Chemical Consequences of Orbital Interactions. II. Ethylene and Butadiene Bridged Polycyclic Hydrocarbons Containing Three- and Four-Membered Rings[1]

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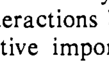
Abstract: Orbital interactions are shown to have significant influence on the chemical behavior of unsaturated, polycyclic hydrocarbons containing small rings. A comparison of the π-type orbital interactions between small ring and ethylene bridge in bicyclo[2.1.0]pent-2-ene and bicyclo[2.2.0]hex-2-ene provides insight into the thermal rearrangements of the compounds as well as cyclopropyl vs. cyclobutyl edge participation in the retro-Diels-Alder reactions of polycyclic azo compounds and in the solvolyses of substituted 7-norbornyl tosylates. Bicyclo[2.1.0]pent-2-ene and bicyclo[2.1.1]hex-2-ene are found to be unique among the compounds studied in having net antibonding interactions between their small ring and bridge π orbitals, reminiscent of the π interactions in cyclobutadiene. The benzene isomers, benzvalene and Dewar benzene, are found to be stabilized by similar interactions, while the 1,3 interactions between the π bonds in Dewar benzene do not appear to have important energetic impact. The butadiene bridged counterparts of the ethylene bridged systems are also analyzed and found to represent the more energetically favorable bridging arrangement in each case. The degree of preference does, however, vary considerably and provides insight into the Diels-Alder reactivities of the dienes. Predictions are also made concerning hyperconjugative stabilizations for a series of related, polycyclic cations. The qualitative arguments are supported by bond orders, energies, and orbital drawings calculated by the EH method, in addition to numerous comparisons with other theoretical and experimental work.

Cyclopropyl and cyclobutyl rings have been found to stabilize adjacent vinyl groups and cationic centers to a degree intermediate between the stabilization obtained from formally saturated and unsaturated systems.[2] In the same way that analogies may be made between the stabilizing π interactions in 1,3-butadiene and vinylcyclopropane or allyl and cyclopropylcarbinyl cations, analogies should also be sought between the destabilizing π interactions in cyclobutadiene (**1**) and bicyclo[2.1.0]pent-2-ene (**2**). Although the elusiveness of **1** is primarily ascribed to its 4π-electron antiaromatic character,[3] the similar importance of electronic interactions in determining the stabilities of small ring polycycles has been overshadowed by concern with their angle strain.



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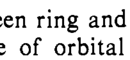

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In previous studies,[1,4] the experimentally observed[5,6] energetic preference for cyclobutane being 1,3-bridged by butadiene rather than ethylene was shown to be consistent with orbital interactions between ring and bridge. Furthermore, the relative importance of orbital interactions between small rings and unsaturated bridges was shown[1,4] to be reflected in bond orders and heats of reaction calculated by molecular orbital methods that include overlap.

The work described in this paper was undertaken to assess the importance of orbital interactions in determining the stabilities and reactivities of the experimentally known, ethylene bridged polycyclic hydrocarbons containing three- and four-membered rings, **2–6.** In addition to obtaining a better understanding of the chemistry of these compounds, insight is also gained in the area of cyclopropyl vs. cyclobutyl edge participation in the solvolyses of substituted 7-norbornyl tosylates and retro-Diels-Alder reactions of polycyclic azo compounds. Another outcome of the study is the prediction of the relative hyperconjugative stabilizations of polycyclic cations related to **2–6.** The butadiene bridged counterparts of **1–6** are also analyzed in order to determine the ethylene vs. butadiene bridging preferences of the three- and four-membered rings. Insight into the Diels-Alder reactivities of the butadiene bridged systems is a straightforward consequence. The available experimental data on the analyzed compounds are seen to be in agreement with the results of the calculations reported here.

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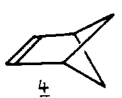

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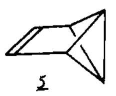

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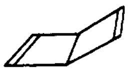

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Cyclobutadiene and 3,4-Dimethylenecyclobutene

It is instructive to pursue the cyclobutadiene analogy since the same type of orbital interactions that destabilize it will be sought in the ethylene bridged polycycles. The π-orbital interactions in rectangular cyclobutadiene are schematized in Figure 1 as the interaction of two ethylene fragments. When the two occupied ethylenic orbitals interact they form a more bonding molecular orbital and a less bonding one. The important feature of the interaction is that the less bonding level has been raised to a greater extent than the more bonding level has been lowered. The result of the four-electron interaction is net destabilization.[7] If, however, the ethylenic bonding levels were only half-filled, a net stabilizing, two-electron interaction would result, i.e., in forming the cyclobutadienyl dication. It is significant that there are no unoccupied π orbitals of the same symmetry as the filled ones in cyclobutadiene to help stabilize the system via two-electron interactions.

The magnitude of the destabilization caused by the mixing of two filled orbitals is proportional to their overlap.[7,9] As a consequence the destabilization can be detected by molecular orbital methods that include overlap, as in extended Hückel (EH) or ab initio calculations. The currently popular, semiempirical MO methods that neglect differential overlap (NDO)[10] predict equal raising and lowering of interacting levels which implies no net interaction of two filled levels.

The net destabilization caused by the interaction of two filled orbitals, in the absence of low-lying unfilled orbitals of the same symmetry, can be detected in bond orders[11] and energies[12] calculated by the EH method.[1] Thus, the $2p-\pi$ bond order calculated by the EH method between carbons 2 and 3 or 1 and 4 (P_a^π) in rectangular cyclobutadiene is

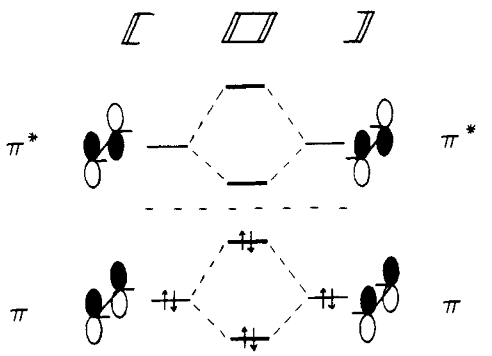


Figure 1. Schematic interaction diagram for the π orbitals of rectangular cyclobutadiene.

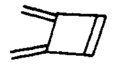
Table I. Bond Lengths[a] and EH Bond Orders

Compd	r_a, Å	r_b, Å	P_a^{π}
1	1.51	1.34	−0.183
2	1.51	1.34	−0.015
3	1.51	1.34	0.073
4	1.537	1.332	−0.007
5	1.497	1.339	0.098
6	1.51	1.34	0.060
7	1.51	1.483	0.158
16	1.51	1.483	0.089
17	1.51	1.483	0.067
18	1.537	1.483	0.078
19	1.497	1.483	0.121
20	1.51	1.483	0.057

[a] r_a is the length of the bond connecting small ring to unsaturated bridge in the polycycles. r_b is the length of the bond between the sp^2 hybrid carbons in the unsaturated bridge.

found to be negative. The P_a^{π} value of −0.183 for **1** recorded in Table I must be considered a lower bound since configuration interaction has not been included in the EH calculations.[13] Nevertheless, the number provides a useful reference value for calculations on the polycycles, **2–6**.

When a butadiene fragment is substituted for one of the ethylene units in **1**, 3,4-dimethylenecyclobutene (**7**) is obtained. The orbital interaction scheme for this molecule shown in Figure 2 is more complex than for **1**. It should first be noticed that the highest occupied MO's of the two fragments are now of opposite symmetry and cannot interact. However, the ethylenic π HOMO will be destabilized by its interaction with the lower lying butadiene orbital, χ_1. Since the two interacting orbitals are of different energy, and χ_1 is more delocalized than π, they do not interact as strongly as the two filled π orbitals in **1**.[7c] Furthermore, the destabilization of π is mitigated by its interaction with χ_3*. The net interaction of π, χ_1, and χ_3* is, in fact, stabilizing according to the EH MO coefficients for the resultant delocalized orbitals in **7**.[14] The butadiene HOMO, χ_2, is also stabilized via its interaction with the ethylenic LUMO, π*, and χ_4*. It is not surprising, therefore, to find that the 2p-π bond order between carbons 1 and 4 in **7** determined by an EH calculation is +0.158.



