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Effects of Electron Repulsion in Conjugated Hydrocarbon Diradicals

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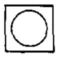
Abstract: It is shown that classification of conjugated diradicals into two types, according to whether their Hückel NBMO's can be confined to disjoint sets of atoms, provides a useful basis for understanding the electronic properties of such diradicals. If the Hückel NBMO's can be so confined, the lowest singlet and triplet states are nearly degenerate at the SCF level, and both SCF wave functions use a common set of MO's. On the other hand, if the Hückel NBMO's cannot be localized to disjoint groups of atoms, then the triplet lies well below the corresponding open shell singlet at the SCF level, and the MO's in the SCF wave functions for the two states differ. These general expectations, which emerge from previous theoretical work on cyclobutadiene (**1**) and trimethylenemethane (**2**), are applied to several other fully conjugated hydrocarbon diradicals. Ab initio SCF and full π space CI calculations on 1,3-dimethylenecyclobutadiene (**7**) and tetramethylenethane (**8**) are reported, which confirm the predictions for each of these molecules. It is demonstrated that PMO analysis of the mode of union of two odd AH's can be used to identify the class to which the resulting diradical belongs. The relationship between NBMO localizability to different sets of atoms in an AH diradical and the number of starred, compared to unstarred, atoms in the AH is also explored.

Diradicals are molecules possessing a pair of nonbonding molecular orbitals (NBMO's) that are occupied by a total of two electrons. One series of diradicals, in which the NBMO's occur in fully conjugated π systems, is comprised of the [4*n*]annulenes. Cyclobutadiene (**1**) is the first member of this series and the one that has received the most attention, both theoretical and experimental.[1] Another type of fully conjugated hydrocarbon diradical consists of those molecules for which no classical Kekulé structures can be written.[2] In this series trimethylenemethane (**2**) is the prototype and also the molecule that has been most studied.[3]



1

2

In this paper we use a PMO approach[4] to show that conjugated diradicals result from the union of two odd alternant hydrocarbon (AH) fragments at a node in the NBMO of at least one of them. The PMO approach is a useful one for dividing diradicals into two classes. In one class the Hückel NBMO's can be chosen so that they are confined to different sets of carbon atoms, as is the case in the [4*n*]annulenes. In the other class, to which **2** belongs, the Hückel NBMO's cannot be so confined. This classification is shown to be of great utility for predicting the important differences in the effects of electron repulsion in the two classes of diradicals. These predictions are compared with the results of ab initio SCF and full π space CI calculations on one molecule from each class.

PMO Analysis of 1 and 2

The π systems of cyclobutadiene (**1**) and trimethylenemethane (**2**) can be analyzed as resulting from the union of an allyl radical (**3**) with a carbon bearing a p-π orbital (**4**), as shown in Figure 1. The existence of a pair of NBMO's in both **1** and **2** emerges clearly from this analysis. Since **3** and **4** are odd alternant hydrocarbons (AH's), each possesses an NBMO.[4] The union of these odd AH fragments to give both **1** and **2** takes place at a nodal plane of the NBMO of **3**. Consequently, the degeneracy of the NBMO's of **3** and **4** is not lifted by their mutual interaction in either mode of union. The noninteraction of the NBMO's of the fragments does not, however, by itself assure the survival of two NBMO's in **1** and **2**, for the p orbital of **4** does interact with the bonding and the antibonding MO of **3**. Nevertheless, the pairing theorem[4,5] guarantees, at least at the level of the Hückel theory, that these latter two MO's of **3** have coefficients of the same magnitude at each carbon and energies that are equally spaced about the energy (α) of the NBMO. This fact is sufficient to ensure that the interaction of the p orbital of **4** with these two MO's of **3**, while lowering the energy of the bonding MO and raising that of the antibonding MO, leaves an MO at the nonbonding level.[6] An orbital interaction diagram is shown in Figure 1.

Figure 1 shows that the π systems of **1** and **2** can both be analyzed in terms of interactions between the same MO's of **3** and **4** and that both **1** and **2** are diradicals. The diagram also illustrates a difference between **1** and **2** that results from the two modes of union of **3** and **4**. Union of **4** to the two terminal carbons of **3** results in a stronger interaction between the p orbital of **4** and the bonding and antibonding MO of **3** than does union of **4** to the central atom of **3**. Consequently, the bonding and antibonding MO's of cyclobutadiene lie respectively at lower and higher energies ($\alpha \pm 2\beta$) than the corresponding MO's in trimethylenemethane ($\alpha \pm 3^{1/2}\beta$).[7] However, a difference between **1** and **2** of much greater significance is in the form taken by the NBMO that arises from the three-orbital interaction in the two different modes of union.

In both **1** and **2** this NBMO results from the p orbital on **4** mixing in the bonding MO of **3** in an antibonding fashion and the antibonding MO in a bonding fashion. Application of the pairing theorem shows that the amount of mixing of these two MO's into the p AO is equal. Moreover, since the pairing theorem requires that the magnitudes of the coefficients of the AO's in these two MO's be the same, mixing of these two MO's into the p orbital of **4** results in a cancellation of their contributions at the carbon atom(s) in **3** where union with **4** occurs.

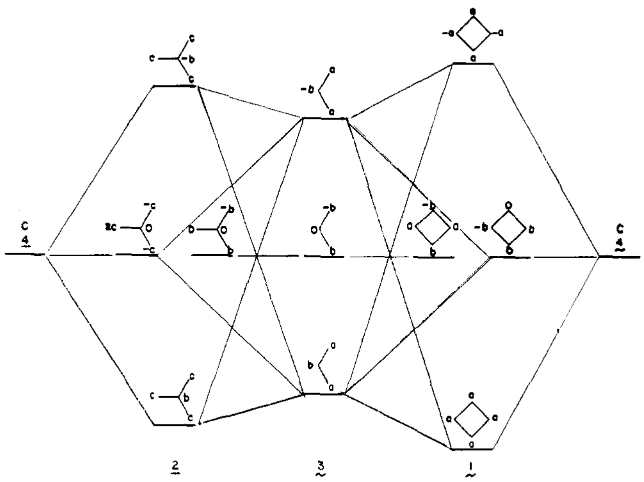


Figure 1. Orbital interaction diagrams for the PMO analysis of cyclobutadiene (**1**) and trimethylenemethane (**2**) in terms of the union of allyl (**3**) with a carbon bearing a p-π orbital (**4**). The normalized coefficients in the MO's are: $a = \frac{1}{2}$, $b = 2^{-1/2}$, and $c = 6^{-1/2}$.

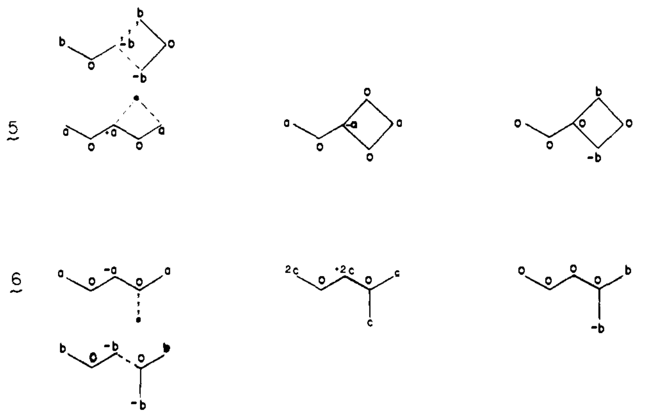


Figure 2. PMO analyses and NBMO's of **5** and **6**. The normalized coefficients in the MO's are: $a = 3^{-1/2}$, $b = 2^{-1/2}$, and $c = 10^{-1/2}$.

