Chemical Consequences of Orbital Interactions in Hydrocarbons Containing Unsaturatively Bridged Small Rings

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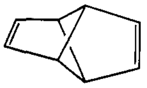
Abstract: The orbital interactions between small rings and unsaturated bridges are examined. The effects of "overlap repulsion" between two filled orbitals, when unmitigated by the presence of a low-lying empty orbital, are discussed. It is shown that overlap repulsion destabilizes molecules containing ethylene bridged three- and four-membered rings relative to their butadiene bridged counterparts. The pseudo Jahn–Teller effect is used to correlate the unusual spectra of molecules containing ethylene bridged small rings with their propensity for undergoing rearrangement. These qualitative considerations are shown to be corroborated by the bond orders and energies calculated by the EH method. The predicted stability of two other unsaturatively bridged cyclobutanes is in accord with experimental data, and the small calculated preference for butadiene over ethylene as a cyclopentane bridging group is in qualitative agreement with the Diels–Alder reactivity of 2,3-dimethylenenorbornane.

Polycyclic hydrocarbons containing small rings have long been a source of topological interest and synthetic challenge for organic chemists.[1] Nevertheless, despite the current interest in all valence electron calculations,[2] few theoretical treatments of molecules belonging to this class of compounds have appeared. The work described in this paper was undertaken to investigate the role of orbital interactions in determining the stability of some hydrocarbons containing small rings spanned by unsaturated bridges.

Our interest in these compounds was prompted by the experimental observation that while tricyclo-$[3.3.0.0^{2,6}]$octadiene (**1**) undergoes rapid rearrangement to semibullvalene at 25°,[3] a similar molecule (**2**), containing a cyclobutane ring 1,3 bridged by butadienes rather than by ethylenes, is formed by pyrolysis at 380°.[4] In addition, the remarkable lack of reactivity of **2** toward Diels–Alder cycloadditions[5] may also be interpreted as reflecting an energetic preference for butadiene over ethylene as the cyclobutane bridging group. Finally, the mechanism by which **1** rearranges suggests that the facility of this reaction[3] is due to the high energy content of the molecule rather than to a transition state of special stability.[5] Although a concerted $_\sigma2_a + _\sigma2_s$ process was at one time suggested[6,7] to rationalize the ease with which this rearrangement occurs, experimental evidence that precludes this pathway for the rapid rearrangement of an ethylene bridged cyclobutane has been recently reported.[5] The available stereochemical[5] and kinetic[8] evidence is consistent with a biradical mechanism[9-12] for the rearrangement of molecules like **1**.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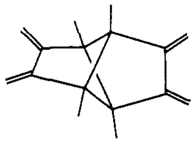
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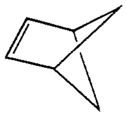
While models suggest that the shorter (≈1.34 Å) bonds in the ethylene bridges of **1** probably introduce more strain into the rigid tricyclic skeleton than the longer (≈1.48 Å) central bonds of the butadiene bridges in **2**, the difference in stability of these molecules might also be due, at least in part, to differences in orbital interactions between ring and unsaturated bridge. The qualitative and semiquantitative results reported in this paper corroborate the hypothesis that interactions between the orbitals of small rings and unsaturated bridges do indeed play a role in determining the relative stabilities of molecules like **1** and **2**.

Bicyclo[2.1.1] Systems. Qualitative Considerations

We begin by considering the orbital interactions between ring and bridge in bicyclo[2.1.1]hexene-2 (**3**) and 2,3-dimethylenebicyclo[2.1.1]hexane (**4**). The largest interactions are expected to occur between the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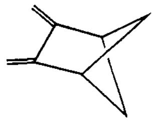
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(1) For reviews, see (a) J. Meinwald and Y. Meinwald, *Advan. Alicyclic Chem.*, 1, 1 (1966); (b) K. B. Wiberg, *ibid.*, 2, 185 (1968).

(2) 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; K. B. Wiberg and O. Sinanoglu, "Sigma Molecular Orbital Theory," Yale University Press, New Haven, Conn., 1970.

(3) J. Meinwald, D. Schmidt, and H. Tsruta, *J. Amer. Chem. Soc.*, **91**, 5877 (1969); H. E. Zimmerman, J. D. Robbins, and J. Schantl, *ibid.*, **91**, 5878 (1969).

(4) W. T. Borden and A. Gold, *ibid.*, **93**, 3830 (1971).

(5) A. Gold and W. T. Borden, *ibid.*, **94**, 7179 (1972).

(6) J. E. Baldwin and A. H. Andrist, *ibid.*, **93**, 3289 (1971).

(7) M. J. Goldstein and R. Hoffmann, *ibid.*, **93**, 6193 (1971).

(8) A. Gold and W. T. Borden, unpublished results.

(9) The experimental evidence does not distinguish between a forbidden concerted and a noninteracting biradical transition state.[10,11]

(10) J. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972).

(11) W. T. Borden and L. Salem, *ibid.*, **95**, 932 (1973).