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The fact that butadiene has low-lying antibonding orbitals of opposite symmetry makes it a very accommodating bridging group. It cannot only interact favorably with symmetric HOMO's of another molecular fragment, e.g., π in **7**, but also with antisymmetric HOMO's in an analogous three-way fashion involving χ_2, χ_4* and the HOMO of the other fragment. This is supported by the calculations on the butadiene bridged polycycles described below.

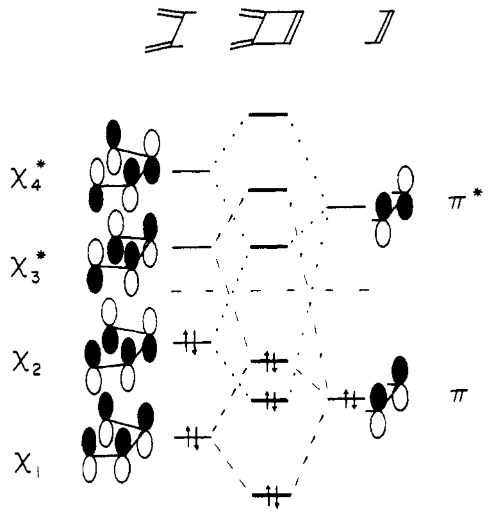


Figure 2. Schematic interaction diagram for the π orbitals of 3,4-dimethylenecyclobutene.

Table II. Hybrid Angles and Charges[a,b]

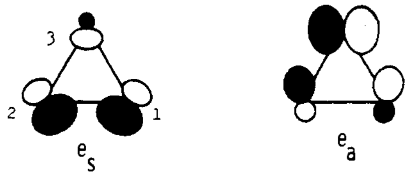
	e_s		e_a	
Compd	θ, deg	ρ_{C_1}	θ, deg	ρ_{C_1}
Ethylene	90.0	1.00	90.0	1.00
Cyclopropane	46.7	0.85	84.7	0.40
Cyclobutane	18.3	0.42	71.7	0.42

[a] EH results. [b] In ethylene, e_s and e_a correspond to π and π*, respectively.

Bicyclo[2.1.0]pent-2-ene and Bicyclo[2.2.0]hex-2-ene

Replacement of an ethylenic unit in **1** by an edge of a cyclopropyl or cyclobutyl ring yields bicyclo[2.1.0]pent-2-ene (**2**) or bicyclo[2.2.0]hex-2-ene (**3**). A comparison of the orbital interactions between small ring and ethylene bridge in these two molecules may be expected to yield some insight into the mechanism and relative extent of cyclopropyl and cyclobutyl edge participation in general.

In a previous study,[1] the important orbital interactions in **2** were shown to occur between the degenerate pair of cyclopropane HOMO's, e_s and e_a, and the π and π* orbitals of the ethylene bridge. In particular, a net repulsive interaction occurs between π and e_s which is unmitigated because of the lack of low-lying, antibonding component orbitals of the same symmetry. The e_a orbital is, however, stabilized by its interaction with π*. The stabilization of e_a is not expected to counterbalance the e_s–π repulsion because: (1) there is a substantial energy separation between e_a and π*; and (2) e_a is less localized on C_1 than e_s and consequently interacts less strongly with opposing π orbitals.



The second point is quantified in Table II where the electron density on C_1 in e_s of cyclopropane is shown to be more than twice that in e_a.[15] Table II also records the directionality of the orbitals expressed as the hybrid angle θ that is determined from eq 1, where c_x and c_y are the 2p$_x$ and 2p$_y$ coefficients on C_1 in the orbitals.

$$\theta = \tan^{-1}|c_y/c_x| \tag{1}$$

For π-like interactions, e_a is seen to have an orientational advantage over e_s.[16,17] Nev-

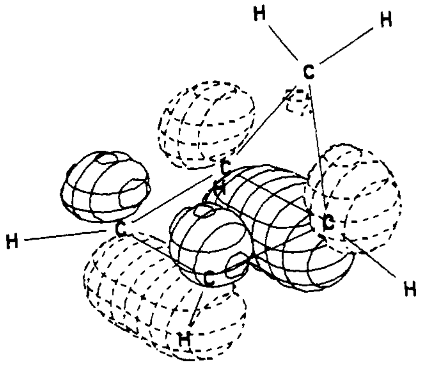


Figure 3. The HOMO of bicyclo[2.1.0]pent-2-ene (2).

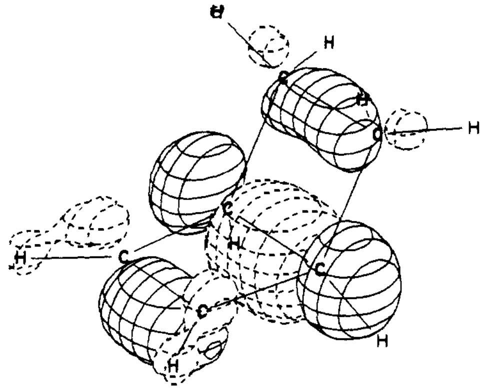
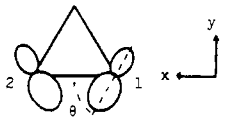
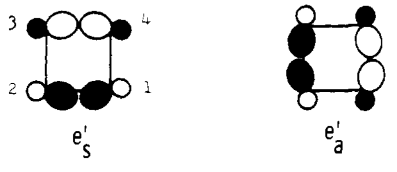


Figure 4. The HOMO of bicyclo[2.2.0]hex-2-ene (3).



ertheless, the dominance of the e_s-π destabilizing interaction is verified by the negative 2p-π bond order between C_1 and C_2 in **2** reported in Table I.

In **3**, the important orbital interactions between small ring and ethylene bridge should occur, by analogy to **2**, between the degenerate pair of cyclobutane HOMO's, e_s' and e_a', and the π and π^* orbitals of the ethylene bridge.[20] Specifically, the e_s'-π, four-electron interaction is destabilizing, and the e_a'-π^*, two-electron interaction is stabilizing. The e_s'-π interaction in **3** is not expected to be nearly as strong as the e_s-π interaction in **2**. The calculations in Table II reveal that ρ_{C_1} in e_s' of cyclobutane[21] is approximately half the ρ_{C_1} value in e_s of cyclopropane.



Furthermore, e_s' in cyclobutane has little π directionality compared with e_s in cyclopropane in agreement with the adage that cyclopropane has roughly three times the bent-bond character of cyclobutane.[22]

The reduction of the destabilizing π interactions between small ring and ethylene bridge in going from **2** to **3** is conveniently illustrated by the accurate drawings of their HOMO's shown in Figures 3 and 4.[23,24] The strong interaction between π and e_s is witnessed by their nearly equal contributions to the HOMO in Figure 3 which bears a striking resemblance to the HOMO of rectangular cyclobutadiene shown in Figure 5. The ethylenic π component in the HOMO of **3** is comparatively subdued. The HOMO of **3** is, in fact, reminiscent of the HOMO to be expected from three parallel σ bonds, i.e., $\sigma_1 - 2\sigma_2 + \sigma_3$ (unnormalized).

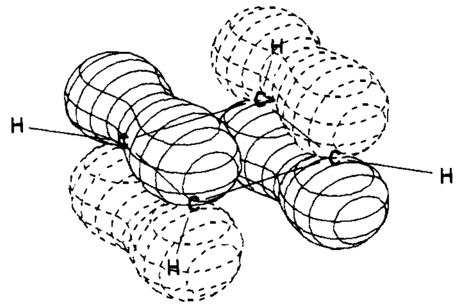


Figure 5. The HOMO of rectangular cyclobutadiene (**1**).

In contrast, the value of θ for the e_a' cyclobutane orbital reported in Table II suggests that it is well suited directionally for interaction with the π^* orbital of the ethylene bridge in **3**. The calculations in Table I verify that this interaction dominates the e_s'-π repulsion. Thus, the net 2p-π interaction between C_1 and C_2 in **3** is attractive with a bond order of +0.073.

