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How Important Is Bishomoaromatic Stabilization in Determining the Relative Barrier Heights for the Degenerate Cope Rearrangements of Semibullvalene, Barbaralane, Bullvalene, and Dihydrobullvalene?[†]

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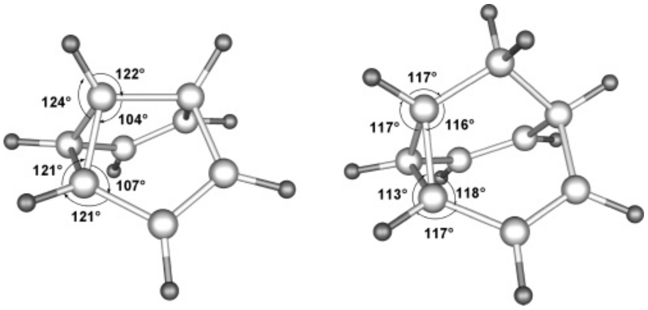
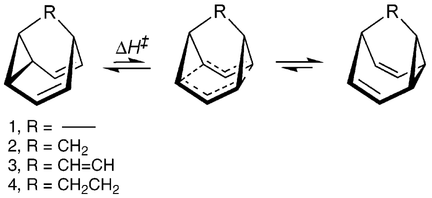


B3LYP/6-31G* calculations have been used to investigate the origins of the relative barrier heights for the degenerate Cope rearrangements of semibullvalene (**1**), barbaralane (**2**), bullvalene (**3**), and dihydrobullvalene (**4**). We conclude from our calculations that, of the four transition structures (TSs), that for rearrangement of **1** has the smallest amount of interallylic bonding. Nevertheless, relief of strain in the reactant confers on **1** the lowest barrier to Cope rearrangement. Conjugation between the cyclopropane ring and the π bond of the etheno bridge in **3** makes the barrier for its Cope rearrangement higher than that for **4** and also contributes to making the barrier for **3** higher than that for **2**. However, the relatively low barrier to the Cope rearrangement of **2** is largely due to the TS for this reaction having the largest amount of interallylic bonding of all four TSs.

Semibullvalene (**1**),[1] barbaralane (**2**),[2] and bullvalene (**3**)[2,3] are three hydrocarbons of considerable interest because they each undergo a degenerate boat Cope rearrangement with a low enthalpy of activation. The low barrier heights have generally been attributed to the fact that the transition structures (TSs) for these reactions benefit from "bishomoaromatic" stabilization.[4]



However, B3LYP and CASPT2 calculations have recently shown that the interallylic stabilization enthalpy

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[†] This manuscript is dedicated to Professor William von Eggers Doering for his seminal contributions, both theoretical and experimental, to the study of fluxional molecules.

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(ISE), due to bonding between the two allyl groups, is about the same size in the TS for boat Cope rearrangement of 1,5-hexadiene as in the TS for Cope rearrangement of **1**.[5] The ca. 40 kcal/mol lower barrier height for boat Cope rearrangement of **1**[6] than of 1,5-hexadiene[7] was shown by the calculations to be due almost entirely to relief of the strain in **1** in the TS for its Cope rearrangement.[5]

The enthalpies of activation for Cope rearrangement, measured for semibullvalene (5.2 kcal/mol)[6b] and barbaralane (7.3 kcal/mol),[8a,b] are both considerably lower than that for bullvalene (13.3 kcal/mol).[9a,b] The differences between the barrier heights have been attributed to differences between the strain energies (SEs) of the reactants and/or differences between the ISEs in the TSs.[10]

To understand quantitatively how differences between the SEs of the reactants and the ISEs of the TSs contribute to the differences between the barrier heights for the Cope rearrangements of **1**−**3**, we have carried out B3LYP/6-31G* calculations. We have also calculated the enthalpy of activation for the Cope rearrangement of dihydrobullvalene (**4**) to analyze why the barrier height (10.0 kcal/mol)[11] for its Cope rearrangement is lower than that for **3**. In this paper, we describe and discuss the results of our calculations.