Consequently, the net contribution of **3** to the resulting NBMO is confined to just the carbon atom(s) not bonded directly to **4**.[8] The mixing of the π orbitals of **3** and **4** to give the MO's of **1** and **2** is shown graphically in Figure 1. Alternatively, the NBMO's of **1** and **2** can be obtained directly from the rule that in each NBMO of an AH the sums of the coefficients of the starred atoms about each unstarred atom must vanish, and vice versa.[4b] Whatever method is used to obtain the NBMO's of **1** and **2**, they differ in that the NBMO's of **1** can be confined to different carbon atoms, while those of **2** cannot. This difference is of paramount significance when the effects of electron repulsion in the open shell π systems of **1** and of **2** are considered.

Effects of Electron Repulsion in 1, 2, and Related Diradicals. In cyclobutadiene (**1**), if the two open shell electrons occupy different NBMO's, because the MO's can be confined to different sets of atoms, these two electrons need never appear in the same AO. Consequently, in the wave function for the lowest singlet state of **1** there are no high energy ionic terms corresponding to the simultaneous occupancy of the same AO by these two electrons. In fact, when differential overlap is ignored, this state and the lowest triplet are accidentally degenerate.[9] When differential overlap is not ignored, the triplet lies slightly below the singlet; but the important effect in correctly resolving the accidental degeneracy of these two states is the correlation between the electrons in the NBMO's and the two electrons that occupy the lowest π MO. When, through CI, this effect is properly included, the singlet is found to lie below the triplet, even at a square molecular geometry.[10]

In contrast, in trimethylenemethane (**2**), because the Hückel NBMO's cannot be confined to separate sets of atoms, the triplet lies below the lowest singlet, since in the former state the Pauli principle keeps the two unpaired electrons from simultaneously appearing in the same AO.[11] In fact, singlet wave functions constructed from the Hückel MO's for **2** contain ionic terms of sufficiently high energy that the SCF wave function for this state utilizes a different set of MO's, sacrificing some of the bonding (in the Hückel sense) of the triplet, in order to reduce the Coulombic repulsion between the open shell electrons.[11] Indeed, the optimum MO's for the planar singlet are essentially those for the noninteracting fragments, allyl (**3**) plus p (**4**).[12,13]

The PMO analysis that allows the deduction of the forms of the NBMO's in **1** and **2** can easily be extended to other conjugated diradicals whose π systems can be dissected into those of an odd AH interacting with a carbon atom bearing a p-π orbital.[8] Again, two types of diradical π systems can result from union between these fragments. If the union occurs at two carbons with opposite signs in the NBMO of the odd AH, [4*n*]annulenes or alkenyl derivatives thereof are obtained.[14] Like cyclobutadiene, these molecules have NBMO's that are confined to different sets of carbon atoms. Consequently, these molecules are, like **1**, expected to use the same set of MO's for both the lowest singlet and triplet state, and, before CI is included, these states are anticipated to be degenerate when differential overlap is neglected. On the other hand, if the union occurs at a nodal (inactive)[4a] carbon atom in the NBMO of the odd AH, alkenylogs of trimethylenemethane are obtained. Like **2**, their NBMO's have atoms in common, and molecules with this type of π system are expected to have the triplet below the lowest singlet in energy and to use different optimal sets of MO's for these states.

The two different types of union between pentadienyl and a carbon atom, which lead, respectively, to **5** and **6**, are shown in Figure 2 as concrete illustrations of these general considerations. The NBMO's of these molecules are also shown. Since the NBMO's in each molecule are degenerate at the Hückel level, any set of orthonormal linear combinations is also an acceptable set of NBMO's. However, one set may lead to a more facile analysis of the effects of electron repulsion than another. For instance, in Figure 2 the set of NBMO's chosen for **5** shows that they can be localized on two different groups of atoms. In **6**, however, no such set of Hückel NBMO's can be found. The pair shown in Figure 2 for **6** was chosen because it suggests the localization of the half-filled MO's in the lowest singlet state of **6** into those of two allyl radicals. This localization should be favored over that into pentadienyl plus p, since the Hückel energy of two allyl radicals is $6\alpha + 5.656\beta$ vs. $6\alpha + 5.464\beta$ for pentadienyl plus p.[15]

Indeed, the π systems of both **5** and **6** can be dissected into two allyl radicals, as also shown in Figure 2. The analysis for the effects of their union is essentially the same as that for the union of **3** and **4** to give the π systems of **1** and **2**. The only difference is that the lowest and highest π MO's of **3** now interact with not just the one π orbital of **4** but with all three π MO's of the second allyl radical. This mode of analysis also leads to the conclusion that the π system of **5** belongs to the same class as that of **1**, while the π system of **6** is of the same type as that of **2**.

1,3-Dimethylenecyclobutadiene (7). The π system of 1,3-dimethylenecyclobutadiene (**7**) can also be analyzed in terms of union of either pentadienyl plus p or two allyl radicals. The π system of **7** differs from that of **5** and **6**, however, in that union in either mode of dissection occurs at *two* nodal (inactive) carbon atoms, as shown in Figure 3. Generalization of the previous discussion of the consequences of union at one inactive

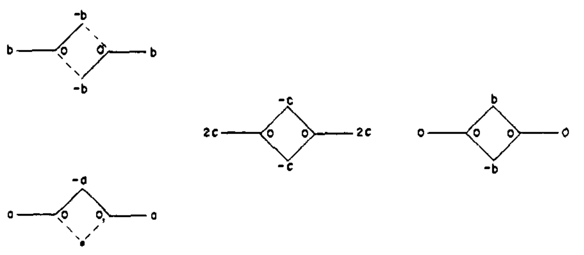


Figure 3. PMO analyses and NBMO's of 1,3-dimethylenecyclobutadiene (7). The normalized coefficients in the MO's are: $a = 3^{-1/2}$, $b = 2^{-1/2}$, and $c = 10^{-1/2}$.

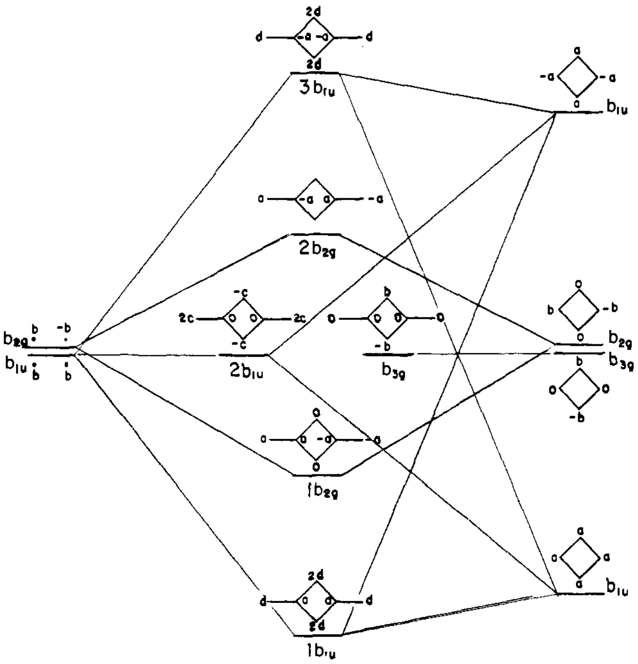


Figure 4. Orbital interaction diagram for the PMO analysis of 1,3-dimethylenecyclobutadiene (7) in terms of the union of cyclobutadiene with two carbons, each bearing a p-π orbital. The normalized coefficients in the MO's are: $a = \frac{1}{2}$, $b = 2^{-1/2}$, $c = 10^{-1/2}$, and $d = 20^{-1/2}$.

