol. Thus, substitution of H in **2a** by F in **2b** and the CH_2 group in **2c** by O in **2d** does, indeed, result in through-bond interactions that stabilize the HOMO, relative to the LUMO, and thus increase the size of ΔE_{HL} .

(26) Review: Borden, W. T. *Chem. Commun.* **1998**, 18, 1919.

we refer to them as the bishomoaromatic stabilization energies (BHASEs) of **2a–d**. We deem the CASPT2 values to be more reliable than the (U)B3LYP values;²⁷ so, again, we base our discussion on the former.

Interestingly, the CASPT2 value of 15.4 kcal/mol for the BHASE in **2a** is almost the same as the interallylic interaction enthalpy in the boat Cope transition structure. Evaluated from experiments, the difference between the heats of formation of two allyl radicals²⁸ and the boat Cope transition structure²⁹ is 14.9 ± 2.1 kcal/mol, which is slightly larger than the (6/6)CASPT2/6-31G* value of 13.5 kcal/mol for the interallylic interaction enthalpy in the boat Cope transition structure.³⁰ Because the boat Cope rearrangement has $\Delta H^\ddagger = 44.7 \pm 2.0$ kcal/mol,²⁹ the 40 kcal/mol lower enthalpy of activation for the degenerate rearrangement of semibullvalene (**1a**)^{1,2} must be the result of a strain energy in **1a** of this size (vide infra).

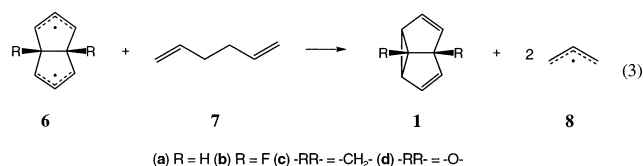
Despite the 0.12 Å longer interallylic bond distance, *d*, in **2b** than in **2a**, the CASPT2 BHASE is computed to be 3.9 kcal/mol larger for **2b** than for **2a**. Apparently, electron donation from the bisallyl HOMO into the low-lying *b*₁ combination of C–F σ^* orbitals provides significantly more stabilization energy for **2b** than the interaction between the allyl SOMO and these σ^* orbitals furnishes for two molecules of **5b**. Presumably, it is this extra through-bond stabilization in **2b** that makes its BHASE greater than that of **2a**.³¹

In **2c**, the BHASE is actually computed to be negative. This is also due to the effect of through-bond interactions, in this case involving the cyclopropane ring in **2c**. As shown in Figure 1, the filled *b*₁ orbital of the ring interacts with the bisallylic HOMO, and, because both orbitals are doubly occupied in the singlet state, this interaction provides no net stabilization for **2c**. In contrast, in **5c** the allyl nonbonding MO is only singly occupied; so the analogous interaction does provide some stabilization. Presumably, it is this extra stabilization for the two molecules of **5c** in eq 2 that makes the isodesmic reaction in this equation slightly exothermic for **2c**.

The through-bond interactions, depicted schematically in Figure 1, involving the C–O σ^* orbitals of the epoxide ring in **2d**, should stabilize **2d**, relative to **2c**. This selective stabilization of **2d** is probably the reason that its CASPT2 BHASE is 4.6 kcal/mol larger than that of **2c**, despite the fact the CASPT2 interallylic bond distance in **2d** is ca. 0.1 Å larger than that in **2c**.

Assessment of the Strain Energies (SEs) in 1. Not only the BHASEs in the *C*_{2v} semibullvalenes (**2**), but also the SEs of the *C*_s semibullvalenes (**1**) contribute to the relative energies of **1** and **2**. The SEs of **1a–d** can be evaluated by computing the

energies necessary to break the unique cyclopropane ring bonds in each semibullvalene, to form the hypothetical diradicals **6a–d**, in which the two allylic radicals do not interact with each other. The energy difference between **6** and **1** can then be compared with the energy necessary to break an unstrained C–C bond in an appropriate reference compound. We chose the central C–C bond in 1,5-hexadiene (**7**), cleavage of which forms two allyl radicals (**8**). Thus, the SEs of **1a–d** are each defined as the energy of the isodesmic reaction in eq 3.



The energies of **6a–d** can be estimated from the energies of **2a–d**, either by adding the relevant ΔE_{ST} value from Table 1 or by adding the appropriate BHASE value from Table 2. Except for **2b**, the two sets of CASPT2 values are nearly the same,³¹ but we prefer to use the thermodynamic BHASE values in Table 2. If the strain energy of **1** is defined by

$$\begin{aligned} SE(\mathbf{1}) &= E(\mathbf{1}) - E(\mathbf{6}) + 2E(\mathbf{8}) - E(\mathbf{7}) \\ &= E(\mathbf{1}) - E(\mathbf{2}) - \text{BHASE}(\mathbf{2}) + 2E(\mathbf{8}) - E(\mathbf{7}) \end{aligned} \quad (4)$$

then adding BHASE(**2**) to SE(**1**) gives the net amount by which bishomoaromaticity and strain combine to make the energy difference between **1** and **2** smaller than that between 1,5-hexadiene (**7**) and two allyl radicals (**8**).