Computational Methodology

B3LYP/6-31G* calculations have been found to give activation enthalpies for Cope rearrangement of **1**[12] and **2**[13] that are in excellent agreement with the experimental values. Therefore, Becke's 3-parameter functional,[14] in conjunction with the correlation functional of Lee, Yang, and Parr[15] and the 6-31G* basis set,[16] was also used in the computational evaluation of **1**−**4**. The unscaled frequencies from B3LYP/6-31G* vibrational analyses were used in order to obtain zero-point energies and heat capacities, integrated to 298 K. The calculations were carried out with the Gaussian 03 suite of programs.[17]

TABLE 1. B3LYP/6-31G* and Experimental Enthalpies (kcal/mol) of Activation for Cope Rearrangements ($\Delta H^{\ddagger}$), B3LYP/6-31G* Singlet−Triplet Energy Differences (ΔE_{ST}), and Interallylic Stabilization Enthalpies (ISE) in the TSs and Bond Dissociation Enthalpies (BDE) in and Enthalpies of Hydrogenation of the Reactants

compd	$\Delta H^{\ddagger}_{calc}$	$\Delta H^{\ddagger}_{exp}$	ΔE_{ST}	ISE	BDE	ΔH (H_2)[a]
1	4.5	5.2[b]	11.6	9.1	13.6	42.8 (42.0)
2	6.4	7.3[c]	21.9	17.0	23.4	31.9 (29.0)
3	12.5	13.3[d]	17.3	13.7	26.2	28.3 (26.0)
4	8.5	10.0[e]	17.1	13.3	21.8	33.1 (31.2)

[a] Enthalpy of hydrogenation to form the more stable 2,6-diene. The enthalpy for forming the less stable 2,7-diene is given in parentheses. [b] Reference 6b. [c] Reference 8a,b. [d] Reference 9a,b. [e] See ref 11.

Results and Discussion

Activation Enthalpies ($\Delta H^{\ddagger}$). The computed barrier heights for the Cope rearrangements of **1**−**4** are given in Table 1. As shown by the comparison with the experimental values in Table 1, B3LYP/6-31G* calculations provide values of $\Delta H^{\ddagger}$ that are in excellent agreement with the values that have been measured. Therefore, there is good reason to believe that B3LYP/6-31G* calculations can also be used to analyze the differences between the barrier heights to Cope rearrangements in **1**−**4**.[18]

Singlet−Triplet Energy Differences (ΔE_{ST}) and Interallylic Stabilization Enthalpies (ISEs). Because there is no bonding between two radicals in a triplet, one possible measure of the ISE of the TS for a Cope rearrangement is the enthalpy difference between the TS

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(11) $\Delta H^{\ddagger} = 12.0$ kcal/mol has been reported for **4** (Oth, J. F. M.; Gilles, J.-M. Unpublished results, cited by: Schröder, G.; Oth, J. F. M. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 414). However, like the values reported in this review for **2** and **3**, this value for **4** is clearly in error. Based on the ratio of rates reported for **3** and **4** at 273 K, the assumption of equal preexponential factors, and $\Delta H^{\ddagger} = 13.3$ kcal/mol for **3**, $\Delta H^{\ddagger} = 10.0$ kcal/mol is obtained for the Cope rearrangement of **4**.

