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Theoretical Studies of Diradicals Containing Four π Electrons

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Among the definitions of a diradical,[1] the broadest considers such a species to be an atom or molecule in which two electrons occupy two degenerate, or nearly degenerate, orbitals. This definition encompasses species as diverse as oxygen atoms and molecules, carbenes, antiaromatic annulenes, conjugated hydrocarbons for which no classical Keklué structures can be written, and the intermediates or transition states in many reactions that are nonconcerted by virtue of orbital symmetry or geometrical restrictions.

The study of diradicals presents some special problems for theoreticians, since adequate wave functions are neither as simple nor as easy to obtain as those for closed-shell molecules. As shown in Figure 1, six electronic configurations are possible when two electrons are placed in two degenerate MO's. It is clear that $|\psi_x{}^\alpha\psi_y{}^\alpha\rangle$ and $|\psi_x{}^\beta\psi_y{}^\beta\rangle$ are triplet configurations and that $|\psi_x{}^\alpha\psi_x{}^\beta\rangle$ and $|\psi_y{}^\alpha\psi_y{}^\beta\rangle$ are singlets. Less obvious is the fact that the sum and difference of $|\psi_x{}^\alpha\psi_y{}^\beta\rangle$ and $|\psi_x{}^\beta\psi_y{}^\alpha\rangle$ represent, respectively, the third ($m_s = 0$) component of the triplet state and a third singlet. Closed-shell self-consistent-field (SCF) techniques cannot be used to obtain the optimal MO's for this type of singlet in which two MO's are each singly occupied. Moreover, closed-shell SCF methods are, in general, inappropriate for finding the other two singlet wavefunctions as well.

At geometries where ψ_x and ψ_y are degenerate by symmetry, these MO's are transformed into linear combinations of each other by some operations of the symmetry group. Consequently, $|\psi_x{}^\alpha\psi_x{}^\beta\rangle$ and $|\psi_y{}^\alpha\psi_y{}^\beta\rangle$ are also mixed by these operations, and the sum and difference of these two configurations must be taken in order to obtain acceptable wave functions. At nearby geometries of lower symmetry, allowance must still be made for mixing of $|\psi_x{}^\alpha\psi_x{}^\beta\rangle$ and $|\psi_y{}^\alpha\psi_y{}^\beta\rangle$. Multiconfigurational SCF (MCSCF) calculations are required in order to determine the optimal MO's with which to construct the proper two-configuration, singlet wave functions.

The presence in a diradical of four low-lying states, a triplet and three singlets, raises the question of which is the ground state. In addition, since at the optimal triplet geometry the three singlets are often in close energetic proximity (symmetry may, in fact, ensure that two of them are exactly degenerate), a molecular distortion that causes mixing between them can result in an energy lowering. Consequently, some of the singlet states may prefer less symmetrical equilibrium geometries than the triplet. The prediction of the geometries and relative energies of the low-lying states in diradicals is a major goal of theory in this area of chemistry. In the event that molecular symmetry results in the existence of several equivalent equilibrium geometries for a particular state, the size of the energy barriers separating these minima becomes a quantity of interest as well.

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The experimental study of diradicals is also complicated by their electronic structure, which generally makes diradicals both thermodynamically and kinetically unstable. Furthermore, the determination of singlet–triplet energy differences poses special problems for experimentalists, as evidenced by the continuing controversy over the value for the $^1A_1$–$^3B_2$ separation in CH_2, the simplest and most studied hydrocarbon diradical.[2]

Diradicals Containing Four π Electrons

Our research on diradicals has been theoretical in nature and has focused on conjugated hydrocarbons containing four π electrons. The molecules studied have been the three smallest antiaromatic annulenes—cyclopropenyl anion, cyclobutadiene, and cyclopentadienyl cation—and the simplest non-Kekulé hydrocarbon—trimethylenemethane. Our goals in this research have been threefold: (1) to determine the type of wave function that provides at least a minimally correct description of each diradical and to interpret these wave functions in physical terms, (2) to understand the potential surfaces of the lowest states of diradicals so that the surface topographies can be predicted without recourse to detailed calculations, and (3) to verify computationally our conclusions regarding wave functions and potential surfaces and to provide ab initio predictions of some of the important properties of diradicals.