(12) L. A. Paquette, M. J. Kukla, and J. C. Stowell [*ibid.*, **94**, 4920 (1972); **94**, 6874 (1972)], following a suggestion of Goldstein and Hoffmann,[7] have proposed that 1 rearranges rapidly because the transition state for this reaction is stabilized by bicycloaromaticity. Theoretical considerations and experimental evidence now available argue against this explanation. First, conversion of 1 to a bicycloaromatic species is equivalent, in terms of orbital symmetry,[13] to its conversion to semibullvalene. Both are forbidden processes,[13] which consequently must involve a diradical species in which two electrons occupy nonbonding MO's. Second, the rapid rearrangement of an ethylene bridged cyclobutane,[5] whose structure rules out bicycloaromatic stabilization of the transition state, provides experimental evidence against the proposal of Paquette, *et al.*

(13) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

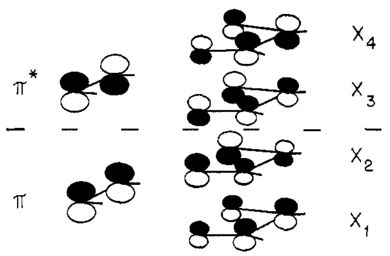

Figure 1. The π orbitals of ethylene and *cisoid*-1,3-butadiene.

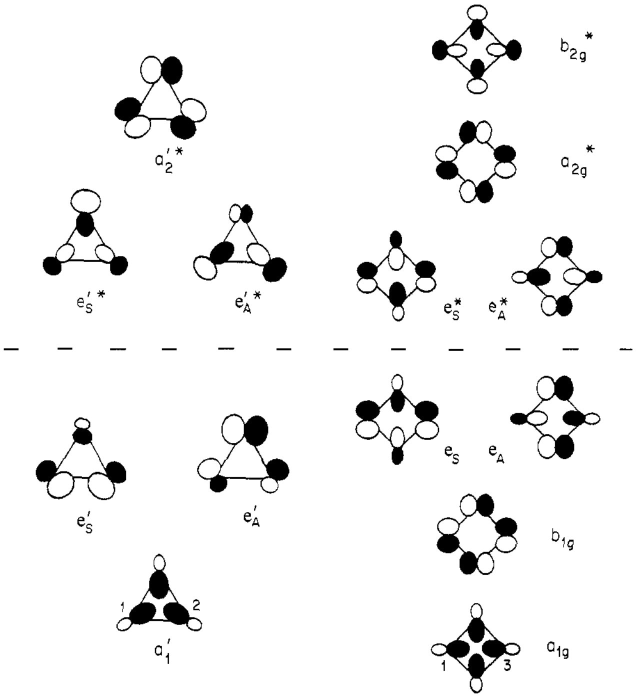

Figure 2. The Walsh orbitals of cyclopropane and cyclobutane.

frontier orbitals [the highest occupied (HOMO) and lowest unoccupied (LUMO) molecule orbitals] of the ring and bridge.[14]

In Figure 1 the π orbitals of ethylene and butadiene have been drawn schematically. It should be noted that the HOMO's, π and χ_2, in the two bridging groups are of opposite symmetry, as are the LUMO's, π* and χ_3. The frontier orbitals for an unpuckered cyclobutane ring are the degenerate e_u Walsh orbitals[15] shown in Figure 2. The e_u and e_u* orbitals that are symmetric to a mirror plane through C_2 and C_4 of the cyclobutane ring in Figure 2 will be referred to as e_s and e_s*, respectively. These two orbitals can undergo π-type interactions with the π orbitals of an unsaturated bridge between C_1 and C_3 that are also symmetric (S) to the mirror plane. The b_{1g} and a_{2g}* orbitals can mix with antisymmetric (A) π MO's of a bridge.

In an ethylene bridged system (**3**), the strongest orbital interaction occurs between the π HOMO of the bridge and the e_s ring orbital, because of their similar energies. The much larger energy separations between π* and b_{1g}, and between π and e_s*, make their mixings comparatively small. A partial interaction diagram is presented in Figure 3.[16]

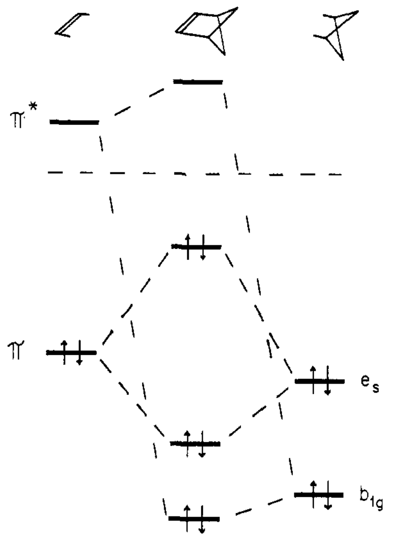

Figure 3. Schematic interaction diagram for the frontier mixings between cyclobutane ring and ethylene bridge orbitals in **3**.