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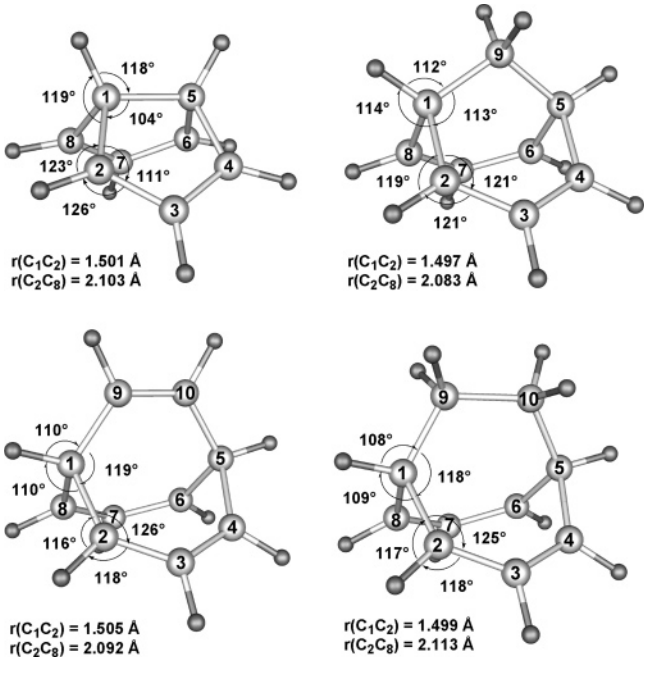
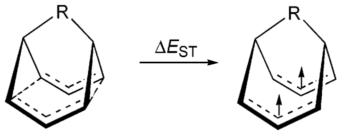


FIGURE 1. B3LYP/6-31G*-optimized transition-structure geometries for the Cope rearrangements of **1**−**4**.

and the triplet diradical formed from it by exciting an electron from the HOMO to the LUMO and inverting the spin of the electron.[5] The (U)B3LYP/6-31G* values of ΔE_{ST} in **1**−**4**, which are given in Table 1, indicate that the bonding between the allylic radicals in the singlet state is strongest in barbaralane (**2**) and weakest in semibullvalene (**1**).



(1)

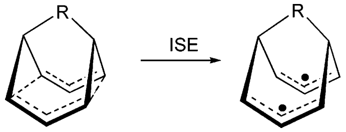
Table 1 also indicates that the value of ΔE_{ST} in **3** and **4** is nearly the same and intermediate between that in **1** and **2**. However, as shown in Figure 1, the interallylic distance, $r(C_2C_8)$, in the Cope TS is computed to be 0.021 Å shorter in **3** than in **4**. Therefore, it is somewhat surprising that **3** does not have the larger value of ΔE_{ST}.

The probable explanation is that the π^* orbital of the double bond in the two-atom bridge in bullvalene (**3**) has the correct symmetry to interact with the out-of-phase combination of allylic nonbonding MOs, which contains one electron in the triplet. In fact, a Mulliken population analysis shows 0.04 unpaired electrons on the carbons of the unsaturated two-atom bridge in triplet **3**. The delocalization of one of the nonbonding electrons in the triplet stabilizes this state relative to the singlet TS.

Thus, the similar values of ΔE_{ST} in **3** and **4** are presumably due to a cancellation of two effects. As suggested by the smaller value of $r(C_2C_8)$ in the TS for Cope rearrangement of **3** than of **4**, there appears to be a larger amount of interallylic bonding in the former TS. However, the resulting stabilization of the TS for Cope rearrangement of **3** is apparently offset in triplet **3** by delocalization of a nonbonding electron into the unsaturated two-atom bridge. Similar stabilization of triplet **4** is, of course, impossible, because in **4** the two-atom bridge is saturated.

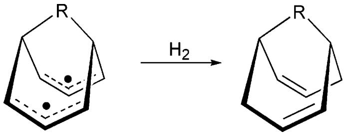
In addition to the possible existence of effects that stabilize the triplet state, there is another problem with using ΔE_{ST} to define the ISE in a Cope TS − there is actually a small, net-antibonding interaction between the two radicals in a triplet. Therefore, a better indication than ΔE_{ST} of the ISE in a Cope TS is the enthalpy difference between the TS and the pair of isolated allylic radicals that interact in the TS.

However, in the case of the TSs for Cope rearrangement of **1**−**4**, the two allylic radicals cannot escape from interacting with each other. Hence, the ISEs must be defined in terms of the enthalpy of the fictional diradical in eq 2, in which the two allylic radicals do not interact.