It is tempting to assess the energetic preference of ethylene as a cyclobutane rather than cyclopropane bridge by calculating the energy of the isodesmic[27] reaction in eq 2.

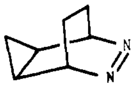
$$2 + \text{cyclobutane} \longrightarrow 3 + \text{cyclopropane} \qquad (2)$$

Although ab initio calculations accurately estimate the heats of reaction of isodesmic processes for, at least, unstrained systems,[27] quantitative significance cannot be attributed to EH results for such reactions. Qualitative verification of the conclusions that have been drawn from the P_a^{π} values for **2** and **3** is, however, expected.[28] An EH calculation does find the heat of reaction for eq 2 to be exothermic by 9.7 kcal/mol. It is noted that MINDO/2 calculations[26] also find eq 2 to be exothermic, however, by a smaller amount, 3.9 kcal/mol. The e_s-π repulsion in **2** is ignored by NDO calculations, as discussed above, and the decreased exothermicity is consistent with this fact.

The calculated energies for eq 2 have bearing on the question of the additivity of strain energies in small ring polycycles.[30] If the component rings of **2** and **3** are considered, then the calculations indicate that the strain energy of **2** is greater than the composite strain energies of cyclopropane and cyclobutene, ca. 57 kcal/mol,[31] and/or the strain energy of **3** is less than the combined strain energies of cyclobutane and cyclobutene, ca. 56 kcal/mol.[31] The differences may be attributed to the "electronic strain" or "electronic relief" caused by the π interactions between the small rings and ethylene bridges in **2** and **3**. Unfortunately, the heats of formation of neither **2** nor **3** have been determined to enable the hypotheses to be tested. The rearrangement mechanism for **3** is also not well established.[32] If the mechanisms for the rearrangements of **2** and **3** are similar, then the calculations are consistent with the observed stabilities of the compounds;[33,34] **2** rearranges to cyclopentadiene with a unimolecular half-life of 40 hr at room temperature,[33b] while **3** remains unchanged after 48 hr under similar conditions.[34] Hopefully, the theoretical work described here will provoke further mechanistic and thermodynamic studies of **2** and **3**.[35]

Cyclopropyl and Cyclobutyl Edge Effects

Other manifestations of the differences between the valence orbitals of cyclopropane and cyclobutane can be found in some related polycycles. For example, the rate of nitrogen extrusion for **8** is enhanced by a factor of 10^{13} relative to **9**.[36] The activation energies for the two processes are 14.9 and 39.2 kcal/mol, respectively.[36] The decompositions of **8** and other azo compounds where the nitrogen leaves anti to the methylene group in the assisting cyclopropane ring have been found to be concerted.[36,37] In contrast, the decomposition of **9** reportedly proceeds via a diradical,[38a] although other cyclobutyl-assisted nitrogen eliminations are apparently concerted.[38b] The striking difference in cyclopropyl vs. cyclobutyl edge participation in **8** and **9** may be rationalized in the context of the preceding observations concerning the orbital interactions in **2** and **3**.



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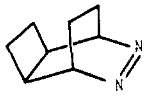

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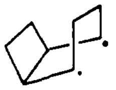
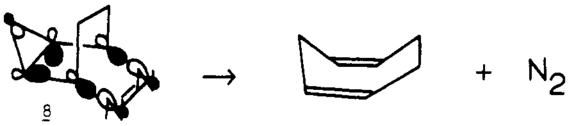
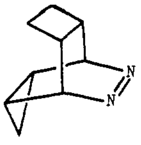


To begin, the retro-Diels–Alder reactions are envisioned as promoted by the mixing of the e_s-type orbital in **8** or e_s' in **9** with the symmetric combination of the unoccupied σ_{CN}^* orbitals. The electronic reorganization corresponding to these interactions agrees with the bonding changes necessary to proceed from reactant to product. It is also noted that the high-lying nature of e_s and e_s' facilitates their interaction with the σ_{CN}^* orbitals. This point is emphasized by photoelectron studies on a series of molecules closely related to **8** which demonstrated that the activation energy for nitrogen expulsion decreases as the energy of the e_s-type orbital in the compounds increases.[39,40]



The critical difference between the orbital interactions in **8** and **9** is revealed in the charge and orientational factors of Table II. Just as the e_s–π mixing in **2** was stronger than e_s'–π in **3**, the mixing of e_s with the symmetric combination of the σ_{CN}^* orbitals in **8** is much more facile than the corresponding interaction with e_s' in **9**. As illustrated, this is the important interaction for the concerted nitrogen extrusion. Naturally, for cases where the cyclopropane ring is syn fused to the nitrogen moiety, the overlap of e_s with the σ_{CN}^* orbitals is markedly reduced, and the rate enhancement for nitrogen elimination is predicted and observed to be curtailed; e.g., $k_8/k_{10} \approx 10^{14}$.[36]



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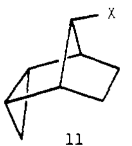
Another area where a significant discrepancy between cyclopropyl and cyclobutyl edge participation is apparent is in the solvolyses of 7-substituted norbornyl compounds.[41,42] Specifically, cyclopropyl and cyclobutyl fused compounds, e.g., **11** and **12**, exhibit solvolyses rates that differ by roughly $10^{9.7}$ at room temperature.[41] The greater anchimeric assistance provided by the cyclopropyl ring is generally ascribed to its increased bent-bond character[22] relative to cyclobutane.[43] In molecular orbital terms, the discrepancy is again consistent with the charge and orientational differences between the cyclopropyl e_s and cyclobutyl e_s' orbitals. The cyclopropyl e_s orbital is more "bent" and more localized in the region where it may interact with the backside of the σ_{CX}^* orbital. This interaction enhances the rate of leaving-group expulsion. It is clear that the endo-anti configuration is essential for the interaction and assistance. The exo-anti and endo-syn analogs of **11** have solvolysis rates 10^{12} to 10^{15} times slower than **11**.[41]



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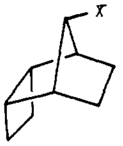

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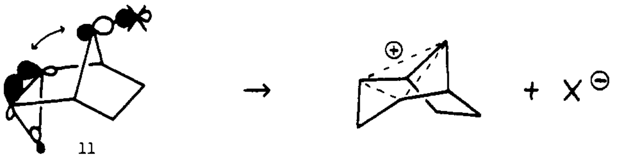

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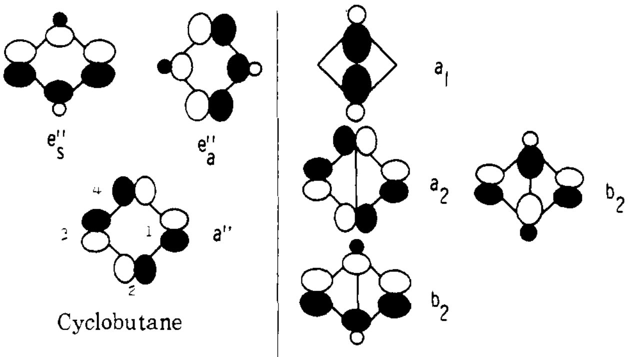
Bicyclo[2.1.1]hex-2-ene and Benzvalene

For the purpose of analyzing orbital interactions between small ring and ethylene bridge, it is convenient to describe bicyclo[2.1.1]hex-2-ene (**4**) and benzvalene (**5**) as a 1,3-ethylene bridged cyclobutane and bicyclobutane, respectively. Although **4** and **5** are closely related structurally, the effect of the additional CC bond in **5** on the orbital interactions between ring and bridge is profound.

In the previous study,[1] the π interactions between ring and ethylene bridge in **4** were found to be destabilizing with a P_a^{π} of −0.007. The destabilization can be traced to the interaction of the bridge π orbital with the high-lying Walsh cyclobutane orbital of the same symmetry. In D_{2d} symmetry with the cyclobutane ring puckered, the highest occupied Walsh orbitals of cyclobutane may be labeled a″, e_s'', and e_a'', with the latter pair being the degenerate HOMO's.