The most important feature of the interaction of π and e_s is that their mixing has a net destabilizing effect on the total energy of **3**, because both orbitals are filled.[18] Since the magnitude of the destabilization caused by the mixing of two filled orbitals depends on their overlap,[19] we shall refer to this effect as "overlap repulsion."[20]

Overlap repulsion should be detectable not only in total energies but also in bond orders[21] calculated by theoretical methods which include overlap.[19] Bond orders are computed from the formula

$$P_{ij} = 2\sum_{\mu} C_{\mu i}C_{\mu j} \qquad (1)$$

where $C_{\mu i}$ is the MO coefficient for the *i*th atomic orbital (AO) in the μth MO and the sum is taken over all filled MO's. In a semiempirical MO approach which neglects differential overlap (NDO), the coef-

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[14] K. Fukui, *Fortschr. Chem. Forsch.*, **15**, 1 (1970); *Accounts Chem. Res.*, 4, 57 (1971), and references therein.

[15] R. Hoffmann and R. B. Davidson, *J. Amer. Chem. Soc.*, **93**, 5699 (1971).

[16] For simplicity, and since their correct ordering is uncertain,[17] the antibonding Walsh orbitals of the ring have been omitted from this diagram. They lie at relatively high energies, so that their mixing with the bonding MO's of the bridge is relatively small. The a_{2g}* ring orbital does, however, mix with π* of the bridge to create a low-lying LUMO in 3.

[17] Compare the ordering in ref 15 with that in J. S. Wright and L. Salem, *J. Amer. Chem. Soc.*, **94**, 322 (1972).

[18] For a brief qualitative discussion, see ref 7.

[19] N. C. Baird and R. M. West, *J. Amer. Chem. Soc.*, **93**, 4427 (1971); K. Muller, *Helv. Chim. Acta*, **53**, 1112 (1970).

[20] The overlap repulsion energy between two completely filled orbitals, that is, the net destabilization resulting from their mixing, is[19]

$$\Delta E = -4S(\beta - \epsilon_0 S)/(1 - S^2)$$

where S is the overlap between them, β is their interaction energy, and ϵ_0 is the mean of their energies before mixing. Note that the dependence on ϵ_0 implies that the overlap repulsion energy between high-lying filled orbitals (ϵ_0 small in magnitude) will have the greatest destabilizing effect on the total energy of the system. This fact provides the rationale for confining our attention primarily to the overlap repulsion between the HOMO's of ring and bridge. It is also clear from the above equation that theoretical methods which neglect differential overlap (NDO) and consequently set $S = 0$ will fail to detect the effect on the energy of overlap repulsions.

[21] In fact, in the EH and simple Hückel methods, the bond order between two AO's is directly proportional to the contribution to the total energy arising from their interaction.[22] If the bond order between two AO's is positive, their interaction is stabilizing; if it is negative, the net overlap repulsion between the AO's destabilizes the molecule.

[22] L. Salem, "The Molecular Orbital Theory of Conjugated Systems," W. A. Benjamin, Reading, Mass., 1966, p 34.

ficients in the bonding and antibonding combinations of two orbitals have the same magnitude. However, when overlap is included, as in *ab initio* or extended Hückel (EH) calculations, the coefficients in the antibonding orbital are larger in magnitude than those in the bonding MO. Thus, when MO's that involve the bonding and antibonding combinations of two atomic orbitals are equally filled, theoretical methods in which overlap is included predict a resulting partial bond order between the AO's that is negative. Therefore, in an EH or *ab initio* calculation the overlap repulsion between e_s and π in **3** should be manifested in a negative contribution to the net bond order ($P_{12}{}^{\pi}$) between the $2p\pi$ orbital at C_2 and the p orbital at C_1 with which it overlaps in a π fashion.

If the only interaction between the MO's of the ring and bridge in **3** was that between e_s and π, then $P_{12}{}^{\pi}$, calculated including overlap, would certainly be negative. However, the effect of overlap repulsion between e_s and π on both $P_{12}{}^{\pi}$ and the total energy in **3** is mitigated by the mixing of b_{1g} with π^*, shown in Figure 3.[23] Since this interaction involves the mixing of a filled with an unfilled orbital, it has a stabilizing effect on the total energy of the molecule and contributes positively to the net bond order, $P_{12}{}^{\pi}$.

The unusual uv spectra of ethylene bridged cyclobutanes[24,25] is also a consequence of orbital interactions, as has been pointed out for **1** by Hoffmann and Davidson[15] and by Gleiter and Kobayashi.[26] As shown in Figure 3, the interaction of the ethylene π with the ring e_s orbital produces a very high lying HOMO in **3**. From the preceding discussion it should be clear that a theoretical relationship exists between the unusual uv spectra and the relative instability of molecules containing a cyclobutane ring 1,3 bridged by ethylene. Baldwin and Andrist have, in fact, noted an experimental correlation between the frequency of the unusual uv absorptions in such molecules and their E_a's for rearrangement[6] and subsequently remarked on this correlation in the context of a discussion of configuration interaction.[27]