carbon, rather than at two active carbons with equal and opposite coefficients in the NBMO, suggests that the NBMO's of **7**, like those of **2** and **6**, have atoms in common. The Hückel NBMO's of **7**, shown in Figure 3, are in accord with this expectation. Therefore, it can be predicted that **7** has a triplet ground state and that the optimum set of MO's for the lowest singlet will differ from those of the triplet.[16]

There are, however, several features of **7** that make it of interest for more detailed theoretical study. The NBMO's of **7** indicate that in the lowest singlet state orbital localization will occur, not as suggested by the dissection into pentadienyl plus p or into two allyl radicals, but as implied by the name of the molecule. Figure 4 shows the π orbital interaction diagram for the union of two methylene groups at C-1 and C-3 of cyclobutadiene (**1**). The in-phase combination of the two methylene p orbitals has b_{1u} symmetry in D_{2h}, the group to which **7** belongs. Consequently, it mixed with both ψ_1 and ψ_4 of **1**, which have the same symmetry. The pairing theorem again guarantees that an NBMO results from the mixing[6] and that the contribution of the cyclobutadiene ring to this NBMO occurs exclusively at C-2 and C-4.[8] The out-of-phase combination of methylene p orbitals has b_{2g} symmetry and can mix with the NBMO of **1**, ψ_3, that also belongs to this representation of D_{2h}. The mixing produces two MO's, which can be described respectively as the out-of-phase combination of two bonding and two antibonding ethylenic π MO's. The remaining NBMO of **1**, ψ_1, is of b_{3g} symmetry and consequently remains unchanged in **7**.

The three-orbital mixing in the b_{1u} manifold, anticipated at the level of Hückel theory, is, with the inclusion of electron repulsion, also expected to occur in the lowest triplet state of **7**. However, in the lowest singlet, in order to keep the electron in the b_{1u} NBMO ($2b_{1u}$) away from the electron of opposite spin in b_{3g}, the mixing should, to a large extent, be "turned off" by the Coulombic repulsion between these two electrons. The MO's of b_{2g} symmetry, in contrast, should remain essentially the same in both states.

In order to test these predictions, we have carried out SCF calculations on **7**, using an STO-3G basis set.[17] An arbitrary geometry[18] for **7** was assumed with all C-C bond lengths 1.41 Å, 1.09 Å C-H bond lengths, 90° internal and 135° external angles for the ring, and 120° bond angles in the methylene groups. The spin-restricted open shell SCF method of Davidson[19] was used to calculate the MO's and energies of the lowest triplet and singlet of the same (B_{2u}) symmetry in **7**. The results are shown in Table I. The triplet is calculated to lie 41.3 kcal/mol below the singlet at this geometry.[18]

The π MO's of the triplet are close to those expected from simple Hückel theory, except in the b_{1u} manifold. The NBMO of this symmetry ($2b_{1u}$) in the triplet has coefficients at C-2 and C-4 that are larger in relative magnitude than those in the Hückel NBMO, and a corresponding reduction in these coefficients occurs in $1b_{1u}$. These changes are favorable in the triplet because the other NBMO (b_{3g}) spans C-2 and C-4. In the triplet the electrons in $2b_{1u}$ and b_{3g} have the same spin; therefore, they never appear simultaneously in the same AO. Thus, an increase in the magnitude of the coefficients at C-2 and C-4 in $2b_{1u}$ causes little increase in Coulomb repulsion energy. The change in these coefficients in $2b_{1u}$ does, however, make possible the corresponding reduction in $1b_{1u}$. The reduction in the coefficients at C-2 and C-4 in $1b_{1u}$ decreases electron repulsion in the triplet, because this MO contains an electron with spin opposite to the one in b_{3g}.

Table I also reveals the expected localization of the MO's of b_{1u} symmetry in the open shell singlet. The lowest b_{1u} MO in the singlet is essentially ψ_1 of cyclobutadiene, and roughly 95% of the electron density in $2b_{1u}$ is localized on the two methylene carbons. However, also as expected, the bonding b_{2g} MO remains virtually unchanged in going from the triplet to the singlet. Therefore, unlike the case in trimethylenemethane (**2**),[12,13] rotation about the bond to either methylene group, although more difficult in the triplet state, remains energetically costly in the singlet.

At the ab initio level the two "nonbonding" MO's no longer have the same energy. Since they are not degenerate by symmetry,[20] there is no reason why they should be so in energy. The degeneracy at the level of simple Hückel theory is a result of its neglect of nonnearest neighbor interactions and, probably even more important, electron repulsion. SCF calculations place $|\ldots(1b_{1u})^2(1b_{2g})^2(2b_{1u})^2\rangle$ 40.3 kcal/mol below $|\ldots(1b_{1u}')^2(1b_{2g}')^2(b_{3g})^2\rangle$, where the primed and unprimed MO's differ because of the different orbital occupancy for the two highest energy π electrons.

Although it is therefore possible that a closed shell (^1A_g) might be lower than the open shell ($^1B_{2u}$) singlet state, the lowest of these two ^1A_g wave functions still lies 30.9 kcal/mol above $^1B_{2u}$. Nevertheless, since the $2b_{1u}$ and b_{3g} MO's are degenerate at the Hückel level, it is to be expected (vide infra) that, in order to satisfactorily describe the lowest closed shell singlet, a two-configuration wave function of the form

$$\Psi = c_1|\ldots(1b_{1u})^2(1b_{2g})^2(2b_{1u})^2\rangle - c_2|\ldots(1b_{1u})^2(1b_{2g})^2(b_{3g})^2\rangle \quad (1)$$

will be necessary, in which the ratio of c_1/c_2, as well as the

Table I. Coefficients at Each Carbon Atom in the Occupied π MO's of $^3B_{2u}$ ($^1B_{2u}$) 1,3-Dimethylenecyclobutadiene[a]

MO	C-1	C-2	C-3	C-4	C-5	C-6
$1b_{1u}$[b]	0.413	0.303	0.423	0.303	0.258	0.258
	(0.404)	(0.407)	(0.404)	(0.407)	(0.052)	(0.052)
$1b_{2g}$[b]	0.454		−0.454		0.468	−0.468
	(0.451)		(−0.451)		(0.472)	(−0.472)
$2b_{1u}$[c]	0.043	−0.445	0.043	−0.445	0.556	0.556
	(0.001)	(−0.171)	(0.001)	(−0.171)	(0.690)	(0.690)
b_{3g}[c]		0.731		−0.731		
		(0.731)		(−0.731)		

[a] SCF energies: $^3B_{2u} = -227.6964$ hartrees ($^1B_{2u} = -227.6361$ hartrees). [b] Doubly occupied MO. [c] Singly occupied MO.

MO's, are optimized. Such wave functions can be obtained by multiconfigurational (MC) SCF calculations. However, recent experience with calculations on methylene, using this type of wave function for the lowest singlet, suggests that it may tend to give an artificially low, closed shell singlet energy, when compared with open shell singlet and triplet wave functions, obtained by single configuration SCF calculations.[21] Therefore, we compared the energies of ^1A_g, $^1B_{2u}$, and $^3B_{2u}$ by using the MO's of the triplet to carry out full π space CI calculations for all three states.[22] This approach, moreover, has the virtue of including the energy differences that arise from correlation of all the π electrons. Differences between states in the correlation of open and closed shell electrons can have important effects on the relative energies of the states in open shell π systems.[10,23]

The full π space CI calculations on **7** show the triplet to be ground state ($E = -227.8140$ hartrees) with the open shell $^1B_{2u}$ state now 29.9 kcal/mol above it and ^1A_g another 9.3 kcal/mol higher still in energy. As is the case in trimethylenemethane,[12b,c] the CI expansions for both singlet states of **7** contain sizable contributions from configurations involving one-electron excitations of the type interdicted by Brillouins' theorem[24] for SCF-MO's. This fact shows that the MO's of the triplet, which were used in the CI, are not the SCF-MO's for either singlet. Thus, both the ab initio SCF and CI results fully confirm the qualitative expectations, based on inspection of the Hückel NBMO's for **7**.[37]

Tetramethylenethane (8). Like 1,3-dimethylenecyclobutadiene (**7**), no classical Kekulé structures can be written for tetramethylenethane (**8**),[25] and **8** too can be dissected into two allyl radicals, as shown in Figure 5. Unlike **7**, however, the union in **8** takes place between the inactive carbon of each allyl radical, rather than between an inactive carbon of one and an active carbon of the other. Consequently, at the level of simple Hückel theory, the NMBO's of the two allylic fragments do not mix with each other nor with any of the other MO's. Thus, the Hückel NBMO's of **8** can be taken as those of the isolated fragments. Since these NBMO's are clearly confined to separate sets of atoms, **8**, like **1**, is anticipated to have a singlet state that, at the SCF level, is approximately degenerate with the triplet, and these states are expected to use a common set of MO's.