Cyclobutane

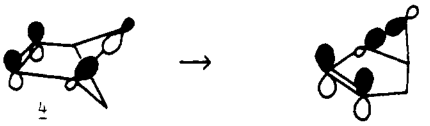
Bicyclobutane

As the pucker is diminished, e_s'' and e_a'' become an equivalent representation of the e_s' and e_a' orbitals of planar cyclobutane.[44,45] The e_a'' HOMO does not have the proper symmetry to take part in any π interactions with an ethylene bridge. The four-electron, destabilizing interaction between e_s'' and π of the bridge dominates the two-electron, stabilizing interaction between a″ and π^*.

The three highest lying filled orbitals of bicyclobutane are represented, in order of increasing energy, as b_2, a_2, and a_1.[4,46] The HOMO, a_1, which is principally composed of the strained σ_{13} bond orbital, is again prohibited by symmetry to interact in a π fashion. On the other hand, a_2 and b_2 are very similar to a″ and e_s'', respectively. Concomitant with the reduction in symmetry and the increase in the pucker angle from 35° in cyclobutane[21] to 58° in bicyclobutane,[47] the ordering of these corresponding orbitals has, however, been reversed. The reversal may be anticipated to be even more pronounced for the a_2 and b_2 components in **5**, where the pucker angle increases to 84°.[48] Reducing the energy gap between a_2 and π^* in **5** permits their stabilizing interaction to more effectively counteract the b_2–π repulsion than in the analogous situation in **4**.

Furthermore, the strain on the C_1–C_6 bond in the bicyclobutane fragment of **5** provides an unusually low-lying, unoccupied orbital of the same symmetry as π. The orbital, b_2^*, is composed primarily of the σ_{16}^* bond orbital (σ_{13}^* in bicyclobutane) but also contains significant components on C_2 and C_5 in **5**.[4,46] The interaction of π, b_2, and b_2^* mitigates the repulsion of the filled orbitals as in the interaction of π with χ_1 and χ_3^* in **7**. Exchanging the cyclobutane fragment of **4** for the bicyclobutane ring in **5** is, therefore, expected to produce a substantial alteration in the orbital interactions between small ring and ethylene bridge. That this is, in fact, the case is verified by the EH calculations reported in Table I. The 2p–π bond order between C_2 and C_3 in **5** is found to be +0.098, the largest value for any of the ethylene bridged compounds treated in this study.[49] Thus, it can be concluded that the orbital interactions between bicyclobutane ring and ethylene bridge in benzvalene enhance the thermodynamic stability of the compound.

Directly comparing the kinetic stabilities of **4** and **5** is not fruitful because of the strain-energy difference in the compounds and the fact that their rearrangements involve different mechanisms. Nevertheless, some mechanistic insight can be gained by considering the influence of the orbital interactions on the rearrangements. On heating, **4** readily isomerizes to bicyclo[3.1.0]hex-2-ene with E_a = 35.2 kcal/mol.[50] The reaction kinetics[50] and studies on substituted compounds[51] indicate the rearrangement is a ${}_{\pi}2_{s} + {}_{\sigma}2_{a}$ concerted process. It is interesting to note that, although the conversion is formally similar to a vinylcyclobutane rearrangement, it also corresponds to a retro-vinylcyclopropane rearrangement.[52] The facility of the rearrangement should be enhanced by the destabilizing orbital interactions between small ring and bridge in **4**. Not only do the orbital interactions destabilize the ground state of 1,3-ethylene bridged cyclobutanes like **4**, but they also yield a high-lying, π-type HOMO. The high energy of the HOMO facilitates its interaction with the antibonding MO's on distortion and enhances the molecules disposition for rearrangement.[40] The electronic destabilization becomes more pronounced in the bis ethylene bridged cyclobutane (**13**) which rearranges rapidly to semibullvalene at 25°.[5] In contrast to the rearrangement of **4** and theoretical proposals of a ${}_{\sigma}2_{a} + {}_{\sigma}2_{s}$ concerted mechanism for the rearrangement of **13**,[7a,53] experimental evidence indicates that the rearrangement for an analog of **13** proceeds via a diradical mechanism.[6b]



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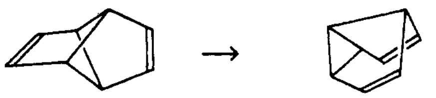

13

Although the isolation of **13** is difficult at room temperature, benzvalene is found to have a half-life of 10 days under the same conditions.[54] The stability of benzvalene is notable in this context as it is 35 kcal/mol more strained than **13**,[55] and the product of its isomerization (benzene) is much more stable than semibullvalene. Further comparison of the two systems is inhibited by a lack of reliable information on the transition states for the rearrangements. For example, benzvalene is expected to rearrange via the prefulvene diradical (**14**),[56] while a diradical mechanism for **13** would involve the bis allylic diradical **15**.[5,6b] The extra allylic unit in **15** favors it over **14** by an allylic resonance energy, ca. 13 kcal/mol. The difference in strain relief in generating the diradicals may, however, be estimated[31,55a] to nullify the resonance-energy advantage of **15**.

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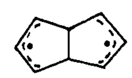


15

In any event, the calculations and qualitative arguments presented here assert that the stability of benzvalene is enhanced by favorable orbital interactions between its bicyclobutane and ethylene fragments. Further comparison can be made with reference to its valence isomer, Dewar benzene, which is the last ethylene bridged polycycle to be treated.

Dewar Benzene

The interactions between highest occupied and lowest unoccupied orbitals in Dewar benzene (**6**) are expected to be similar to those in bicyclo[2.2.0]hex-2-ene (**3**) with the addition of the mixing of the ethylenic π orbitals. In the fashion of the previous analyses, it is convenient to treat Dewar benzene as an ethylene bridged cyclobutene. The critical interactions are then expected between the ethylenic π and π^* orbitals of the bridge and the Walsh and ethylenic orbitals of the cyclobutene ring. The interaction between the Walsh and bridging orbitals is reflected in the P_a^{π} bond order presented in Table I.[57] The similarity of the P_a^{π} values for **3** and **6** represents a balance of two effects. The e_a' analog for cyclobutene is at higher energy than the e_s' analog, so the e_a' analog can mix more constructively with the π^* orbital of the bridge in **6**. The increased stabilization is, however, balanced by the greater concentration of the cyclobutene e_s' orbital on the C_1–C_4 bond in **6** than in the cyclobutane e_s' orbital of **3**.[60] This yields increased e_s'–π destabilization in **6** relative to **3**.

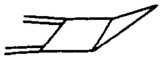
The other important question in analyzing the frontier orbital interactions for Dewar benzene is the extent of the destabilization caused by the mixing of the two filled, ethylenic π orbitals. One measure of the degree of interaction of two orbitals is the splitting of their delocalized MO's. For Dewar benzene, the less bonding and more bonding combinations of the filled, ethylenic π orbitals differ in energy by only 0.38 eV according to an EH calculation, even though the more bonding combination is further depressed by interaction with the σ_{14} bond orbital. The EH number compares favorably with an ab initio value of 0.48 eV.[59] As a model for a destabilizing interaction, the splitting between the more and less bonding combinations of e_s and π in **2** should provide an appropriate reference. The EH value for this splitting is 1.7 eV, while an ab initio calculation yields a value nearly twice as large.[61] On this basis, it is reasonable to predict that the destabilization due to the 1,3 interaction between the π bonds in **6** is not nearly as significant as for the 1,2, π-type interactions in molecules like **2** and **4** that have been the focus of the present study. This assessment is further supported by the calculations on the butadiene bridged analogs of **2–6** discussed below.