An elegant theoretical framework for correlating the unusual uv spectra of ethylene bridged cyclobutanes with the facility with which these molecules undergo rearrangement is provided by the pseudo, or second-order, Jahn–Teller effect.[28] This theoretical treatment shows that a molecule in which there exists a small energy gap between an occupied and an unoccupied orbital can undergo facile rearrangement along a vibrational mode which allows their mixing. The vibrational mode that is required for the mixing of two such orbitals must have the same symmetry as an electronic transition between them. The long wavelength uv absorption of **1** shows that in this molecule there is a relatively small energy difference between the HOMO and LUMO. Accepting the theoretical interpretation of the uv spectrum of this molecule,[15,26] it is possible to predict that **1** will decompose in a vibrational mode of e symmetry. A drawing of this mode reveals that a relaxed vibration along it leads to creation of the diradical that has been implicated[5] in the thermal rearrangement of **1**. From the theoretical perspective of the pseudo Jahn–Teller effect, the proclivity toward rearrangement of **1** is seen as a consequence of the interaction between the HOMO's of bridge and ring, unmitigated by mixing of the LUMO of the bridges. This creates a system in which there exist high-lying filled and low-lying empty orbitals. Mixing between them can be brought about by an asymmetric vibration which destroys the symmetry that prevents their interaction; and rearrangement along such a pathway, which in the case of **1** leads to cleavage of one ring bond, is consequently favorable.

Replacing the ethylene bridge in **3** by butadiene, as in **4**, results in a reversal of symmetry of the HOMO and LUMO of the unsaturated bridge, as noted above. The HOMO of the bridge, χ_2, no longer has the same S symmetry as e_s, the HOMO of the ring; consequently, they do not mix, so there is no overlap repulsion between them. However, χ_3, the LUMO of the butadiene bridge in **4**, has the symmetry requisite for mixing with the HOMO of the ring, and this interaction lowers the energy of e_s while raising that of χ_3. Since only the former is filled, this mixing has an important stabilizing effect on the total energy of **4** and makes a positive contribution to the bond order, $P_{12}{}^{\pi}$, between the ring and bridge in this molecule. Another consequence of the fact that χ_3 and e_s have the same symmetry is that, using the theory of the pseudo Jahn–Teller effect, **4** can be predicted to be relatively stable to rearrangement. Unlike the case in **3**, in **4** the HOMO of the ring is already mixed with the LUMO of the bridge. Thus **4** does not possess an asymmetric vibrational mode that can be "relaxed" by permitting an interaction between these orbitals that does not already exist in the most symmetrical molecular configuration.

Results of Calculations

The above analysis, based almost exclusively on consideration of the interaction between the HOMO of the cyclobutane ring and the HOMO and LUMO of the unsaturated bridge in **3** and **4**, represents an oversimplification of the orbital interactions that exist in these compounds.[29] Nevertheless, the results of calculations indicate the above analysis, based on these qualitative considerations, to be substantially correct.

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(23) The overlap repulsion between e_s and π is itself mitigated to a small extent by mixing in of $e_s{}^*$ which is not shown in Figure 3. Because $e_s{}^*$ lies quite high in energy, it consequently mixes only slightly with the bonding π orbital.

(24) J. Meinwald and F. Uno, *J. Amer. Chem. Soc.*, **90**, 800 (1968).

(25) M. B. Robin, H. Basch, N. A. Kuebler, B. E. Kaplan, and J. Meinwald, *J. Chem. Phys.*, **48**, 5037 (1968).

(26) R. Gleiter and T. Kobayashi, *Helv. Chim. Acta*, **54**, 1081 (1971). These authors have constructed an orbital interaction diagram for **3**, as well as for **1**.

(27) J. E. Baldwin, A. H. Andrist, and R. K. Pinschmidt, Jr., *Accounts Chem. Res.*, **5**, 402 (1972).

(28) R. F. W. Bader, *Can. J. Chem.*, 40, 1164 (1962); L. S. Bartell, *J. Chem. Educ.*, **45**, 754 (1968); L. Salem, *Chem. Phys. Lett.*, **3**, 99 (1969); R. G. Pearson, *J. Amer. Chem. Soc.*, **91**, 1252, 4947 (1969).

(29) For instance, in the above analysis of the interaction between e_s of the ring and χ_3 of the bridge in **4** we ignored the fact that χ_1 also mixes with the former orbital; and we totally neglected the mixing between χ_2, the HOMO of the bridge, and b_{1g} of the ring. In both cases the mixing has a destabilizing effect, since it occurs between two filled orbitals. However, in each case the overlap repulsion that results from the mixing of two filled orbitals is mitigated by the presence of an unfilled bridge orbital (χ_3 in the former and χ_4 in the latter) of appropriate symmetry for mixing with the filled orbital of the ring. Only when two filled orbitals interact in the absence of a low-lying orbital of the same symmetry does the overlap repulsion between them become the dominant effect of orbital mixing. Some examples of systems where such an empty orbital is absent so that overlap repulsion becomes important are: two atoms with nonbonding orbitals, each containing a lone pair of electrons; rectangular cyclobutadiene, viewed as two interacting ethylenes; and a cyclobutane ring, spanned by an ethylene bridge (**3**).