The (U)B3LYP/6-31+G(d) bond dissociation energy of 1,5-hexadiene to two allyl radicals is computed to be 54.8 kcal/mol, and the corresponding enthalpy change for this reaction is calculated to be 49.6 kcal/mol. The use of a UB3LYP wave function for the radicals underestimates the energy of this reaction. The (6/6)CASPT2/6-31+G(d) value of 58.0 kcal/mol for the bond dissociation energy is higher than the (U)B3LYP value but lower than the previously published (6/6)CASPT2/6-31G* value of 61.6 kcal/mol. The latter CASPT2 energy gives a value for the bond dissociation enthalpy in 1,5-hexadiene that is in better agreement with experiment than the former.³² Therefore, we have chosen to use $2E(\mathbf{8}) - E(\mathbf{7}) = 61.6$ kcal/mol in computing the CASPT2 SEs in Table 2.

Using the above UB3LYP and CASPT2 values for $2E(\mathbf{8}) - E(\mathbf{7})$, together with the values of $E(\mathbf{1}) - E(\mathbf{2})$ in Table 1 and the BHASE values for **2** in Table 2, we obtained the SEs for **1** in Table 2. For each type of calculation, $2E(\mathbf{8}) - E(\mathbf{7})$ is an additive constant to all of the strain energies. Thus, eq 4 confirms that the difference between the SEs for any two semibullvalenes, plus the difference between their BHASEs, is equal to the difference between the relative energies of the *C*_s (**1**) and *C*_{2v} (**2**) geometries of the two semibullvalenes.

Whether the B3LYP energies or enthalpies or the CASPT2 energies are used, the data in Table 2 show that for each semibullvalene, relief of strain in **1**, rather than bishomoaromatic stabilization in **2**, is the major reason the energy difference between **2** and **1** is much smaller than the energy difference

(27) Because of the fact that the B3LYP wave functions for **2a** and **2b** are restricted, whereas the wave functions for **5a** and **5b** are not, the endothermicity of the reaction in eq 2 is underestimated by (U)B3LYP. In contrast, because the B3LYP wave functions for **2c** and **2d**, like those for **5c** and **5d**, are unrestricted, the UB3LYP BHASEs for **2c** and **2d** are much closer to the CASPT2 values than the (U)B3LYP are for **2a** and **2b**.

(28) Roth, W. R.; Bauer, F.; Beitat, A.; Ebbrecht, T.; Wüstefeld, M. *Chem. Ber.* **1991**, *124*, 1453.

(29) Goldstein, M. J.; Benzon, M. S. *J. Am. Chem. Soc.* **1972**, *94*, 7147.

(30) Hrovat, D. A.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1994**, *116*, 1072.

(31) It is probably significant that, although the CASPT2 values of ΔE_{ST} and the BHASEs are nearly the same for **2a**, **c**, and **d**, ΔE_{ST} is larger than the BHASE by 2.1 kcal/mol in **2b**. In two molecules of **5b**, both nonbonding electrons are stabilized by their interaction with the C–F σ^* orbitals. However, in contrast, in the triplet state of **2b** the unpaired electron in the LUMO cannot interact at all with these σ^* orbitals. It seems likely that this is the reason why in **2b** that ΔE_{ST} is larger than the BHASE value.

(32) It has previously been found³⁰ that use of a 6-311(2d,2p) basis set, which gives a bond dissociation energy of 66.0 kcal/mol, is necessary to obtain a bond dissociation enthalpy that agrees well with the experimental value of 59.6 ± 0.7 kcal/mol.²⁸

between 1,5-hexadiene (**7**) and two allyl radicals (**8**). However, for a more detailed discussion of the results in Table 2, we again use the presumably more accurate CASPT2 values for the BHASEs and SEs.

As noted in the previous section, because the CASPT2 BHASE in **2a** and the experimental allyl radical interaction enthalpy in the boat Cope transition structure are nearly the same, the difference of some 40 kcal/mol between the experimental activation enthalpies for the boat Cope²⁹ and semibullvalene^{1,2} degenerate rearrangements must be due to roughly 40 kcal/mol of strain relief in going from **1a** to **2a**. This is, probably fortuitously, exactly the SE for **1a** found by our CASPT2 calculations.³³

The (U)B3LYP calculations find the SEs of **1a** and **1b** to be almost identical. Thus, these calculations ascribe the negative activation enthalpy for the Cope rearrangement of **1b** entirely to a larger BHASE in **2b** than in **2a**. However, the CASPT2 results indicate that, on going from R = H to R = F, 3.1 kcal/mol of the 7.0 kcal/mol lower energy of **2**, relative to **1**, is due to greater relief of strain in **1b** than in **1a**. Because fluorine substituents are known to increase the strain in cyclopropane rings,³⁴ the CASPT2 finding seems more reasonable.