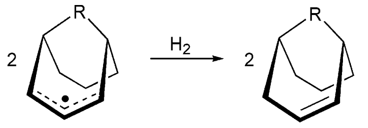
(2)

The enthalpy of the fictional diradical in eq 2 can neither be measured nor computed directly. However, since the allylic radicals in the diradical are, by definition, noninteracting, the enthalpy of the hydrogenation reaction of the diradical to the diene,



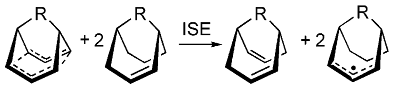
(3)

should be nearly the same as the enthalpy of hydrogenation of two moles of the monoradical to two moles of the monoene in eq 4.



(4)

Combining eqs 3 and 4 and substituting for the diradical in eq 2 gives the ISE of the TS in eq 2 as the enthalpy of the isodesmic reaction in eq 5.[5]



(5)

The ISEs of the TSs for the Cope rearrangements of **1**−**4** are defined in eq 5 as the difference between the hydrogenation enthalpy of the two interacting allylic radicals in the TS and the hydrogenation enthalpy of the pair of noninteracting allylic radicals in two moles of the monoradical in eq 4. The ISEs of the TSs are given in Table 1.

There is reasonable agreement of the differences between the singlet−triplet splittings in the four TSs

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(18) CASPT2 calculations have shown that the necessity of using (U)B3LYP calculations for triplets in computing ΔE_{ST} values, and for radicals in computing ISE values, leads to the underestimation of the sizes of both of these measures of the interallylic interaction enthalpy in a Cope TS.[5] However, when comparing (U)B3LYP values of ΔE_{ST} or ISE for two different Cope TSs the errors in each should tend to cancel.

with the differences between their ISEs. However, the net antibonding interaction between the allylic radicals in the triplet makes ΔE_{ST} larger than the ISE for each of the hydrocarbons in Table 1.

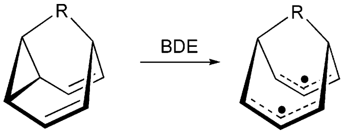
If the difference between the ΔE_{ST} and the ISE for each of the hydrocarbons is taken as a measure of the degree to which the allylic radicals interact in each triplet diradical, the results in Table 1 indicate that the largest amount of antibonding interaction occurs in the triplet diradical formed from **2** and the smallest amount in the triplet diradical formed from **1**. This conclusion is consistent with the interallylic distances, computed for the triplet diradicals. These distances are 2.584, 2.539, 2.548, and 2.550 Å for **1**−**4**, respectively.

Of the four TSs for Cope rearrangement, that for semibullvalene (**1**) has the lowest ISE and that for barbaralane (**2**) has the highest. The reason why the TS for **2** is computed to have the largest ISE and the TS for **1** the smallest is indicated by Figure 1, which depicts the geometries of the TSs for the Cope rearrangements of **1**−**4**. The zero bridge in **1** prevents the terminal atoms of the two allylic moieties from approaching each other as closely in the TS for Cope rearrangement of **1** [$r(C_2C_8)$ = 2.103 Å] as in the TS for Cope rearrangement of **2** [$r(C_2C_8)$ = 2.083 Å]. In addition, the geometry of the TS for Cope rearrangement of **2** also allows the overlap between the 2p−π AOs on the terminal atoms to have more σ and less π character than in the TS for Cope rearrangement of **1**.

The TSs for the Cope rearrangements of bullvalene (**3**) and dihydrobullvalene (**4**) are calculated not only to have very similar values of ΔE_{ST} but also very similar ISEs, despite the fact that the interallylic distance of $r(C_2C_8)$ = 2.092 Å in the former TS is 0.021 Å shorter than that in the latter. The explanation of the similar ISEs is analogous to that for the similar values of ΔE_{ST}. The monoradical in eq 5, whose enthalpy is used to compute the ISE, is stabilized by some delocalization of the electron in the nonbonding MO into the π^* MO of the unsaturated two-atom bridge in bullvalene.