Benzvalene (**5**) and Dewar benzene (**6**) were the first $(CH)_6$ structural isomers to be isolated after benzene. The stability of **5** and **6** is largely due to the fact that their concerted aromatizations are symmetry forbidden. It is interesting to note that, although benzvalene is a higher energy isomer than Dewar benzene, the half-life of benzvalene[54] is

10 days at room temperature as compared with 2 days for Dewar benzene.[62,63] Similarily, the activation energy for the thermal aromatization of the hexatrifluoromethyl derivative of benzvalene is 0.9 kcal/mol higher than for the corresponding Dewar benzene.[64] The difference in stabilities is small and is, no doubt, to a large extent attributable to differences in the transition states for the two aromatizations. Nevertheless, the relative stability of benzvalene is consistent with the highly favorable π interactions between its bicyclobutane fragment and ethylene bridge.

Butadiene Bridged Compounds. Diels–Alder Reactivities

As in the transformation from **1** to **7**, replacing the ethylene bridges in **2–6** by butadiene is expected to have a profound effect on the π-type orbital interactions. The EH calculations reported in Table I for the resultant molecules, **16–20**, support the assertion that 1,3-butadiene is a very accommodating bridging group. In each case, the calculated $P_a{}^\pi$ bond order is significantly positive.[65] This may be attributed to the fact that butadiene has low-lying unfilled orbitals of opposite symmetry. Both high-lying symmetric and antisymmetric, π-type orbitals of the small rings are stabilized by their interactions with the unfilled bridge orbitals, $\chi_3{}^*$ and $\chi_4{}^*$, in a manner analogous to the interactions analyzed for **7** above.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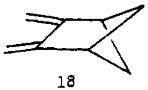
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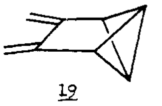
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20

The energetic preference of butadiene over ethylene as a bridging group can, in principle, be estimated by calculating the heats of reaction for isodesmic processes such as eq 3.[1,4] The EH results for these reactions that relate the ethylene bridged compounds **1–6** to their butadiene bridged counterparts are reported in Table III. Again, quantitative significance should not be attached to the EH heats of reaction.[28] The results do, however, support the bond-order values for the compounds and the qualitative description of the orbital interactions that has been presented.

$$\mathbf{1} + \text{ethylene} \longrightarrow \mathbf{7} + \textit{cisoid}\text{-butadiene} \qquad (3)$$

Specifically, the most exothermic reactions in Table III are found, as expected, for the ethylene bridged compounds with unfavorable π-orbital interactions, i.e., **1**, **2**, and **4**. The fact that the butadiene bridged compounds are energetically favored in each reaction may be traced to two factors. First, the replacement of the shorter ethylene bond in the bridges of **1–6** with the longer central bond of butadiene provides some strain relief. For the reaction involving **4**, the strain relief was previously calculated to account for approximately 3 kcal/mol of the EH heat of reaction.[1] Secondly, the 1,3-π interactions between ring and bridge are more favorable in the butadiene bridged systems. This results from the butadiene LUMO, $\chi_3{}^*$, being symmetric, so when it mixes with filled ring orbitals net 1,3 bonding is produced as well as 1,2 bonding. The LUMO of ethylene is, however, antisymmetric, so when it interacts with filled ring orbitals, 1,3 antibonding is produced concomitantly with the 1,2 bonding.[67]

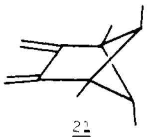
The heats of reaction in Table III should provide some insight into the Diels–Alder reactivities of the butadiene bridged compounds, **16–20**. The more exothermic the reaction, the more the diene bridge is preferred to ethylene, and the less receptive the diene should be toward dienophiles. From this standpoint, **16** and **18** are anticipated to be poor dienes as compared with **17**, **19**, and **20** which should have roughly comparable Diels–Alder reactivities. The situation is, however, complicated for **16**, **17**, and **20** which are all expected to undergo facile disrotatory openings to stabilized bis allylic diradicals or for **20** to *o*-xylylene. This has been verified for the known molecules, **17**[68a] and **20**,[68b] which both open with activation enthalpies of approximately 17 kcal/mol.[68] Nevertheless, **17** and **20** may be trapped with the highly reactive dienophile, 1-phenyl-1,3,4-triazoline-2,5-dione at room temperature.[68] Experiments with a series of less reactive dienophiles would be interesting.

Table III. Heats of Reaction[a] for A + *cisoid*-1,3-Butadiene → B + Ethylene

A	B	ΔH
1	7	−37.2
2	16	−16.8
3	17	−6.1
4	18	−17.1
5	19	−8.4
6	20	−7.2

[a] EH results in kcal/mol.

The Diels–Alder reactivities of molecules like **18** and **19** are more easily contrasted since they are less prone to rearrangement. In particular, **21**, like another molecule containing a butadiene bridged cyclobutane,[6b] reacts sluggishly with TCNE, the reaction requiring 20 hr at 55° for completion.[69] On the other hand, the reaction of the butadiene bridged bicyclobutane **22** with TCNE proceeds in less than 1 min at room temperature.[69] These experimental observations are in accord with the arguments and calculations presented here that point out the thermodynamic disadvantage in replacing an ethylene for a butadiene as a 1,3-cyclobutane bridging group as compared with a 2,4-bicyclobutane bridging group. Further support is gained from noting that the difference in π bond order between **5** and **19** and the energy for their interrelation in Table III are very similar to the corresponding quantities calculated for unsaturatively bridged cyclopentane.[1] Since 2,3-dimethylenenorbornane readily undergoes a Diels–Alder reaction with maleic anhydride,[70] the Diels–Alder reactivity of **22** is not surprising.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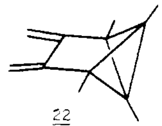
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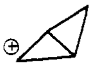
Before leaving this section, another comment on the 1,3 interaction between the π bonds in Dewar benzene is in order. Particularly, the heat of reaction reported in Table III for the Dewar benzene (**6**) to Dewar xylylene (**20**) conversion is very close to the value for the **3** to **17** reaction and significantly smaller than the values for the reactions involving the π-destabilized molecules **2** and **4**. This reinforces the conclusion made above based on orbital splittings that the 1,3 interactions between the unsaturated fragments in **6** are not nearly as energetically important as the 1,2-π interactions in **2** and **4**. Otherwise, the exchange of the unfavorable 1,3-π interactions in **6** for the favorable ones in **20** would produce a much more negative heat of reaction for their conversion in Table III.

Related Cations

The destabilizing π interactions between small ring and ethylene bridge in **2** and **4** have been traced to the interaction of a high-lying, filled, symmetric orbital of the ring with the filled π orbital of the bridge. If this four-electron, destabilizing interaction were reduced to a two-electron interaction, significant stabilization could occur. The appropriate transformation is achieved by replacing the ethylene bridges in **2** and **4** with a cationic center yielding **23** and **24.** The filled π orbital of the ethylene bridge is thereby supplanted by the empty 2p orbital of the electron-deficient carbon. Although calculations on **23** and **24** are not reported here, both molecules may be anticipated to receive substantial stabilization via the interaction of their vacant 2p orbitals with the e_s and e_s'' ring orbitals, respectively.



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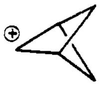
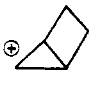


24

Little comment on **23** and **24** has been made in the literature. Devaquet and Hehre have, however, performed an important theoretical study on the mechanism of circumambulation in **23.**[71] The hyperconjugative stabilization of **23** should lower the energy of its ground state and reduce its tendency to rearrange. Devaquet's and Hehre's calculations[71] indicate, however, that a highly stabilized, symmetry-forbidden, cyclopropenylcarbinyloid transition state exists for the circumambulation process. The activation energy, if any, for disrotatory opening of **23** to cyclobutenyl cation would be of interest but was not reported.[71] Padwa and Alexander[72] have also found the solvolytic reactivity of 2-phenylbicyclo[1.1.1]pentan-2-ol *p*-nitrobenzoate to be anomalously high when compared with a series of model compounds. Although it is tempting to attribute at least part of the enhanced reactivity to the stability of phenyl substituted **24,** it is possible that the anomaly results from differences in σ participation accompanying the ionizations of the various compounds.[72]