Through-bond interactions between the bisallylic HOMO and the bonds of the cyclopropane ring actually destabilize the lowest singlet state of **2c**, making the CASPT2 BHASE 21.0 kcal/mol smaller in **2c** than in **2b**. However, the 25.7 kcal/mol increase in strain on going from R = F to $-\text{RR}- = -\text{CH}_2-$ makes the CASPT2 energy difference between **2c** and **1c** 4.7 kcal/mol larger than that between **2b** and **1b**.

Replacement of $-\text{RR}- = -\text{CH}_2-$ in **2c** by $-\text{RR}- = -\text{O}-$ in **2d** results in through-bond interactions that stabilize the latter (see Figure 1). However, the resulting difference between the BHASEs of **2c** and **2d** accounts for only 4.6 kcal/mol of the 16.5 kcal/mol difference between the relative energies of **1c-2c** and **1d-2d**. The balance of 11.9 kcal/mol is due to the increase in strain that occurs when $-\text{RR}- = -\text{CH}_2-$ in **1c** is replaced by $-\text{RR}- = -\text{O}-$ in **1d**.

Conclusions

Our calculations find that 1,5-annelated semibullvalenes **1c** and **1d** each have a large energetic preference for a C_{2v}

equilibrium geometry, respectively, **2c** and **2d**. However, **2c** and **2d** both have significantly reduced BHASEs, relative to the C_{2v} transition state (**2a**) for the degenerate Cope rearrangement of the parent semibullvalene (**1a**).³⁵ The driving force for conversion of **1c** to **2c** and **1d** to **2d** is not bishomoaromatic stabilization of the C_{2v} geometries, but rather relief of strain in the C_s geometries of the semibullvalenes. Therefore, the common practice of describing all semibullvalenes that prefer a C_{2v} geometry as "bishomoaromatic" is misleading.

In fact, interallylic bonding through space is so small in **2c** that through-bond interactions are predicted to make the ground state of this diradical a triplet. We hope that this prediction will be tested experimentally.

On the other hand, our CASPT2 calculations find that through-bond interactions in **2b**, involving the fluorines, make the BHASE in this semibullvalene greater than that in **2a**. The increased BHASE in **2b**, coupled with an increased SE in **1b**, relative to **1a**, are predicted to make the C_{2v} structure the equilibrium geometry, albeit by only 1–2 kcal/mol. Like the prediction of a triplet ground state for **2c**, we hope that the prediction that semibullvalene **1b** will prefer a geometry (**2b**) which not only has C_{2v} symmetry but is also bishomoaromatic will be subject to experimental test.

Acknowledgment. The research reported here was made possible through grants from the National Science Foundation (CHE-9909892 and CHE-9808182) and a generous allotment of computer time provided by the University of Washington Student Technology Fund. D.K.H. thanks the Mary M. Gates Foundation for generous support.

Supporting Information Available: The optimized geometries and energies of **1-8** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JA027392P

(33) Dewar and Lo⁶ were thus correct in conjecturing that strain relief is a major factor in the low barrier to degenerate rearrangement of **1a**.

(34) Reviews: (a) Dolbier, W. R., Jr. *Acc. Chem. Res.* **1981**, *14*, 195. (b) Smart, B. E. In *Molecular Structure and Energetics*; Liebman, J. F., Greenberg, A., Eds.; VCH: Deerfield Beach, FL, 1986; Vol. 3, p 141.

(35) Unlike the case in **2c** and **2d**, the interallylic bond lengths at the optimized C_{2v} geometry of 2,8:4,6-bis(ethano)semibullvalene are actually slightly shorter than those in **2a**,¹⁵ suggesting that the BHASE in the doubly bridged C_{2v} semibullvalene is actually larger than that in **2a**. In fact, the (U)B3LYP singlet-triplet splitting of $\Delta E_{\text{ST}} = 17.0$ kcal/mol that we compute for the bis(ethano)semibullvalene is larger by 4.7 kcal/mol than ΔE_{ST} in **2a**. Part of the larger value of ΔE_{ST} in the former semibullvalene is probably due to some residual repulsion between the two allyl radicals in the triplet. The ethano bridges constrain the interallylic distance in this state to be 2.301 Å, which is 0.284 Å shorter than the interallylic distance in the triplet state of **2a**. However, there is no doubt that bishomoaromatic stabilization, as well as strain relief, lead to 2,8:4,6-bis(ethano)semibullvalene being predicted computationally to have a C_{2v} equilibrium geometry.^{9,14,15}