It must be noted, however, that these localized NBMO's are not eigenfunctions of the symmetry operators in the D_{2h} point group to which planar **8** belongs. Linear combinations of the localized NBMO's must be taken to obtain MO's that transform as irreducible representations of D_{2h}. In the planar molecule the in-phase combination of localized NBMO's lies slightly below the out-of-phase,[27] due to nonnearest neighbor π interactions between the allylic fragments, which simple Hückel theory ignores. The question then arises, which set of NBMO's should be used in classifying **8**, the localized set that confines the nonbonding electrons to different sets of atoms, or the delocalized set, which has the correct symmetry properties?

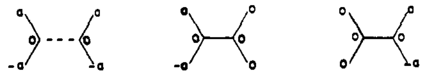


Figure 5. PMO analysis of tetramethylenethane (**8**), in terms of the union of two allyl radicals, and NBMO's of **8**. Normalization requires $a = 2^{-1/2}$.

A similar type of question can be raised in cyclobutadiene (**1**). Consider the MO's for rectangularly distorted **1** as it approaches a square geometry. At a rectangular geometry, where r_{12} and r_{34} are the short bond lengths, the MO

$$\psi_2 = (\phi_1 + \phi_2 - \phi_3 - \phi_4)/2 \tag{2}$$

lies below

$$\psi_3 = (\phi_1 - \phi_2 - \phi_3 + \phi_4)/2 \tag{3}$$

As a square geometry is approached, the use of a CI wave function of the form

$$\Psi = c_1|\ldots\psi_2^2\rangle - c_2|\ldots\psi_3^2\rangle \tag{4}$$

becomes increasingly important for the singlet. The physical reason for this fact is that, as a square geometry is approached, little π bonding is gained by placing both electrons in ψ_2, and having both electrons in the same MO results in substantial Coulombic repulsion between them. The effect of the second term in the wave function on decreasing the Coulombic repulsion energy can easily be appreciated by looking at the limit of a square geometry, where, by symmetry, $c_1 = c_2$. The wave function, Ψ, can then be rewritten as

$$\begin{aligned}\Psi = (|\ldots\psi_2^2\rangle - |\ldots\psi_3^2\rangle)/2^{1/2} = (|\ldots(\psi_2 \\ + \psi_3)^\alpha(\psi_2 - \psi_3)^\beta\rangle + |\ldots(\psi_2 - \psi_3)^\alpha(\psi_2 \\ + \psi_3)^\beta\rangle)/2(2^{1/2}) = (|\ldots\psi_{2'}^\alpha\psi_{3'}^\beta\rangle \\ + |\ldots\psi_{3'}^\alpha\psi_{2'}^\beta\rangle)/2^{1/2}\end{aligned} \tag{5}$$

where

$$\psi_{2'} = (\phi_1 - \phi_3)/2^{1/2} \tag{6}$$

$$\psi_{3'} = (\phi_2 - \phi_4)/2^{1/2} \tag{7}$$

Thus, CI increasingly restricts these two electrons in the lowest singlet to different sets of atoms, until at a square geometry their confinement is complete. Although both the primed and unprimed MO's are, from the point of view of symmetry, equally valid choices for square cyclobutadiene,[29] in terms of giving the most readily interpretable wave function for the singlet, the primed set of MO's is certainly the better of the two. Indeed, if the unprimed set of MO's were chosen for the classification of the π system of **1**, one might erroneously conclude that, since these NBMO's span common sets of atoms, the π system of **1** belongs to the same class as that of **2**.

This illustrates a potential pitfall in using the Hückel NBMO's of a diradical to classify it, rather than dissecting it into two odd AH fragments and determining their mode of union. If the Hückel NBMO's have atoms in common, one must take care to form orthonormal linear combinations of them in order to see if the resulting MO's can be confined to different sets of atoms. Linear combinations of the unprimed NBMO's of **1** in eq 2 and 3 can be so localized, since their sum and difference yields the primed set of NBMO's in eq 6 and 7. In contrast, in molecules like **2**, **6**, and **7** no orthogonal linear combinations of the Hückel NBMO's can be found that are confined to different sets of atoms. Since localization is clearly possible for the Hückel NBMO's in **8**, this diradical belongs to the same class as **1**, rather than to the class containing **2**, despite assertions to the contrary in the literature.[26]

As noted above, only at geometries of **1** where the C–C bonds all have the same length do c_1 and c_2 in eq 4 have exactly the same magnitude; consequently, only at such geometries can it be accurately said that in the lowest singlet state one electron is localized in $\psi_{2'}$ and the other in $\psi_{3'}$.[29,30] Of course, at nonsquare geometries there is no MO degeneracy, and **1** is not truly a diradical. Similarly, in **8** only at some nonplanar geometry do the symmetry combinations

$$\psi_S = (\psi_2 + \psi_{2'})/2^{1/2} \tag{8}$$

$$\psi_A = (\psi_2 - \psi_{2'})/2^{1/2} \tag{9}$$

of the localized allyl NBMO's, ψ_2 and $\psi_{2'}$, have the exact same energy.[27] Consequently, only at this geometry do the coefficients, c_1 and c_2, in the normalized two-configuration wave function for the lowest singlet state of **8**

$$\Psi = c_1|\ldots\psi_S{}^2\rangle - c_2|\ldots\psi_A{}^2\rangle \tag{10}$$

have the same magnitude, so that the nonbonding electrons each occupy one of the localized allyl NBMO's. In eq 10 the wave function for the electrons in ψ_S and ψ_A may be rewritten in terms of the localized NBMO's as

$$\begin{aligned} c_1|\psi_S{}^2\rangle - c_2|\psi_A{}^2\rangle &= (c_1|(\psi_2 + \psi_{2'})^2\rangle - c_2|(\psi_2 \\ &\quad - \psi_{2'})^2\rangle)/2 = [(c_1 - c_2)(|\psi_2{}^2\rangle + |\psi_{2'}{}^2\rangle) \\ &\quad + (c_1 + c_2)(|\psi_2{}^\alpha\psi_{2'}{}^\beta\rangle + |\psi_{2'}{}^\alpha\psi_2{}^\beta\rangle)]/2 \end{aligned} \tag{11}$$

The relative magnitudes of $c_1 - c_2$ and $c_1 + c_2$ are thus indicative of the extent to which in planar **8** these electrons each occupy a separate, localized, allyl NBMO and also of the extent to which planar **8** may, strictly speaking, be called a diradical.