Similar transformations for the other ethylene bridged compounds, **3, 5** and **6,** can be performed to yield cations **25, 26,** and **27,** respectively. The cationic centers in these systems are, by analogy, not expected to receive substantial hyperconjugative stabilization since the stabilization in the parent olefins of **25–27** was dominated by the interaction of a high-lying, filled, antisymmetric ring orbital with the π^* orbital of the ethylene bridge. Loss of this interaction plus the lack of strong interactions between symmetric orbitals of ring and bridge for the cations is expected to result in little stabilization for **25–27.**



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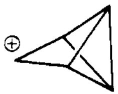

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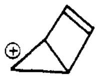
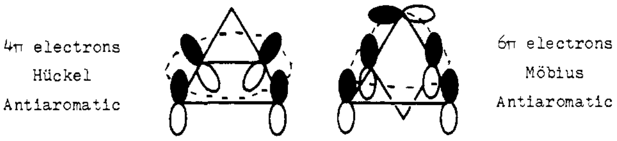


27

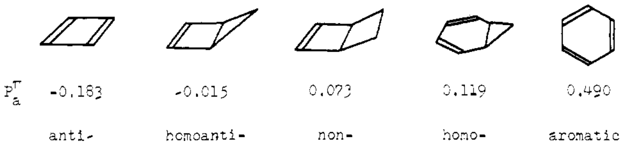
This proposition gains support from both semiempirical[73] and ab initio[74] calculations that conclude that neither **26** nor **27** represents minima on the $(CH)_5^+$ potential surface. Additional calculations to assess the extent of hyperconjugative stabilization in **23–27** and the validity of the brief qualitative arguments in this section are warranted.

Aromaticity

In closing, it is appropriate to consider the relationship of the present study to other work in the area of homoaromaticity and antihomoaromaticity.[16,75,76] Two of the ethylene bridged polycycles, **2** and **4,** have been shown to be unique among the compounds studied here in having net antibonding interactions between their small ring and bridge π orbitals reminiscent of cyclobutadiene. This has been rationalized by the qualitative consideration of detailed orbital interactions. Hehre[16] has found that Möbius-Hückel descriptions[76] of homotropylium cation and bicyclo[3.1.0]hexenyl cation are consistent with the homoaromatic and homoantiaromatic characters of the compounds. Applying the same orbital model to **2** and **4,** it is predicted that both compounds have antiaromatic character, as Hehre previously indicated for **2.**[16] The problem with the Möbius-Hückel description in the present context occurs with compounds **3** and **5** for which Möbius-Hückel diagrams could be constructed similar to those for **2** and **4** with the same antiaromatic conclusions. To rationalize the results presented in Tables I and III in a Möbius-Hückel fashion, it would be necessary to propose different conjugative abilities for the four-membered rings in **3, 4,** and **5.** This is in essence what has been shown above by a more complete and classical description of the orbital interactions in these compounds. The two approaches are, therefore, related. The Möbius-Hückel method[76] is, however, generally applied to reacting systems for which an aromatic-antiaromatic or forbidden-concerted answer is sought. It is not well suited to describe subtle differences in orbital interactions for molecules in their ground states.



Perhaps a more general gauge of aromaticity may be formulated along the lines of P_a^{π} values or an energetic criterion. As illustrated below, increasing aromatic character is reflected in increasing P_a^{π} values.[77] Further work in this area is being pursued.



Conclusion

This study has been aimed at pointing out the importance of orbital interactions in determining the chemical behavior of polycycles containing small rings. Two of the ethylene bridged polycycles, **2** and **4,** were found to be destabilized by antibonding interactions between their small ring and bridge π orbitals. On the other hand, the highly strained benzvalene (**5**) was found to be stabilized by similar interactions, while the 1,3 interactions between the π bonds in Dewar benzene (**6**) were not found to have important energetic impact. The calculations and analyses have also led to a better understanding of numerous chemical phenomena from cyclopropyl vs. cyclobutyl edge effects to the Diels-Alder reactivities of butadiene bridged, small ring polycycles and the stabilizations of some related polycyclic cations. Nevertheless, further study on the molecules discussed here at the ab initio level is desirable to obtain accurate heats of reaction for the isodesmic processes that were considered. A better quantitative estimate of the energetic influence of the orbital interactions would then be obtained.

Acknowledgments. The author thanks Professor W. T. Borden for provoking his interest in small ring compounds and for many of the underlying ideas in this work. Receipt of experimental data concerning compound **3** from Professor R. N. McDonald is also greatly appreciated. Professor H. Hogeveen kindly provided a preprint of his studies[71] on compound **21.** Support from the Department of Chemistry at Harvard is gratefully acknowledged.

References and Notes

(1) Part I: W. L. Jorgensen and W. T. Borden, *J. Am. Chem. Soc.*, **95**, 6649 (1973).

(2) (a) R. Hoffmann, *Pure Appl. Chem., Suppl.*, **2**, 233 (1971); (b) R. Hoffmann and R. B. Davidson, *J. Am. Chem. Soc.*, **93**, 5699 (1971); (c) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **92**, 6380 (1970); (d) W. J. Hehre, *ibid.*, **94**, 6592 (1972).

(3) For reviews, see: M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds", Academic Press, New York, N.Y., 1967; R. Petit, *Pure Appl. Chem.*, **17**, 253 (1968).

(4) W. L. Jorgensen and W. T. Borden, *Tetrahedron Lett.*, 223 (1975).

(5) J. Meinwald and D. Schmidt, *J. Am. Chem. Soc.*, **91**, 5877 (1969); J. Meinwald and H. Tsuruta, *ibid.*, **91**, 5877 (1969); H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

(6) (a) W. T. Borden and A. Gold, *J. Am. Chem. Soc.*, **93**, 3830 (1971); (b) A. Gold and W. T. Borden, *ibid.*, **94**, 7179 (1972).

(7) For qualitative discussions, see: (a) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971); (b) R. Hoffmann, *Acc. Chem. Res.*, **4**, 1 (1971); (c) ref 8, p 10.

(8) W. L. Jorgensen and L. Salem, "The Organic Chemist's Book of Orbitals", Academic Press, New York, N.Y., 1973.

(9) N. C. Baird and R. M. West, Jr., *J. Am. Chem. Soc.*, **93**, 4427 (1971); K. Müller, *Helv. Chim. Acta*, **53**, 1112 (1970).

(10) For reviews, see: J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Hill, New York, N.Y., 1970; J. N. Murrell and A. J. Harget, "Semiempirical SCF-MO Theory of Molecules", Wiley-Interscience, London, 1972.

(11) Bond orders are computed as

$$P_{ij} = 2\sum_{\mu} c_{\mu i}c_{\mu j}$$

where $c_{\mu i}$ is the MO coefficient for the ith atomic orbital in the μth MO, and the sum is taken over all filled MO's.

(12) Total energies and bond orders are directly proportional in the EH and simple Hückel methods: L. Salem, "The Molecular Orbital Theory of Conjugated Systems", W. A. Benjamin, Reading, Mass., 1966, p 34.

(13) The EH parameters are from: R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *J. Am. Chem. Soc.*, **92**, 7091 (1970).

(14) The ethylenic π orbital may be thought of as a perturber that causes polarization and remixing of χ_1^* and χ_3^*. For a related discussion, see: L. Libit and R. Hoffmann, *J. Am. Chem. Soc.*, **96**, 1370 (1974).

(15) The cyclopropane geometry used in the calculations was from: O. Bastiansen, F. N. Fritsch, and K. Hedberg, *Acta Crystallogr.*, **17**, 538 (1964); W. J. Jones and B. P. Stoicheff, *Can. J. Phys.* **42**, 2259 (1964).

(16) This has been noted qualitatively by W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 5207 (1974).

(17) Our experience has indicated that the agreement in the coefficients of EH and ab initio wave functions is generally excellent for occupied orbitals.[18] For example, the value of θ for e_s in cyclopropane from an ab initio calculation[19] is 43.3°. This only differs from the EH value in Table II by 3.4°.

(18) Reference 8, pp 54-55.

(19) R. M. Stevens, E. Switkes, E. A. Laws, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **93**, 2603 (1971).

(20) The representation of the frontier orbitals of cyclobutane follows Salem and Wright.[44] See also ref 2b.