The fact that cyclopropenyl anion, cyclobutadiene, cyclopentadienyl cation, and trimethylenemethane can all adopt geometries of high symmetry greatly simplifies finding the wave functions for and predicting the equilibrium geometries of these diradicals. For example, the Hückel molecular orbitals (MO's) of each of these four diradicals are completely determined by symmetry at the most symmetrical molecular geometry. At this geometry in each diradical there exist a pair of degenerate π MO's that are occupied by two electrons.

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(1) L. Salem and C. Rowland, *Angew. Chem., Int. Ed. Engl.*, **11**, 92 (1972).

(2) For a recent review, see W. T. Borden and E. R. Davidson, *Annu. Rev. Phys. Chem.*, **30**, 125 (1979).

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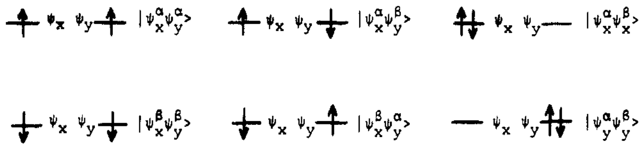

Figure 1. Configurations possible for the occupancy of two orbitals by two electrons.

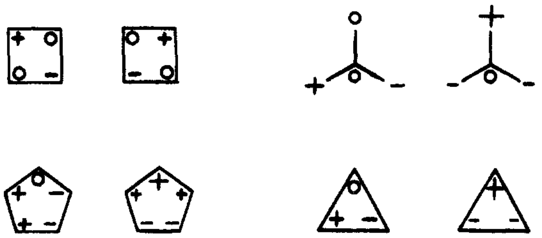

Figure 2. Schematic representation of the degenerate Hückel MO's that are partially occupied in cyclobutadiene, trimethylenemethane, cyclopentadienyl cation, and cyclopropenyl anion. Although the MO degeneracy in these diradicals is symmetry determined, any orthogonal linear combination of the orbitals shown is also a satisfactory representation of the degenerate MO's.

These degenerate Hückel MO's are depicted schematically in Figure 2.

Inspection of these orbitals reveals an important difference between the degenerate MO's of cyclobutadiene and those of the other three diradicals. Because of the D_{4h} symmetry of cyclobutadiene, its degenerate π MO's can be chosen so that they have no atoms in common. The degenerate MO's for the other three diradicals do not have this property, nor can linear MO combinations be found that do. Many of the differences between cyclobutadiene and the other three molecules can be traced to this symmetry-related distinction between their partially occupied, degenerate MO's.[3]

For example, since in cyclobutadiene the degenerate MO's can be localized to different sets of atoms, an electron in one of these MO's will not appear in the same atomic orbital (AO) as an electron in the other MO, *regardless of* the spins of the two electrons. Consequently, the lowest singlet and triplet states of cyclobutadiene should, to a first approximation, have nearly the same energies at square geometries, because the Coulombic repulsion energies between the two nonbonding electrons in both states are almost identical.[4] In contrast, in the other three diradicals, where the degenerate Hückel MO's do have atoms in common, the triplet state is anticipated to lie well below the singlet in the geometry of highest symmetry.[4] In these molecules two electrons in the degenerate Hückel MO's are prevented from appearing simultaneously in the same AO *only if* their spins are triplet coupled so that the Pauli principle is operative. Since there is a high Coulombic repulsion energy associated with the simultaneous occupancy of an AO by two electrons, the triplet ground states found for both cyclopentadienyl cation[5] and trimethylenemethane[6] can be attributed[4] to the fact that their degenerate MO's have atoms in common.[7]

Cyclobutadiene

The near-degeneracy of the triplet and lowest singlet state in square cyclobutadiene, anticipated by inspection of the degenerate MO's, provides an economical explanation[4] of why this antiaromatic annulene, unlike those with non-D_{4h} symmetry,[5,7] has a singlet ground state.[2,8] However, a complete understanding requires elucidation of the mechanism by which the singlet falls below the triplet in cyclobutadiene, since, when AO overlap is included, SCF calculations at square geometries find that the triplet actually lies a few kcal/mol below the singlet.