Table I. Bond Orders[a,b] between p Orbitals, Oriented for π Overlap, on Adjacent Carbons of Rings and Bridges

Compd	r_{12}, Å	r_{23}, Å	P_{12}^{π}
3	1.537	1.332	−0.007
4	1.537	1.483	0.078
5	1.537	1.397	0.036
6	1.537		0.098
7	1.510	1.340	−0.015
8	1.510	1.483	0.089
9	1.537	1.343	0.036
10	1.537	1.483	0.059

[a] EH results. [b] Multiplication by the overlap integral (S = 0.193 at 1.537 Å and 0.202 at 1.51 Å) converts the bond orders to overlap populations.

As shown in Table I, a net negative π-bond order is found between C-1 and C-2 in **3**[30] by an EH calculation.[33] The negative value of P_{12}^{π} shows that the negative contribution of the overlap repulsion between e_s and π to the net bond order outweighs the positive contribution of the mixing between π^* and b_{1g}. It is of some interest that a MINDO/2 calculation[34] erroneously predicts a large (0.227)[35] *positive* π-bond order between C-1 and C-2. This anomaly results from the method's neglect of differential overlap (NDO) and its consequent failure to take account of the overlap repulsion arising from the interaction of the filled orbitals, π and e_s.[36] Any concern that the negative value of P_{12}^{π} predicted by an EH calculation is in error and somehow arises from the failure of the EH method to deal explicitly with electron repulsion should be laid to rest by the finding of Wipff and Lehn[39] that an *ab initio* calculation predicts an even more negative value of P_{12}^{π} in **3**. Clearly, where overlap repulsion is important, the EH method, which includes overlap, will provide a more accurate qualitative picture of bonding, or rather the lack of it, than NDO methods, which are less approximate in other ways, but achieve some of their greater sophistication at the expense of neglecting overlap and hence overlap repulsions.

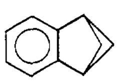
As expected, in the butadiene bridged cyclobutane (**4**)[40] an EH calculation predicts a positive P_{12}^{π} bond order. An *ab initio* calculation[39] gives a value of P_{12}^{π} very close to that in Table I. Thus the P_{12}^{π} bond orders, obtained from both EH and *ab initio* calculations, confirm the stabilizing nature of the orbital interactions in molecules (*e.g.*, **2** and **4**) containing a cyclobutane ring bridged 1,3 by butadiene compared with the net slightly destabilizing interaction between the orbitals of ring and bridge in molecules (*e.g.*, **1** and **3**) containing a cyclobutane ring similarly spanned by ethylene.

A quantitative estimate of the energetic preference for butadiene over ethylene as the cyclobutane bridge can, in principle, be obtained from a calculation of the energy of the isodesmic[42] reaction shown in eq 2. However,

$$\mathbf{3} + \textit{cisoid}\text{-butadiene} \longrightarrow \mathbf{4} + \text{ethylene} \qquad (2)$$

for such a calculation to be quantitatively meaningful, accurate structural data on **3** and **4** are required. In the absence of such data we resorted to use of the same geometry for the cyclobutane ring in both **3** and **4**[32] for the purpose of verifying qualitatively the conclusions, drawn from the values of P_{12}^{π}, regarding the relative stabilities of these molecules. As anticipated, an EH calculation shows reaction 2 to be exothermic. No quantitative significance should be attached to the value of −17 kcal/mol that is computed for the energy of this process. To test that the calculated exothermicity is not due merely to better orbital overlap in the σ bonds between ring and bridge in **4** than in **3**, the reaction in eq 2 was recalculated using the C-2–C-3 bond length of **3** for the corresponding bond in **4** and the central bond in butadiene.[43] The calculated exothermicity of the reaction becomes 14 kcal/mol, a decrease of only 3 kcal/mol.

The method of analysis described above is easily applied to other unsaturatively bridged cyclobutanes. For example, if the two Kekulé structures for benzene are considered, one would expect benzobicyclo[2.1.1]-hexene (**5**) to possess orbital interactions intermediate between those of an ethylene and a butadiene bridged cyclobutane. The value of P_{12}^{π} in Table I from an EH calculation[44] verifies this; in fact, the bond order in **5**



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(30) The geometry of **3** used in the calculations was taken from electron diffraction results[31] except for the geometry of the cyclobutane ring. Some doubt regarding the reliability of the reported structure of **3**[31] seems warranted. When the coordinates[32] of the cyclobutane ring in bicyclo[2.1.1]hexane are used in place of those published for the same ring in **3**,[31] the total energy of **3**, calculated *via* the MINDO/2 and EH methods, drops by 14.2 and 28.9 kcal/mol, respectively. Thus, the cyclobutane geometry used in all the calculations is taken from the structure determination of bicyclo[2.1.1]hexane.[32]

(31) D. L. Zebelman, S. H. Bauer, and J. F. Chiang, *Tetrahedron*, **28**, 2727 (1972).