Since the nonnearest neighbor π interactions in planar **8** that cause ψ_S to lie below ψ_A are relatively small, it seemed reasonable to expect the magnitude of $c_1 + c_2$ to be much greater than that of $c_1 - c_2$. To confirm this expectation, we carried out ab initio calculations on planar **8**, using the same bond length as in **7** for the C–C bonds within each allylic fragment, 1.50 Å for the bond joining the fragments, and assuming 120° bond angles about each carbon. The values of $c_1 + c_2$ and $c_1 - c_2$ can be obtained from the coefficients in the CI expansion for the lowest singlet state of **8**, using either the localized allyl or delocalized symmetry NBMO's to form the CI matrix. We carried out calculations using both sets of NBMO's.

The delocalized symmetry NBMO's were obtained from an SCF calculation on the triplet state of **8**, despite the fact that the MO's were required to have, rather than D_{2h}, only C_{2v} symmetry with the C_2 axis along the unique C–C bond. All the π MO's are listed in Table II, labeled by the representation of C_{2v} to which each belongs. Note that $1b_1$ and $2b_1$ are not just the in- and out-of-phase combinations of the π bonding MO's of each allylic fragment, because of the mixing between the bonding MO of one fragment and the antibonding MO of the other. The normalization coefficients of ψ_S and ψ_A differ because of the net difference between them of 0.019 in nonnearest neighbor π overlap integrals. The greater positive overlap of this type in ψ_S ($1a_2$) is responsible for its orbital energy being computed as 6.8 kcal/mol below that of ψ_A ($2a_2$).

Also shown in Table II are the localized allyl NBMO's. They were obtained from an SCF calculation on the lowest singlet, in which two electrons were constrained to occupy orthogonal a_2 MO's.[31] This singlet is calculated to have the same SCF energy as the triplet to within 0.01 kcal/mol. As expected, the doubly occupied MO's ($1b_1$ and $2b_1$) found by the SCF calculation on the singlet are identical with those that emerged from the calculation on the triplet. The very small amount of delocalization in the NBMO's of the singlet is a consequence of the orthogonality requirement, since the totally localized allyl NBMO's in planar **8** are not orthogonal to each other, because of the nonzero π overlap between them.

Full π space CI calculations were carried out for the singlet and the triplet, using both the localized and delocalized NBMO's to form the CI matrices. Diagonalization of the matrices formed from either set of MO's gives the same energy. At the CI level the singlet ($E = -228.9794$ hartrees) is calculated to lie below the triplet by 5.3 kcal/mol. Previous semiempirical π electron calculations on planar **8**, including extensive (but not complete) π space CI, have also shown that these two states are close in energy but found the triplet to lie lowest.[28]

Although the lower energy of the singlet at the CI level can in part be attributed to the possibility of the double occupancy of ψ_S in this state, greater nonnearest neighbor bonding in the singlet cannot be totally responsible for its lower energy. Given the difference of only 6.8 kcal/mol in the orbital energies of ψ_S and ψ_A, the occupation number of ψ_S would have to be nearly two and that of ψ_A zero, if this effect were to account for the singlet–triplet energy difference. This would require c_1 in eq 10 to approach 1 and c_2 to approach zero, which would give a ratio of $c_1 + c_2$ to $c_1 - c_2$ of 1. Our CI results indicate that this is not at all what obtains, for both sets of CI calculations on the singlet give $c_1 + c_2 = 1.238$ and $c_1 - c_2 = 0.066$. The ratio of covalent to ionic terms of nearly 20 to 1 in the wave

Table II. Coefficients at Each Atom in the π MO's of Triplet (Singlet)[a] Tetramethylenethane[b]

MO	C-1	C-2	C-3	C-4	C·5	C-6
$1b_1$[c]	0.242	0.470	0.242	0.242	0.470	0.242
$2b_1$[c]	0.366	0.399	0.366	−0.366	−0.399	−0.366
$3b_1$[d]	0.454	−0.474	0.454	0.454	−0.474	0.454
$4b_1$[d]	0.369	−0.741	0.369	−0.369	0.741	−0.369
$1a_2$[e]	0.504		−0.504	0.504		−0.504
	(0.716)		(−0.716)	(−0.004)		(0.004)
$2a_2$[e]	0.509		−0.509	−0.509		0.509
	(0.004)		(−0.004)	(−0.716)		(0.716)

[a] The singlet and triplet SCF calculations lead to the same set of b_1 MO's. [b] SCF energy for both states = −228.8389 hartrees. [c] Doubly occupied MO. [d] Unoccupied MO. [e] Singly occupied MO.

function for the two electrons in the highest occupied MO's reflects the near degeneracy of ψ_S and ψ_A and justifies the appellation of diradical for planar **8**. In addition, this ratio suggests that nonnearest neighbor bonding, resulting from double occupancy of ψ_S in the singlet, can play only a minor role in causing its energy to be lower than that of the triplet. Indeed, when $c_1 - c_2$ is set equal to zero by omitting $|\ldots\psi_2{}^2\rangle$ and $|\ldots\psi_{2'}{}^2\rangle$ from the CI expansion for the singlet, the energy of this state is computed to be only 0.4 kcal/mol higher than when these configurations are included.

Another contributor to the lower energy calculated for the singlet at the CI level is an effect invoked several years ago by Dewar[32] in an ingenious attempt to explain why triplet trimethylenemethane (**2**) prefers a planar geometry but the corresponding singlet does not. Dewar argued that if one considers **2** as resulting from union of an allyl radical with a carbon bearing a p-π orbital, then the p-π orbital on the central carbon of the allyl radical contains some spin density of the opposite sign from that possessed by the unpaired electron in its NBMO. In triplet **2** the electron in the p orbital on the lone carbon also has spin opposite to that induced at the central carbon, so π bonding between these two carbons can occur. In contrast, in the singlet the spins in the p-π orbitals at these two carbons are the same, so π bonding between them cannot occur. However, since negative spin density only appears in MO calculations at the CI level, the effect invoked by Dewar does not explain his own SCF results.[32,33] Nevertheless, the effect described by him does exist in **2** *at the CI level.*[12b,c]

The same argument, applied to planar **8**, predicts greater π bonding between the central carbon atoms of the allylic fragments in the singlet than in the triplet. In fact, the π bond order between these carbons, calculated from the CI wave function for each state, is greater in the singlet (0.179) than in the triplet (0.135).[34] Configuration interaction of the type that correlates the two electrons in the NBMO's with those in the bonding π MO's thus does appear to play a crucial role in making the singlet the calculated ground state of planar **8**. This is another feature that **8** shares with cyclobutadiene,[10] in addition to a degenerate (or nearly degenerate) lowest singlet and triplet state at the SCF level and a common set of MO's[29] for both states.

Starred and Unstarred Atoms. Diradicals **1** and **8** have still another property in common. They are both AH's[4,5] with equal numbers of starred and unstarred atoms. This is another feature that sets them apart from **2** and **7**, which are also AH's, but in which the starred outnumber the unstarred atoms by two. As shown in Figure 6, molecules **5** and **6** are similarly differentiated. The fact that molecules belonging to the cyclobutadiene (**1**) class have the same number of starred and unstarred atoms, while molecules of the trimethylenemethane (**2**) type do not, is no accident. Rather, as shown in the Appendix, it is a necessary consequence of the fact that the Hückel NBMO's of the former class can be chosen to have no atoms in common, whereas those of the latter cannot. When the number of starred and unstarred atoms in a diradical is equal, one NBMO can be confined to the former set and the other to the latter set of atoms. However, when the starred outnumber the unstarred atoms by two, the Hückel MO's are both confined to atoms of the starred set.

Nevertheless, even if the Hückel NBMO's of a diradical both span the starred set of atoms, there still exists the possibility that they can be localized to different atoms of this set. This will occur when a diradical can be analyzed as resulting from union of two odd AH's at an inactive carbon of each, provided that in one and only one of the odd AH fragments the inactive carbon belongs to the same (starred) set as the active carbons of the NBMO. An example of such a molecule is 1,1,2,3,3-pentamethylenepropane (**9**). Note that in this diradical the starred outnumber the unstarred atoms by two; nevertheless, the NBMO's can be taken as those of two isolated allyl radicals.