Bond Dissociation Enthalpies (BDEs) and Strain Energies. Since the ISE is computed to be 7.9 kcal/mol smaller in the TS for Cope rearrangement of **1** than of **2**, the ca. 2 kcal/mol lower enthalpy of activation for the former reaction is certainly not due to the greater electronic stabilization of the TS for **1**. Instead, the 2 kcal/mol lower barrier to Cope rearrangement in **1** than in **2** must be due to **1** releasing about 10 kcal/mol more strain energy than **2** in the TS for Cope rearrangement.

One way to compute the strain energies of hydrocarbons **1**−**4**, relative to each other, is to calculate the difference between the dissociation enthalpies of the doubly allylic C−C bonds in the three-membered rings of these hydrocarbons. Of course, to ensure that the BDEs do not contain a contribution from stabilizing interactions between the pair of allylic radicals thus formed, the BDEs must be defined in terms of the same fictional diradicals, containing two noninteracting allylic radicals, as in eq 2. With the definition of ISE in eq 2 and BDE in eq 6, $\Delta H^{\ddagger}$ = BDE − ISE, or BDE = $\Delta H^{\ddagger}$ + ISE.



(6)

The BDEs of hydrocarbons **1**−**4** are given in Table 1. The fact that semibullvalene (**1**) is calculated to have the lowest BDE means that it has the highest strain energy of the four hydrocarbons. It is apparent from the B3LYP-optimized structures in Figure 2 that the necessity in **1** of connecting the bridgehead carbons (C1 and C5) with a bond, rather than with a CH_2 group (as in **2**) or two bridging carbons (as in **3** and **4**), results in severe distortions of the angles between the exocyclic bonds and the endocyclic bonds of the three-membered ring in **1**. These bond angle distortions are presumably responsible for the 9.8 kcal/mol lower BDE and the 0.023 Å larger C2−C8 bond length in semibullvalene (**1**) than in barbaralane (**2**).

However, **2** does not have the highest BDE in Table 1. Replacing the methano group that connects the bridgehead carbons in **2** with the etheno group in **3** increases the calculated BDE by 2.8 kcal/mol. In contrast, replacing methano in **2** with ethano in **4** decreases the calculated BDE by 1.6 kcal/mol. Thus, saturating the etheno bridge makes the BDE of **4** 4.4 kcal/mol lower than that of **3**. Since the ISEs of the TSs for the Cope rearrangements of **3** and **4** differ by only 0.4 kcal/mol, it is the higher BDE of **3** that makes the calculated $\Delta H^{\ddagger}$ for its Cope rearrangement 4.0 kcal mol/mol higher than $\Delta H^{\ddagger}$ for the Cope rearrangement of **4**.

The bond angles in Figure 2 suggest that **3** is less strained than **4**. However, we believe that at least some of the higher BDE in **3** is due to stabilizing conjugation between the cyclopropane ring and the π bond of the etheno bridge in **3**. Similar types of conjugation have been invoked to explain why the barriers to Cope rearrangement of 9-methylenebarbaralane,[19] barbaralone,[19−21] and protonated barbaralone[21] are all higher than that of barbaralane. Upon replacement of the etheno bridge in