(32) J. F. Chiang, *J. Amer. Chem. Soc.*, **93**, 5044 (1971).

(33) The EH parameters are from: R. Hoffmann, S. Swaminathan, B. G. Odell, and R. Gleiter, *ibid.*, **92**, 7091 (1970).

(34) The MINDO/2 method and parametrization used are described in: M. J. S. Dewar and D. H. Lo, *J. Amer. Chem. Soc.*, **94**, 5296 (1972).

(35) The absolute magnitude of the MINDO/2 bond orders, P_{ij}, calculated from (1) are expected to be larger than the EH or *ab initio* bond orders, calculated from the same formula, because overlap is not included in normalizing the MINDO/2 MO coefficients. For example, P^{π} in ethylene is 1.00 in MINDO/2 or any other NDO method, while the EH value is 0.785.

(36) The closely related inadequacy of NDO calculations in representing the repulsion between lone pairs on adjacent centers also arises from the NDO approximation.[37] Similar errors also occur in the rotational barriers for some anions. For instance, in cyclopropylcarbinyl the interaction between the lone pair and the filled cyclopropane e'_A Walsh orbital (Figure 2) is not calculated to be destabilizing in the bisected configuration by an NDO method. We find that a MINDO/2 calculation favors the bisected form of this anion by 3.4 kcal/mol over the eclipsed, while EH and *ab initio*[38] calculations both favor the eclipsed form by small amounts.

(37) N. Bodor, M. J. S. Dewar, A. Harget, and S. Haselbach, *J. Amer. Chem. Soc.*, **92**, 3854 (1970).

(38) W. J. Hehre, *ibid.*, **94**, 6592 (1972).

(39) G. Wipff and J. M. Lehn, unpublished results. We wish to thank Dr. Wipff and Professor Lehn for communicating their results to us privately before publication.

(40) The butadiene geometry used for **4** was adapted *via* rigid rotation from electron diffraction results[41] for transoid 1,3-butadiene except the $C_2C_3C_8$ angle was maintained at 127.2°, the C_2C_3H value in **3**. The remaining parameters for **4** were obtained from **3**.[30]

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

(42) Isodesmic processes are reactions in which the same number and types of bonds appear in the reactants and products. Since in such a reaction electron correlation effects are expected to be about the same in reactants and products, the heats of such reactions can be estimated accurately by *ab initio* calculations employing single Slater determinants: W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

(43) Shortening the C-2–C-3 bond in **4** increases the calculated energy of the butadiene bridge in this molecule, but this should be balanced by a comparable increase in the calculated energy of butadiene itself.

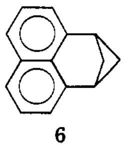
(44) The benzene geometry for **5** was taken from an electron diffraction study: A. Langseth and B. P. Stoicheff, *Can. J. Phys.*, 34, 350 (1956).

is almost exactly the average of those in **3** and **4**. The reaction shown in eq 3 is also predicted to be less exo-

$$\mathbf{3} + \text{benzene} \longrightarrow \mathbf{5} + \text{ethylene} \qquad (3)$$

thermic than that in eq 2; an EH calculation yields a value of -5 kcal/mol for its energy. A bisbenzene bridged cyclobutane of little stability has been proposed as an intermediate in the thermal rearrangement of dibenzocyclooctatetraenes.[45]

The final unsaturatively bridged cyclobutane we considered is **6**, the product of the thermal rearrangement of 1,8-divinylnaphthalene.[46a] The stability of **6** is reflected in the bond order from an EH calculation, which yields a value of P_{12}^{π} of 0.098. Such a large bond order might be deemed rather surprising in view of the fact that e_s of the ring has the wrong symmetry for mixing with the LUMO of the naphthalene bridge. However, e_s also has the wrong symmetry for mixing with the HOMO of the bridge, so that there is no overlap repulsion between them. In addition, b_{1g} of the ring does mix with the naphthalene LUMO,[46b] and e_s mixes with an empty orbital of only slightly higher energy than the LUMO of the bridge.



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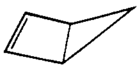
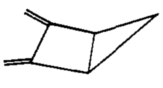
Bicyclo[2.1.0] Systems

Analysis of the interactions between bridge π orbitals and the cyclopropane Walsh orbitals (Figure 2) in bicyclo[2.1.0]pentene (**7**) and 2,3-dimethylenebicyclo[2.1.0]pentane (**8**) is a straightforward extension of that for the corresponding bridged cyclobutanes. The e_s' orbital of cyclopropane ring in **7** interacts strongly with the ethylene π HOMO. This results in overlap repulsion between them with concomitant destabilization of **7**, ameliorated by the mixing of e_a' with π^*. Note, however, that the coefficients of e_a' at C_1 and C_4 are smaller in magnitude than those of e_s'. Therefore, despite the fact that the e_s' and the e_a' orbitals of the cyclopropane ring in **7** are closer in energy than the e_s and b_{1g} orbitals of the cyclobutane ring in **3**, the net effect of orbital interactions between ring and bridge should be qualitatively similar in both molecules. A correspondence is also expected between the orbital interactions in **4** and those present in **8**. That this is, in fact, the case is shown by the results in Table I.[47] An *ab initio* calculation[39] gives essentially the EH value for P_{12}^{π} in **8** but predicts a bond order of zero in **7**. The energy calculated by the EH method for the isodesmic reaction below, corresponding to eq 2, is also -17 kcal/mol.