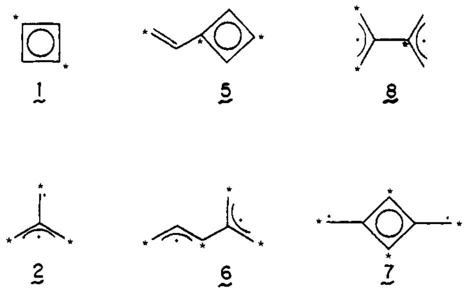
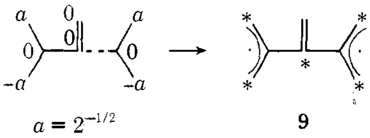


Figure 6. Starred and unstarred atoms in **1**, **2**, **5**, **6**, **7**, and **8**.



$a = 2^{-1/2}$

9

Conclusions

Although just counting the number of starred and unstarred atoms in an AH diradical does not provide an infallible method for determining whether its Hückel NBMO's necessarily have atoms in common, the zero sum rule for NBMO's in AH's can always be used to find the NBMO's directly. Alternatively, the molecule may be divided into two odd AH fragments and the mode of their union analyzed to see whether it involves (a) two active atoms (with equal and opposite coefficients in the NBMO) of one fragment with an active carbon of the other, as in **1**; (b) an active carbon of one fragment with an inactive of the other, as in **2**; or (c) two inactive carbons, as in **8** and **9**. No matter which method is chosen to ascertain whether the Hückel NBMO's necessarily span common atoms, it is clear that such a classification is of the utmost utility in determining the electronic properties of diradicals. It should be noted, however, that such a classification may not lead to the correct prediction of the ground state of *every* diradical.[35] For instance, the effects of CI[23] and/or geometrical distortions[9] can cause a singlet to become the ground state of large molecules with a half-filled pair of MO's that are degenerate at the most symmetrical molecular geometry, even if these MO's have atoms in common. Nevertheless, by determining whether the Hückel NBMO's necessarily span common atoms, it is always possible to deduce whether the triplet and corresponding open shell singlet state of a diradical use the same set of orbitals. This determination can be crucial to the correct understanding of the differences in the chemical behavior of these states.[12,13]

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Appendix

The localizability of the NBMO's of diradicals onto disjoint sets of atoms may be investigated by using some properties of the nonzero parts of the adjacency matrices for the starred and unstarred atoms in AH's. This approach draws on recent work by Hall.[36]

Suppose the atoms in an AH are starred so that, as is customarily the case, the number of starred atoms, n, is greater than the number of unstarred atoms, m. The Hückel equation for an AH can be cast in the form

$$\left(\begin{array}{c|c} 0 & \mathbf{A}_{\mathrm{su}} \\ \hline \mathbf{A}_{\mathrm{us}} & 0 \end{array}\right) \left(\begin{array}{c} c_{\mathrm{s}i} \\ \hline c_{\mathrm{u}i} \end{array}\right) = \left(\begin{array}{c} c_{\mathrm{s}i} \\ \hline c_{\mathrm{u}i} \end{array}\right) \epsilon_i \qquad (12)$$

Here $\mathbf{A}_{\mathrm{su}}$ is the nonzero part of the adjacency matrix for the starred atoms, in which 1 is entered in a row, corresponding to a starred atom, and column, corresponding to an unstarred atom, if the atoms are nearest neighbors. Otherwise, zero is entered, which is why two blocks of the full adjacency matrix in eq 12 are zero, since in an AH each starred atom has only unstarred atoms as its nearest neighbors and vice versa. $\mathbf{A}_{\mathrm{us}}$ is the nonzero part of the adjacency matrix for the unstarred atoms, which is just the transpose of $\mathbf{A}_{\mathrm{su}}$; $c_{\mathrm{s}i}$ and $c_{\mathrm{u}i}$ are respectively the coefficients of the starred and unstarred atoms in the ith MO; and ϵ_i is the orbital energy, relative to α, in units of β. Equation 12 can be divided into two separate matrix equations

$$(\mathbf{A}_{\mathrm{su}})(c_{\mathrm{u}i}) = (c_{\mathrm{s}i})\epsilon_i \qquad i = 1 \ldots n \qquad (13)$$

$$(\mathbf{A}_{\mathrm{us}})(c_{\mathrm{s}i}) = (c_{\mathrm{u}i})\epsilon_i \qquad i = 1 \ldots m \qquad (14)$$

Multiplication of the first of these equations by $(\mathbf{A}_{\mathrm{us}})$ and substitution from the second into the right-hand side of the resulting equation gives

$$(\mathbf{A}_{\mathrm{us}})(\mathbf{A}_{\mathrm{su}})(c_{\mathrm{u}i}) = (c_{\mathrm{u}i})\epsilon_i^2 \qquad i = 1 \ldots m \qquad (15)$$

Similarly

$$(\mathbf{A}_{\mathrm{su}})(\mathbf{A}_{\mathrm{us}})(c_{\mathrm{s}i}) = (c_{\mathrm{s}i})\epsilon_i^2 \qquad i = 1 \ldots n \qquad (16)$$

The rank, r, of any matrix $(\mathbf{A})$ is the number of linearly independent rows (or columns) of $(\mathbf{A})$ and is also equal to the number of nonzero eigenvalues of $(\mathbf{A})(\mathbf{A}^{\mathrm{T}})$ and $(\mathbf{A}^{\mathrm{T}})(\mathbf{A})$, where $(\mathbf{A}^{\mathrm{T}})$ is the transpose of $(\mathbf{A})$. Moreover, the nonzero eigenvalues of $(\mathbf{A})(\mathbf{A}^{\mathrm{T}})$ and $(\mathbf{A}^{\mathrm{T}})(\mathbf{A})$ are identical. Therefore, for each distinct nonzero eigenvalue, ϵ_i^2, of $(\mathbf{A}_{\mathrm{us}})(\mathbf{A}_{\mathrm{su}})$ with associated eigenvector $(c_{\mathrm{u}i})$, there is an identical eigenvalue of $(\mathbf{A}_{\mathrm{su}})(\mathbf{A}_{\mathrm{us}})$ with associated eigenvector $(c_{\mathrm{s}i})$. This suffices to show that the eigenvalues of (12) are $\pm\epsilon_i$, with associated eigenvectors

$$\begin{pmatrix} c_{\mathrm{s}i} \\ c_{\mathrm{u}i} \end{pmatrix} \text{ and } \begin{pmatrix} c_{\mathrm{s}i} \\ -c_{\mathrm{u}i} \end{pmatrix}$$

and thus constitutes an alternate proof of the pairing theorem.[4,5]

In addition to the r nonzero eigenvalues of $(\mathbf{A}_{\mathrm{us}})(\mathbf{A}_{\mathrm{su}})$, there are $m - r$ with $\epsilon_i = 0$, whose eigenvectors can be seen, from eq 15, to span only the unstarred atoms. Similarly, there are $n - r$ eigenvalues of $(\mathbf{A}_{\mathrm{su}})(\mathbf{A}_{\mathrm{us}})$ with $\epsilon_i = 0$, whose eigenvectors span only the starred atoms. If $m - r = n - r = 1$, then there are two NBMO's one of which is localized on the unstarred atoms, while the other is confined to the starred atoms. As pointed out in the text, the NBMO's are so localized in cyclobutadiene (**1**). In this molecule $m = n = 2$ and

$$(\mathbf{A}_{\mathrm{su}}) = \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix} \qquad (17)$$

so $r = 1$. Thus, $m - r = n - r = 1$, as expected. Similarly, in tetramethylenethane (**8**) $m = n = 3$ and

$$(\mathbf{A}_{\mathrm{su}}) = \begin{pmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 1 & 1 \end{pmatrix} \qquad (18)$$

so $r = 2$. Thus, again, $m - r = n - r = 1$, and the existence of two NBMO's, confined to different sets of atoms, is predicted.