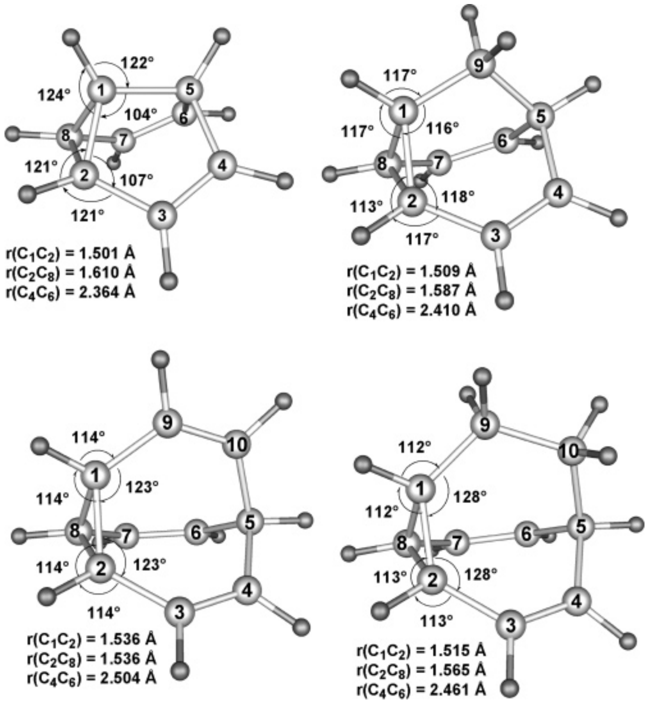


FIGURE 2. B3LYP/6-31G*-optimized geometries of **1**−**4**.

3 with the ethano bridge in **4**, the conjugation between the cyclopropane ring and the π bond of the etheno bridge is, of course, lost.

The differences between the bond lengths in the cyclopropane rings of **3** and **4** are consistent with loss of the stabilizing interaction between one of the degenerate pair of highest occupied MOs of the three-membered ring and the π^* orbital of a double bond on going from **3** to **4**. The loss of this interaction should result in an increase in the electron density in **4** in the ring orbital that interacts with the π^* orbital in **3**. The increase in the electron density in this ring orbital would be expected to strengthen the ring bonds that are proximal to the saturated bridge in **4** (C1−C2 and C1−C8) but to weaken the ring bond that is distal to it (C2−C8).[22] As shown in Figure 2, not only is the C1−C2 bond 0.021 Å shorter in **4** than in **3**, but the C2−C8 bond is, indeed, 0.029 Å longer.

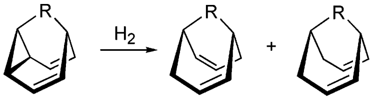
The results in Table 1 show that the differences in Cope barrier heights between **1** and **2**, as well as between **3** and **4**, are due to the differences between the BDEs in the reactant. However, although the BDE of **2** is computed to be 1.6 kcal/mol higher than that of **4**, nevertheless, the barrier height for Cope rearrangement is computed to be 2.1 kcal/mol lower in **2**. The reason is obviously that the ISE of the TS for Cope rearrangement of **2** is computed to be 3.7 kcal/mol greater than that of the TS for Cope rearrangement of **4**.

As already discussed, the TS for Cope rearrangement of **2** has the largest ISE of all four TSs. The 3.3 kcal/mol higher ISE of the TS, combined with the 2.8 kcal/mol lower BDE makes the calculated barrier for the Cope rearrangement of **2** 6.1 kcal/mol lower than the barrier computed for **3**.

Calculated Differences between Enthalpies of Hydrogenation [ΔH (H_2)]. Measurement of either the ISEs or BDEs in **1**−**4** would allow experimental tests of the explanations in the previous section for the differences between the barrier heights for the Cope rearrangements of these hydrocarbons. However, both the ISEs in eq 2 and BDEs in eq 6 are defined in terms of a fictional diradical in which there is no interaction between the allylic moieties. Therefore, although the ISEs and the BDEs can, through the use of eq 5, be computed, neither of these quantities can be measured directly.

As a substitute for measuring the ISEs, it is possible, at least in principle, to measure the singlet−triplet splittings in **1**−**4** using transition state spectroscopy.[23] However, these measurements of ΔE_{ST} would require the preparation of the radical anions of **1**−**4**, and it is unlikely that any of these hydrocarbons would bind an electron in the gas phase.

Probably the best hope of testing the explanations in the previous section would be to measure the differences between the enthalpies of hydrogenation of the cyclopropane rings in **1**−**4**, because these differences would be expected to be similar to the differences between the BDEs. Therefore, we computed the enthalpies of hydrogenation of **1**−**4** to both the more stable 2,6-dienes and to the less stable 2,7-dienes. The results are given in Table 1.