(21) The planar cyclobutane used in the calculations employed the structural parameters of A. Almenningen, O. Bastiansen, and P. N. Skancke, *Acta Chem. Scand.*, **15**, 711 (1961).

(22) C. A. Coulson and T. H. Goodwin, *J. Chem. Soc.*, 2851 (1962); *ibid.*, 3161 (1963).

(23) The drawings were constructed from the EH wave functions.[17] For details, see ref 8.

(24) The structural parameters of **3** have not been reported. The geometry used in the calculations was adapted from that of **2**[25] and cyclobutane.[21] In addition, the C_1C_4 bond length and $C_1C_2C_4C_5$ dihedral angle were calculated via the MINDO/2[26] method yielding values of 1.553 Å and 118.6°.

(25) S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, and J. E. Baldwin, *J. Am. Chem. Soc.*, **92**, 5250 (1970).

(26) M. J. S. Dewar and D. H. Lo, *J. Am. Chem. Soc.*, **94**, 5296 (1972).

(27) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Am. Chem. Soc.*, **92**, 4796 (1970).

(28) The processes for which EH heats of reaction are reported in this paper are a restricted subset of isodesmic reactions. In particular, the reactants and products not only contain the same numbers and types of atoms and bonds,[27] but also the same numbers and types of hybridized atoms and hybrid bond types, e.g., sp^2-sp^3, sp^3-1s, etc. Although the EH heats of reaction for the restricted processes are not quantitatively useful, they are qualitatively significant and reproduce anticipated and observed trends.[1,4,29]

(29) W. L. Jorgensen, unpublished results.

(30) K. B. Wiberg, *Adv. Alicyclic Chem.*, **2**, 185 (1968); P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Am. Chem. Soc.*, **92**, 2377 (1970).

(31) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, N.Y., 1968.

(32) The mechanism of the rearrangement of **2** has been the topic of much debate: J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970); S. McLean, D. M. Findlay, and G. I. Dmitrienko, *J. Am. Chem. Soc.*, **94**, 1380 (1972); J. E. Baldwin and G. D. Andrews, *ibid.*, **94**, 1775 (1972); M. C. Flowers and H. M. Frey, *ibid.*, **94**, 8636 (1972); J. I. Brauman, W. E. Farneth, and M. B. D'Amore, *ibid.*, **95**, 5043 (1973); G. D. Andrews, M. Davalt, and J. E. Baldwin, *ibid.*, **95**, 5044 (1973).

(33) (a) J. I. Brauman, L. E. Ellis, and E. E. van Tamelen, *J. Am. Chem. Soc.*, **88**, 846 (1966); (b) J. I. Brauman and D. M. Golden, *ibid.*, **90**, 1920 (1968).

(34) R. N. McDonald and C. E. Reineke, *ibid.*, **87**, 3020 (1965); *J. Org. Chem.*, **32**, 1878 (1967); R. N. McDonald, private communication.

(35) **2**, **3**, and **6** owe much of their stability to the fact that a thermally allowed conrotatory cyclobutene opening is sterically impeded in these cases.

(36) J. C. Hinshaw and E. L. Allred, *Chem. Commun.*, 72 (1969); E. L. Allred, J. C. Hinshaw, and A. L. Johnson, *J. Am. Chem. Soc.*, **91**, 3382 (1969); E. L. Allred and J. C. Hinshaw, *Chem. Commun.*, 1021 (1969); E. L. Allred and K. J. Voorhees, *J. Am. Chem. Soc.*, **95**, 620 (1973).

(37) J. A. Berson and S. S. Olin, *J. Am. Chem. Soc.*, **91**, 777 (1969); R. Askani, *Tetrahedron Lett.*, 3349 (1970); L. A. Paquette, *J. Am. Chem. Soc.*, **92**, 5765 (1970).

(38) (a) E. L. Allred and J. C. Hinshaw, *Tetrahedron Lett.*, 387 (1972); (b) J. A. Berson, E. W. Petrillo, Jr., and P. Bickart, *J. Am. Chem. Soc.*, **96**, 636 (1974).

(39) H. Schmidt, A. Schweig, B. M. Trost, H. B. Neubold, and P. H. Scudder, *J. Am. Chem. Soc.*, **96**, 622 (1974).

(40) A correlation between long wavelength uv absorptions and propensity for rearrangement has also been noted for other strained polycycles: J. E. Baldwin and A. H. Andrist, *J. Am. Chem. Soc.*, **93**, 3289 (1971). This observation is concisely rationalized in the context of the second-order Jahn-Teller effect.[1]

(41) H. Tanida, T. Tsuji, and T. Irie, *J. Am. Chem. Soc.*, **89**, 1953 (1967); M. A. Battiste, C. L. Deyrup, R. E. Pincock, and J. Haywood-Farmer, *ibid.*, **89**, 1954 (1967); J. Haywood-Farmer and R. E. Pincock, *ibid.*, **91**, 3020 (1969); M. Sakai, A. Diaz, and S. Winstein, *ibid.*, **92**, 4452 (1970).

(42) See also: M. A. Battiste and J. W. Nebzydoski, *J. Am. Chem. Soc.*, **92**, 4450 (1970); M. A. Battiste, J. Haywood-Farmer, H. Malkus, P. Seidl, and S. Winstein, *ibid.*, **92**, 2144 (1970); R. M. Coates and J. L. Kirkpatrick, *ibid.*, **90**, 4162 (1968); **92**, 4883 (1970); L. A. Paquette, O. Cox, M. Oku, and R. P. Henzel, *ibid.*, **96**, 4892 (1974); R. M. Coates and K. Yano, *Tetrahedron Lett.*, 2289 (1972).

(43) The 1.4 kcal/mol strain energy difference between cyclopropane and cyclobutane[31] is insufficient to account for the difference in solvolysis rates. Assuming equal *A* factors, the $10^{9.7}$ rate quotient corresponds to an activation energy difference of 13.3 kcal/mol.

(44) L. Salem and J. S. Wright, *J. Am. Chem. Soc.*, **91**, 5947 (1969).

(45) The apparent difference simply results from defining the orbitals to be symmetric or antisymmetric with respect to planes through opposite bonds[44] or atoms.[2b]

(46) Reference 8, pp 203-205.

(47) K. W. Cox, M. D. Harmony, G. Nelson, and K. B. Wiberg, *J. Chem. Phys.*, **50**, 1976 (1969).

(48) R. D. Suenram and M. D. Harmony, *J. Am. Chem. Soc.*, **95**, 4506 (1973).

(49) The geometry of **5** used in the calculations was taken from the microwave determination of ref 48.

(50) H. M. Frey, R. G. Hopkins, and H. E. O'Neal, *Chem. Commun.*, 1069 (1969).

(51) W. R. Roth and A. Freidrich, *Tetrahedron Lett.*, 2607 (1969).

(52) Both vinylcyclopropane and vinylcyclobutane rearrangements are, however, considered to be diradical processes: M. C. Flowers and H. M. Frey, *J. Chem. Soc.*, 3547 (1961); H. M. Frey and D. C. Marshall, *ibid.*, 3981 (1962); D. G. Retzlhoff, B. M. Coull, and J. Coull, *J. Phys. Chem.*, **74**, 2455 (1970); R. J. Ellis and H. M. Frey, *Trans. Faraday Soc.*, **59**, 2076 (1963); H. M. Frey, *Adv. Phys. Org. Chem.*, **4**, 147 (1966).

(53) J. E. Baldwin and A. H. Andrist, *J. Am. Chem. Soc.*, **93**, 6193 (1971).

(54) K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Am. Chem. Soc.*, **89**, 1031 (1967); L. Kaplan and K. E. Wilzbach, *ibid.*, **90**, 3291 (1968); H. R. Ward and J. S. Wishnok, *ibid.*, **90**, 1085 (1968); T. J. Katz, E. J. Wang, and N. Acton, *ibid.*, **93**, 3782 (1971); B. M. Trost and R. M. Cory, *ibid.*, **93**, 5573 (1971).