In diradicals where the NBMO's are both confined to atoms of the starred set, it is still possible that the NBMO's can be localized to different atoms within this set. To see if this is the case, it is useful to look at $(\mathbf{A}_{\mathrm{us}})$, the matrix whose elements multiply the unknown coefficients of the starred atoms in eq 14. A sufficient condition for localizability of the NBMO's to disjoint groups of atoms is the existence of two pairs of columns in $(\mathbf{A}_{\mathrm{us}})$ that are disjoint. For example, in trimethylenemethane (**2**), where $m = 1$ and $n = 3$,

$$(\mathbf{A}_{\mathrm{us}}) = \begin{pmatrix} 1 & 1 & 1 \end{pmatrix} \qquad (19)$$

so $r = 1$, $m - r = 0$, and $n - r = 2$. Thus, there are two NBMO's in **2**, both confined to the starred set of atoms. The NBMO's of **2** cannot be localized onto different atoms of this set, since the columns of $(\mathbf{A}_{\mathrm{us}})$ in eq 19 cannot be partitioned into two pairs that are disjoint. The same is true of the columns of $(\mathbf{A}_{\mathrm{us}})$ for 1,3-dimethylenecyclobutadiene (**7**), where again $m - r = 0$, $n - r = 2$, and

$$(\mathbf{A}_{\mathrm{us}}) = \begin{pmatrix} 1 & 1 & 1 & 0 \\ 0 & 1 & 1 & 1 \end{pmatrix} \qquad (20)$$

However, for 1,1,2,3,3-pentamethylenepropane (**9**)

$$(\mathbf{A}_{\mathrm{us}}) = \begin{pmatrix} 1 & 1 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 1 & 1 \end{pmatrix}$$

and the columns can be partitioned into pairs (1,2 and 4,5) that are disjoint. Consequently, despite the fact that $m - r = 0$ and $n - r = 2$, the NBMO's of this molecule can be chosen so that they have no common atoms.

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(1) Review: G. Maier, *Angew. Chem., Int. Ed. Engl.*, **13**, 425 (1974).

(2) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

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(4) (a) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969, pp 191–247; (b) W. T. Borden, "Modern Molecular Orbital Theory for Organic Chemists", Prentice-Hall, Englewood Cliffs, N.J., 1975, pp 78–104.

(5) C. A. Coulson and G. S. Rushbrooke, *Proc. Cambridge Philos. Soc.*, **36**, 193 (1940).

(6) Although it is not difficult to show that $\epsilon = \alpha$ is a root of the secular equation for this type of three-orbital interaction, a general proof, using second-order perturbation theory, is perhaps more instructive. Let $\psi_i = \Sigma_{\mathrm{s}} c_{i\mathrm{s}}\phi_{\mathrm{s}} + \Sigma_{\mathrm{u}} c_{i\mathrm{u}}\phi_{\mathrm{u}}$ be a bonding MO of any AH with energy $\epsilon_i = \alpha + n_i\beta$, where s spans the starred set of atoms and u the unstarred. Then the pairing theorem for AH's[5] guarantees the existence of an antibonding MO of the form $\psi_j = \Sigma_{\mathrm{s}} c_{i\mathrm{s}}\phi_{\mathrm{s}} - \Sigma_{\mathrm{u}} c_{i\mathrm{u}}\phi_{\mathrm{u}}$ with $\epsilon_j = \alpha - n_i\beta$. Let us suppose that the AH is odd and that the starred set of atoms is the more plentiful. Then the NBMO of the odd AH will be confined to the starred set of atoms.[4] Therefore, the union between the odd AH and a carbon bearing a p orbital ($\epsilon = \alpha$) will result in no interaction between the NBMO's of the two fragments if the union occurs either at two starred atoms, *k and l*, with equal coefficients of opposite sign in the NBMO of the AH, and/or at one or more unstarred (inactive) atoms, say m and n. In second-order perturbation theory the interaction of the p orbital with all the other MO's of the odd AH on union at k and l results in a change in its energy that is given by the expression

$$\Delta\epsilon = \sum_i \frac{1c_{ik} + c_{il})^2\beta^2}{\alpha - (\alpha + n_i\beta)} + \frac{1c_{ik} + c_{il})^2\beta^2}{\alpha - (\alpha - n_i\beta)}$$

where the first set of terms give the energy change on interaction with the bonding MO's of the odd AH and the second set the energy change on interaction with the antibonding MO's. The two sets of terms differ only in the sign of the denominators; therefore, they cancel, and $\Delta\epsilon = 0$. If union occurs at m and n, c_{ik} and c_{il} are replaced by c_{im} and c_{in} in the first set of terms and by $-c_{im}$ and $-c_{in}$ in the second. Again $\Delta\epsilon = 0$. However, if union occurs at the starred atoms c_k and c_l and also at the unstarred atom c_m, then, although there is no interaction between the NBMO's of the fragments, the interaction of the p orbital with the bonding and antibonding MO's of the odd AH does not leave the resulting MO at the nonbonding ($\epsilon = \alpha$) level. The expression for $\Delta\epsilon$ is

$$\Delta\epsilon = \sum_i \frac{(c_{ik} + c_{il} + c_{im})^2\beta^2}{\alpha - (\alpha + n_i\beta)} + \frac{(c_{ik} + c_{il} - c_{im})^2\beta^2}{\alpha - (\alpha - n_i\beta)} = \sum_i -4c_{im}(c_{ik} + c_{il})\beta/n_i$$

which will not in general be zero. Thus, the π system of bicyclobutadiene, which results from the union of **4** to all three carbon atoms of **3**, has only one NBMO (that present in **3**) which survives unchanged.

(7) Second-order perturbation theory gives these MO energies as respectively $\alpha \pm 1.414\beta \pm (\beta/2 + \beta/2)^2/1.414\beta = \alpha \pm 2.121\beta$ and $\alpha \pm 1.414\beta \pm (\beta/2^{1/2})^2/1.414\beta = \alpha \pm 1.768\beta$.

(8) Again, a general proof using perturbation theory is offered. Suppose the union of the carbon atom to the odd AH takes place at the starred atoms

k and l. The mixing coefficient of ψ_i into the p orbital of the carbon atom is given by the expression $(c_{ik} + c_{il})\beta/[\alpha - (\alpha + n_i\beta)] = -(c_{ik} + c_{il})/n_i$, while that of ψ_j, the antibonding MO paired with ψ_i, is given by $(c_{ik} + c_{il})/n_i$. Therefore, these MO's are mixed into the p orbital to the same extent but with opposite signs. Since ψ_i and ψ_j have the same coefficients at the starred atoms and coefficients of the same magnitude but opposite sign at the unstarred atoms, the contribution of the odd AH to the resulting NBMO occurs only at the unstarred atoms, the set to which the lone carbon is not bonded. If the carbon is instead bonded to one or more of the unstarred atoms, the mixing coefficients for ψ_i and ψ_j are the same. Thus, the NBMO that results from the mixing has coefficients only at the starred atoms of the odd AH, just those atoms where the NBMO of the odd AH, which survives unaltered after union, also has nonzero coefficients.

(9) W. T. Borden, *Chem. Commun.*, 881 (1969).

(10) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 5968 (1975).

(11) W. T. Borden and L. Salem, *J. Am. Chem. Soc.*, **95**, 932 (1973).