7



8

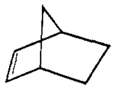
$$\mathbf{7} + \textit{cisoid}\text{-butadiene} \longrightarrow \mathbf{8} + \text{ethylene} \qquad (4)$$

A comparison of the experimental stabilities of **7** and **8** is not possible, since the latter is an unknown molecule. Moreover, when and if **8** is prepared, the fact that it can open to a highly stabilized bis-allylic diradical in order to relieve the large strain present in the bicyclo[2.1.0]pentane ring system[1b] makes a comparison of kinetic stabilities inappropriate. However, it can be predicted that **8** like **2** should prove to be relatively unreactive toward Diels–Alder cycloadditions. Bicyclo[2.1.0]pentene is known and is found to undergo rearrangement to cyclopentadiene with E_a = 26.9 kcal/mol.[48] The mechanism of this process has aroused much interest.[49–52] The theory of the pseudo Jahn–Teller effect predicts that **7** will decompose most easily in a vibrational mode that removes the plane of symmetry present in the molecule and allows mixing between e_s' and π^*. As would be expected, **7** possesses a long wavelength uv absorption.[6]

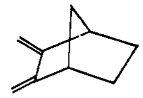
It is of some interest to note that the interactions between the orbitals of the cyclopropane ring and the π bonds in semibullvalene,[53] the molecule to which **1** rearranges, are qualitatively similar to those in **8**. Thus, the rearrangement is thermodynamically favored by the exchange of the unfavorable orbital interactions between ring and bridges in **1** for the much more favorable ones present in the product.[54]

Bicyclo[2.2.1] Systems

The next logical step in our survey of small rings with unsaturated bridges is to compare the orbital interactions in molecules containing a five-membered ring bridged by ethylene and by butadiene; *e.g.*, norbornene (**9**) and 2,3-dimethylenenorbornane (**10**).



9



10

The results of EH calculations[55] show that the values of P_{12}^{π} in **9** and **10** are much more comparable than in the unsaturatively bridged cyclobutanes (**3** and **4**) or cyclopropanes (**7** and **8**). The fact that the HOMO of a puckered cyclopentane ring is antisymmetric and consequently interacts relatively strongly with the π^* orbital of the ethylene bridge in **9** but not with χ_3 of the butadiene bridge in **10** is responsible for the increased π-bond order in the former and the decreased value of

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(45) M. Stiles and U. Burckhardt, *J. Amer. Chem. Soc.*, **86**, 3396 (1964).

(46) (a) J. Meinwald and J. A. Kapecki, *ibid.*, **94**, 6235 (1972); S. F. Nelsen and J. P. Gillespie, *ibid.*, **94**, 6237, 6238 (1972). (b) After this manuscript was submitted, Nelsen and Gillespie published a paper [*ibid.*, **95**, 2940 (1973)] showing how this mixing can explain the epr spectrum of the anion radical of a derivative of **6**.

(47) The experimentally determined coordinates were used for **7**: S. L. Hsu, A. H. Andrist, T. D. Gierke, R. C. Benson, and J. E. Baldwin, *ibid.*, **92**, 5250 (1970). They were modified for **8** in the same fashion that those of **4** were obtained from **3**.[40]

(48) J. I. Brauman and D. M. Golden, *ibid.*, **90**, 1920 (1968).

(49) J. E. Baldwin and A. H. Andrist, *Chem. Commun.*, 1561 (1970).

(50) S. McLean, D. M. Findlay, and G. I. Dmitrienko, *J. Amer. Chem. Soc.*, **94**, 1380 (1972).

(51) J. E. Baldwin and G. D. Andrews, *ibid.*, **94**, 1775 (1972).

(52) M. C. Flowers and H. M. Frey, *ibid.*, **94**, 8636 (1972).

(53) The valence orbitals of semibullvalene have been constructed: R. Hoffmann and W.-D. Stohrer, *J. Amer. Chem. Soc.*, **93**, 6941 (1971).

(54) The lower strain energy calculated for semibullvalene, compared to that calculated for **1**, also favors the rearrangement: H. Iwamura, K. Morio, and T. L. Kuni, *Chem. Commun.*, 1408 (1971).

(55) The geometry of **9** was estimated from that of norbornane[56] and norbornadiene[57] and was modified for **10** in the same fashion that **4** was obtained from **3**.

(56) J. F. Chiang, C. F. Wilcox, Jr., and S. H. Bauer, *J. Amer. Chem. Soc.*, **90**, 3149 (1968).

(57) G. Dallinga and L. H. Toneman, *Recl. Trav. Chim. Pays-Bas*, **87**, 805 (1968).