(55) (a) N. C. Baird and M. J. S. Dewar, *J. Am. Chem. Soc.*, **91**, 352 (1969); (b) H. Iwamura, K. Morio, and T. L. Kuii, *Chem. Commun.*, 1408 (1971).

(56) L. T. Scott and M. Jones, Jr., *Chem. Rev.*, **72**, 181 (1972).

(57) Although an experimental determination of the structure of the hexamethyl derivative of **6** has been reported,[58] structural parameters for the parent compound have not appeared in the literature. Using the bicyclic structure of the hexamethyl compound for a calculation on the parent appears to be a poor approximation on the basis of ab initio calculations.[59] Discrepancies for the C_1–C_4 bond length are particularly notable. The geometry of **6** used in the EH calculations was adapted from the structure of **3**.[24]

(58) M. J. Cardillo and S. H. Bauer, *J. Am. Chem. Soc.*, **92**, 2399 (1970).

(59) M. D. Newton, J. M. Schulman, and M. M. Manus, *J. Am. Chem. Soc.*, **96**, 17 (1974).

(60) See ref 8, pp 200-202, for accurate drawings of the valence orbitals of cyclobutene.

(61) G. Wipff, Dissertation, Strasbourg, 1974.

(62) E. E. van Tamelen and S. P. Pappas, *J. Am. Chem. Soc.*, **85**, 3297 (1963); E. E. van Tamelen, S. P. Pappas, and K. L. Kirk, *ibid.*, **93**, 6092 (1971).

(63) Prismane is the most recent $(CH)_6$ isomer to be synthesized and is stable at room temperature: T. J. Katz and N. Acton, *J. Am. Chem. Soc.*, **95**, 2738 (1973).

(64) D. M. Lemal and L. H. Dunlap, *J. Am. Chem. Soc.*, **94**, 6562 (1972).

(65) The geometries of **16-20** used in the calculations were adapted from the geometries of their ethylene bridged counterparts and electron diffraction results for 1,3-butadiene.[66] Additional details may be found in ref 1.

(66) A. Almenningen, O. Bastiansen, and M. Traetteberg, *Acta Chem. Scand.*, **12**, 1221 (1958).

(67) For a more detailed discussion, see ref 1, ref 58.

(68) (a) C.-S. Chang and N. L. Bauld, *J. Am. Chem. Soc.*, **94**, 593, 7594 (1972); (b) F. R. Farr and N. L. Bauld, *ibid.*, **92**, 6695 (1970).
(69) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 3747 (1973); H. Hogeveen and W. F. J. Huurdeman, *ibid.*, 1255 (1974); C. Capozzi and H. Hogeveen, *J. Am. Chem. Soc.*, **97**, 1479 (1975).
(70) K. Alder and W. Roth, *Chem. Ber.*, **88**, 407 (1955).
(71) A. J. P. Devaquet and W. J. Hehre, *J. Am. Chem. Soc.*, **96**, 3644 (1974).
(72) A. Padwa and E. Alexander, *J. Am. Chem. Soc.*, **92**, 1796, 5674 (1970).
(73) H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5834 (1973); M. J. S. Dewar and R. C. Haddon, *ibid.*, **95**, 5836 (1973).
(74) W. J. Hehre and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5837 (1973).
(75) S. Winstein, *Q. Rev., Chem. Soc.*, **23**, 141 (1969).
(76) M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, **10**, 761 (1971); H. E. Zimmerman, *Acc. Chem. Res.* **4**, 272 (1971).
(77) EH results.

Determination of Triplet-Energy Levels in Azomethine Dyes by Energy-Transfer Measurements

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Abstract: Because the triplet-energy levels in azomethine dyes could not be observed directly, we attacked the problem of locating the azomethine dye triplet levels by applying an indirect experimental method. Flash kinetic spectrophotometry was used to measure the rate constants for energy transfer from a graded series of triplet sensitizers to a variety of azomethine dyes. Triplet-energy levels in the dyes can be assigned near that point where the efficiency of the energy-transfer process begins to drop. The results unexpectedly revealed dye triplet states of very low energy. The yellow azomethine dyes derived from pivaloylacetanilide, benzoylacetanilide, dibenzoylmethane, diacetylmethane, and dipivaloylmethane all have triplet energies in the range between 40 and 50 kcal/mol. With sensitizers having triplet energies lower than the dyes, the rate of drop in the efficiency of the energy-transfer process is characteristic of molecules that can twist about an essential double bond in the lowest excited state. The triplet energies of the cyan dyes derived from phenol and 1-naphthol and the magenta dyes derived from 2-pyrazolin-5-one are so low that these dyes quench our lowest energy triplet sensitizers at the maximum rate. The cyan dyes have triplet energies of less than or equal to 21 kcal/mol and the magenta dyes of less than or equal to 23 kcal/mol. Because of these low-energy triplet states in azomethine dyes, electronic energy transfer must be considered to be a contributor to the mechanism of the previously observed quenching of singlet oxygen by azomethine dyes.[1]

The longest lived excited electronic state in an organic molecule is almost always the lowest triplet state. On this basis, the triplet state must be considered to be a likely candidate for the reactive state in molecules that undergo photochemical reactions. Because of the possible role of triplet states in the light-fading reactions of azomethine dyes, one of the goals of our experimental investigations has been to gain information about these dye triplet states.

Several experimental methods failed to allow direct observation of the triplet states in azomethine dyes. To try to determine triplet-energy levels in azomethine dyes, both phosphorescence spectroscopy in rigid solvents at liquid nitrogen temperature and electronic absorption spectroscopy in heavy-atom solvents at room temperature were attempted, but without success. In addition, flash photolysis experiments were attempted to monitor triplet–triplet absorption, but the azomethine dye triplets appear to be too short-lived to permit detection.

To obtain a measure of the triplet energy levels in azomethine dyes, we applied an indirect experimental technique involving the measurement of rates of energy transfer from a graded series of triplet sensitizers to each individual dye. Triplet-energy levels in the dyes can be assigned near that point where the efficiency of the energy-transfer process begins to drop. The rule is that energy transfer from the triplet sensitizer remains diffusion controlled[2] until the sensitizer has less than 3 kcal/mol energy in excess of that required to excite the quencher from the ground state to its lowest triplet state.[3,4] The energy-transfer process is depicted in eq 1, where S is the sensitizer and Q is the quencher or

$$S^{*3} + Q \rightleftharpoons S + Q^{*3} \qquad (1)$$

dye. As the energy-transfer step becomes progressively more endothermic, the rate of decrease in the measured rate constant is dependent upon the nature of the quencher. In plots of the logarithm of the measured rate constant vs. the difference in triplet energy between sensitizer and quencher, the final slope is that predicted by the Arrhenius equation provided the quencher remains in its ground-state geometry following its acceptance of excitation energy. With quenchers that can change their geometries concomitantly with the excitation process, the slopes of such plots are shallower than the Arrhenius equation predicts, provided that these geometrical changes lower the energy of the quencher triplet states and thus reduce the energy requirements for their excitation.[3-5] "Nonvertical energy transfer" is the name assigned to this phenomenon.[3,4,6,7] Triplet-energy levels normally refer to molecules in their ground-state geometries.

Lamola reports the utility of the energy-transfer technique for triplet-energy determination, particularly after other methods had either failed or yielded erroneous or equivocal results.[8] Examples of molecules whose triplet energies were determined by energy-transfer measurements are biacetyl,[9] some aliphatic and aromatic azides,[10,11] as well as the geometric isomers of stilbene,[3] α-methylstilbene,[3] and some azastilbenes.[12] Plots of the logarithm of the measured rate constant vs. the difference in triplet energy between sensitizer and quencher yield slopes in accord with the Arrhenius equation when the quenchers are biacetyl and *trans*-stilbene.[3,5] Apparent deviations from this equation obtain for the remaining examples listed above by virtue of "nonvertical energy transfer".

Results and Discussion

Flash Kinetic Spectrophotometry. Flash kinetic spectrophotometry was the experimental technique employed for measurement of rates of energy transfer from a graded se-