(12) (a) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2906 (1975); (b) W. T. Borden, *J. Am. Chem. Soc.*, **98**, 2695 (1976); (c) W. T. Borden and E. R. Davidson, *J. Chem. Phys.*, **64**, 663 (1976).

(13) Planar D_{3h} trimethylenemethane actually possesses a pair of degenerate singlet states of E′ symmetry. Although one of them may be described as having an allyl plus p wave function,[12] the other resembles an ethylene weakly interacting with two radicals.[12b,c] However, it is easily shown[12b,c] that the latter is merely a linear combination of two other allyl plus p type wave functions in which the two remaining peripheral carbons are chosen to bear the noninteracting p orbital. A physical explanation of this mathematical fact can be given in terms of the potential surface for the singlet: E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, **99**, 2053 (1977).

(14) In the NBMO's of odd AH's carbon atoms with coefficients of opposite sign are separated by $4n - 3$ others. If the union of an additional carbon to two such atoms occurs, a ring of $4n$ atoms is formed.

(15) The experimental results of A. S. Kende and E. E. Riecke, *J. Am. Chem. Soc.*, **94**, 1397 (1972), on the preferred course of thermal rearrangement of a 2-vinyl-1-methylenecyclopropane are consistent with this expectation.

(16) Obvious routes for the laboratory preparation of **7**, necessary to test experimentally these theoretical predictions, include cleavage, either thermal or photochemical, of the very weak σ bond of the zero bridge in 2,4-dimethylenebicyclo[1.1.0]butane, and extrusion of nitrogen, again either thermally or photochemically induced, from 5,6-dimethylene-3,4-diazabicyclo[2.1.1]hexene.

(17) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(18) Since the MO's for the singlet and triplet differ, the optimum geometries for these two states are also expected to differ.[12,13] More specifically, the π bonding between the ring and the exocyclic methylene groups is stronger in the triplet than in the singlet; consequently, the bonds to these groups should be shorter in the former than in the latter state. A determination of the optimum geometry for each state is planned.

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(20) The NBMO's do not transform together to form the basis for a degenerate representation of the point group; indeed, D_{2h} has no degenerate representations.

(21) J. H. Meadow and H. F. Schaefer III, *J. Am. Chem. Soc.*, **98**, 4383 (1976).

(22) Ab initio studies of trimethylenemethane[12c] indicate that in AH's like **2** and **7**, either the MO's of the triplet or the lowest open shell singlet can be used to carry out CI, since both give the same calculated energy.

(23) J. N. Murrell and A. Hinchcliffe, *Mol. Phys.*, **11**, 101 (1966), have shown that in dinegative ions of aromatic π systems intraorbital electron correlation plays an important role in causing a ^{1}A state to fall below the triplet in some large molecules.

(24) Brillouin's theorem in open shell systems is discussed by R. Manne, *Mol. Phys.*, **24**, 935 (1972).

(25) This diradical, also known as 2,2′-bisallyl, is implicated in the degenerate rearrangement of 1,2-dimethylenecyclobutane and the dimerization of allene.[26] Triplet **8** has been observed by P. Dowd, *J. Am. Chem. Soc.*, **92**, 1066 (1970).

(26) J. J. Gajewski, *J. Am. Chem. Soc.*, **97**, 3457 (1975), and references therein.

(27) As the molecule twists about the bond connecting the two allylic fragments, the out-of-phase combination of localized NBMO's is progressively stabilized by spiroconjunction, relative to the in phase, until at 90° the former combination lies below the latter. At a twist angle of about 40° they are calculated to be degenerate.[28]

(28) B. G. Odell, R. Hoffmann, and A. Imamura, *J. Chem. Soc. B*, 1675 (1970).

(29) The choice of the set of NBMO's for the triplet is arbitrary, since for two electrons of the same spin any orthonormal linear combination of their MO's gives the same wave function. See ref 4b, pp 176–178, for a discussion.

(30) At rhomboid, as well as at square, geometries of **1** there is a singlet state in which the electrons are so localized.

(31) Although this calculation was carried out with an open shell SCF program,[19] the wave function in eq 10 for this singlet shows that it is really a closed shell state of A_g symmetry in D_{2h}. While it is obvious that the first two terms on the second line of eq 11 have this symmetry, it is perhaps less apparent that the second two terms possess it as well. However, since any D_{2h} symmetry operation that does not take ψ_2 and $\psi_{2'}$ each into a multiple of itself takes them into each other, and since open shell singlets have spatial wave functions that are invariant to orbital interchange, it is clear that these latter two terms also have A_g symmetry, as of course they must. The triplet wave function changes sign on interchange of ψ_2 and $\psi_{2'}$; so it does not belong to A_g in D_{2h}. The singlet wave function $|\psi_S{}^\alpha\psi_A{}^\beta\rangle + |\psi_A{}^\alpha\psi_S{}^\beta\rangle$ has the same symmetry in D_{2h} as the triplet but is of much higher energy, since it is equivalent to $|\psi_2{}^2\rangle - |\psi_{2'}{}^2\rangle$.

(32) M. J. S. Dewar and J. W. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971).

(33) As noted previously,[12] Dewar's SCF results for the planar singlet grossly overestimate its energy, since the half-electron method, used in setting up the Fock operator, does not lead to the correct set of MO's for this species.

(34) The π bond order between the cisoid terminal atoms in **8** is negative, a consequence of the positive bond orders within the allylic fragments and between the central atoms. The negative π bond order between these terminal atoms suggests a preference for a conrotatory mode of interconversion of **8** with 1,2-dimethylenecyclobutane, in agreement with the results of stereochemical studies.[26] It should be noted, however, that the preferred geometry for **8** is probably not a planar one.[26,28]

(35) For example, 1,8-naphthoquinodimethane belongs to the same class of diradical as trimethylenemethane (**2**). Nevertheless, in a bridged 1,8-naphthoquinodimethane that has been recently studied experimentally [C. R. Watson, R. M. Pagni, J. R. Dodd, and J. E. Bloor, *J. Am. Chem. Soc.*, **98**, 2551 (1976)] the triplet appears to be 0.2 kcal/mol higher in energy than the lowest singlet.

(36) G. Hall, private communication.

(37) NOTE ADDED IN PROOF. Geometry optimization for the different states of 1,3-dimethylenecyclobutadiene (**7**) shows that the triplet is, indeed, the ground state but that ^1A_g, rather than $^1B_{2u}$, is the singlet state of lowest energy. A detailed description of the potential surface for this very interesting molecule will be submitted for publication shortly.

P-Type Delayed Fluorescence from Rubrene

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Abstract: An absorbance transient assigned to the lowest rubrene triplet can be sensitized by energy transfer from flash-excited anthracene or benzophenone. In acetonitrile this transient showed a first-order lifetime of 80–120 μs. Delayed fluorescence from rubrene was observed, and its intensity at all times was proportional to the square of the triplet absorbance. These results show that rubrene undergoes triplet–triplet annihilation to produce the emitting singlet. An attempt was made to locate the energy of the rubrene triplet by using various electron acceptors as quenching agents. The results are consistent with a triplet energy between 1.04 and 1.29 eV.

Delayed fluorescence from fluid solutions of aromatic hydrocarbons generally arises as the result of bimolecular triplet–triplet annihilation. This type of emission, known as P-type delayed fluorescence,[1,2] requires that the sum of the excitation energies of the interacting triplets at least approximate that of the first excited singlet. Whether the lowest rubrene (5,6,11,12-tetraphenylnaphthacene) triplet possesses sufficient energy to undergo this process has long been questioned.[3-6] Despite electrochemiluminescence studies[4] that seem to indicate that rubrene does yield delayed fluorescence, direct