P_{12}^{π} in the latter. With values of P_{12}^{π} that differ between **9** and **10** by less than a third as much as those in **3** and **4** or **7** and **8**, it is somewhat surprising to find that the reaction

$$\mathbf{9} + \textit{cisoid}\text{-butadiene} \longrightarrow \mathbf{10} + \text{ethylene} \qquad (5)$$

is calculated by the EH method to be exothermic by as much as 8 kcal/mol.[58] It is not at all inconceivable that EH theory overestimates the difference in interaction energy between ring and bridge in **9** and **10** and that comparison of the values of P_{12}^{π} in these molecules is a better semiquantitative indicator of the effect of orbital interactions between ring and bridge on their relative stability. Be that as it may, comparison of either bond orders or energies allows the qualitative prediction that **10** should be a much more reactive diene toward Diels–Alder cycloadditions than either **4** or **8**. In fact, **10** does undergo a Diels–Alder reaction with maleic anhydride readily.[59]

Conclusions

In this paper we have shown that the experimental stability of molecules containing unsaturatively bridged small rings correlates well with the type of orbital interactions between ring and bridge that exist in each of these systems. The conclusions drawn from simple frontier orbital interaction schemes have been verified by calculations. Although our work does not allow a reliable quantitative estimate of the contribution of orbital interactions to the energy differences between molecules containing unsaturatively bridged small rings,[60] in the absence of evidence to the contrary there appears to be no reason to assume that orbital interactions between ring and bridge are not the principal factor in determining the relative stabilities of such systems.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. Support by the National Science Foundation of the experimental work which led to this theoretical study is also gratefully acknowledged.

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(58) The explanation of this apparent anomaly is that the antibonding π interaction between C-1 of the ring and C-3 of the bridge that is found by EH calculations in the other ethylene bridged molecules (**3** and **7**) still persists in **9**. This 1,3 antibonding π interaction arises from the fact that π^*, the empty orbital of the ethylene bridge, is antisymmetric. Thus, when it mixes with a filled ring orbital in a fashion that is bonding between C-1 and C-2, antibonding between C-1 and C-3 is concomitantly produced. This effect is superimposed upon the negative π-bond order between C-1 and C-3 that exists as a consequence of the overlap repulsion between π and filled ring orbitals of the same symmetry. Therefore, the bond order, P_{13}^{π}, is calculated to be quite negative in the ethylene bridged systems; for instance in **9** it is -0.16. In contrast, because χ_3, the LUMO of the butadiene bridge, is a symmetric orbital, its mixing with filled ring orbitals contributes positively to P_{13}^{π}, as well as to P_{12}^{π}. This tends to cancel the negative contributions to the π-bond order between C-1 and C-3 from overlap repulsions between filled orbitals and from the mixing of the antisymmetric χ_4 orbital of the bridge with the ring. Thus, the value of P_{13}^{π} in a butadiene bridged molecule is expected to be smaller in magnitude than that in the corresponding ethylene bridged system. Indeed, the value of P_{13}^{π} in **10** is -0.047. Although the π overlaps between C-1 and C-3 in **9** and 10 are relatively small (only about a fifth the size of those between C-1 and C-2), nevertheless, the difference in the values of P_{13}^{π} in these molecules is relatively large. In fact, the difference in 1,3 π bonding between **9** and 10 is sufficient to account for a substantial part of the predicted exothermicity of the reaction of eq 5, as computed by EH theory.

(59) K. Alder and W. Roth, *Chem. Ber.*, **88**, 407 (1955).

(60) Although the qualitative results of EH calculations regarding the relative stabilities of nonpolar species are generally reliable, the magnitudes of energy differences are poorly reproduced. NDO calculations are also not expected to yield quantitatively reliable results for the difference in energy between small rings bridged by ethylene and by butadiene, for, as discussed above, such calculations fail to detect the overlap repulsion that acts to destabilize the former type of molecule relative to the latter. High quality *ab initio* calculation[61] of the energies of the isodesmic reactions in eq 2–5 is most likely to yield reasonably accurate quantitative estimates of the difference in energy between bridging groups. The contribution of π-type orbital interactions between ring and bridge to these figures may be estimated by compressing the central bond in both a butadiene bridge and butadiene itself to the ethylene bond length and using identical geometries for the ring in a pair of bridged compounds. It should be noted that the EH results reported above, using a compressed central bond in **4**, suggest that the orbital contribution to the calculated energy difference between bridged cyclobutanes **3** and **4** is large compared to that of strain.

(61) W. Hehre [*J. Amer. Chem. Soc.*, **94**, 6592 (1972)] has used *ab initio* calculations to show that the energy of the π-type interaction of a vinyl group with a small ring to which it is attached is intermediate between that of vinyl with methyl and vinyl with vinyl. However, this result does not allow the estimation of the π-interaction energy of butadiene with a small ring, relative to that of ethylene, since, as a cyclopropane or cyclobutane bridging group, ethylene is calculated to undergo no or slightly destabilizing π interactions.