(7)

As expected, **1**, which is predicted to have the lowest BDE, is computed to have the highest ΔH (H_2). The BDEs of **2**−**4** are computed to be, respectively, 9.8, 12.6, and 8.2 kcal/mol higher than those of **1**, whereas the enthalpy for hydrogenating **1** to the more stable diene is computed to be, respectively, 10.9. 14.5, and 9.7 kcal/mol higher than the enthalpies of hydrogenation of **2**−**4**. In each case the $\Delta\Delta H$ (H_2) value is higher than the corresponding ΔBDE value, indicating that addition of a pair of hydrogen atoms to C2 and C6 of the fictional diradicals, shown in eqs 3 and 6, is more exothermic for **1** than for **2**−**4**. However, the differences between the $\Delta\Delta H$ (H_2) values and the corresponding ΔBDE values are only 1−2 kcal/mol, so both sets of values give a consistent picture of the relative strain energies of these four hydrocarbons.

If the less stable dienes are used instead of the more stable dienes, the calculated value of ΔH (H_2) for **1** decreases by 0.8 kcal/mol; whereas, that for **2** decreases by 2.9 kcal/mol. The larger enthalpy difference between the dienes formed from **2** than from **1** indicates that there are larger destabilizing transannular interactions in the 2,7-diene formed from **2** than from **1**. This finding is consistent with the larger interallylic repulsion and smaller interallylic distance in the triplet state of **2** than of **1**.

Conclusions

Our computational results show that the methano bridge between C1 and C5 in barbaralane (**2**) allows much more interallylic interaction in the TS than does the C−C bond between these bridgehead carbons in semibullvalene (**1**). The 1.9 kcal/mol lower calculated enthalpy of activation for Cope rearrangement of **1** than of **2** is, therefore, not due to the ISE in the TS for Cope rearrangement being greater in **1** than **2**. On the contrary, **1** is computed to have a TS ISE that is 7.9 kcal/mol smaller than that of **2**.

The ca. 2 kcal/mol lower value of $\Delta H^{\ddagger}$, both calculated and measured, for **1** is due to the strain in its three-membered ring being considerably greater than the strain in the three-membered ring of **2**. Based on the calculated BDEs, the strain energy of **1** is 9.8 kcal/mol greater than that of **2**, and based on the predicted enthalpies of hydrogenation to the 2,6-dienes, the strain energy of **1** is 10.9 kcal/mol higher than that of **2**.

The enthalpy of activation for Cope rearrangement of bullvalene (**3**) is both computed and found to be ca. 6 kcal/mol higher than that of barbaralane (**2**). Favorable interaction between the double bond of the etheno bridge

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and the cyclopropane ring in **3** is probably responsible, at least in part, for making its strain energy 2.8 kcal/mol smaller than that of **2**, based on calculated BDEs, and 3.0−3.6 kcal/mol smaller, based on predicted enthalpies of hydrogenation. In addition, the ISE of the TS for Cope rearrangement is calculated to be 3.3 kcal/mol smaller for **3** than for **2**.

Both the ISE and ΔE_{ST} values are calculated to be nearly the same in dihydrobullvalene (**4**) as in bullvalene (**3**). Consequently, it is the higher BDE of **3** that is responsible for making $\Delta H^{\ddagger}$ for its Cope rearrangement larger than that of **4**. The calculated BDE is 4.4 kcal/mol higher for **3** than for **4**, and the enthalpy of hydrogenation is predicted to be 4.8−5.2 kcal/mol lower for the former than for the latter. At least part of these enthalpy differences is attributable to the loss of a stabilizing interaction with the cyclopropane ring on replacing the etheno bridge in **3** with the ethano bridge in **4**.

The ca. 2 kcal/mol lower barrier to Cope rearrangement in **2** than in **4**, is due to the 3.7 kcal/mol greater ISE in the TS for the former reaction than the latter. However, with this exception, the differences between the barrier heights to Cope rearrangements in **1**−**4** are dominated by differences between BDEs in the reactants, rather than by differences between ISEs in the TSs. Thus, “bishomoaromatic stabilization” plays but a minor role in the qualitative differences between the barrier heights to Cope rearrangements in **1**−**4**.

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Supporting Information Available: Optimized geometries and energies for the localized and delocalized singlet states, and the delocalized triplet states for **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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