One possible mechanism by which the energy of the singlet could fall below that of the triplet would be a distortion of singlet cyclobutadiene to lower symmetry. This would allow the triplet to be lower in energy than the singlet at square geometries, but the ground state of the diradical could still be a singlet that preferred a nonsquare geometry. The triplet would then be metastable, and it might be possible to populate it photochemically at low temperatures.[9]

That such an experiment is unlikely to succeed and that the triplet is, in fact, likely to enjoy only a fleeting existence were suggested by an early calculation in which configuration interaction (CI) involving the π electrons of cyclobutadiene was included.[10] Subsequent, more sophisticated, ab initio calculations[11-14] have confirmed the earlier finding that, when CI is included, the energy of the singlet falls below that of the triplet, even at a square geometry.

Despite the fact that one must go beyond SCF calculations in order to obtain the correct state ordering in square cyclobutadiene, the very interesting violation of Hund's first rule that is found at the π CI level is amenable to a physical interpretation.[15] Each of the degenerate MO's that is singly occupied in the two lowest states of cyclobutadiene resembles the nonbonding MO that is singly occupied in the allyl radical. In the allyl radical the nonuniform distribution of spin in this MO perturbs the wave functions for the pair of

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(3) W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **99**, 4587 (1977).

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

(5) M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffman, C. Perchonok, E. Wasserman, R. S. Hutton, and V. J. Kuck, *J. Am. Chem. Soc.*, **95**, 3017 (1973).

(6) R. J. Baseman, D. W. Pratt, M. Chow, and P. Dowd, *J. Am. Chem. Soc.*, **98**, 5726 (1976). Derivatives of trimethylenemethane also have been found to have triplet ground states [M. S. Platz, J. M. McBride, R. D. Little, J. J. Harrison, A. Shaw, S. E. Potter, and J. A. Berson, *J. Am. Chem. Soc.*, **98**, 5725 (1976)], and a triplet EPR signal has been detected in a nitrogen analog [H. Quast, L. Bieber, and W. C. Danen, *J. Am. Chem. Soc.*, **100**, 1306 (1978)].

(7) Several other diradicals with this property are also known to have triplet ground states. Among these are another antiaromatic annulene, the hexachlorobenzene dication [E. Wasserman, R. S. Hutton, V. J. Kuck, and E. A. Chandross, *J. Am. Chem. Soc.*, **96**, 1965 (1974)], and another non-Kekulé hydrocarbon, 1,8-naphthoquinodimethane [M. Gisin, E. Rommel, J. Wirz, M. N. Burnett, and R. M. Pagni, *ibid.*, **101**, 2216 (1979); M. S. Platz, *ibid.*, **101**, 3308 (1979)].

(8) For a recent review of cyclobutadiene, see T. Bailey and S. Masamune, *Tetrahedron*, **36**, 343 (1980).

(9) M. J. S. Dewar and H. W. Kollmar, *J. Am. Chem. Soc.*, **97**, 2933 (1975).

(10) D. P. Craig, *Proc. R. Soc. London, Ser. A*, **202**, 498 (1950).

(11) R. J. Buenker and S. D. Peyerimhoff, *J. Chem. Phys.*, **48**, 354 (1968).

(12) H. Kollmar and V. Staemmler, *J. Am. Chem. Soc.*, **99**, 3583 (1977).

(13) W. T. Borden, E. R. Davidson, and P. Hart, *J. Am. Chem. Soc.*, **100**, 388 (1978).

(14) J. A. Jafri and M. D. Newton, *J. Am. Chem. Soc.*, **100**, 5012 (1978).

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

Figure 3. Degenerate MO's suitable for describing rectangular distortions in cyclobutadiene.

electrons in the bonding π orbital.[16] This effect, which enters at the CI level for a restricted Hartree–Fock (RHF) wave function, lowers the energy of the RHF wave function by reducing the Coulombic repulsion between the nonbonding electron and those in the bonding π MO. CI allows the bonding π electrons to become "polarized" so that the electron of spin opposite to that in the nonbonding MO becomes more confined to the central carbon, where the nonbonding orbital has a node, while the other electron becomes more confined to the terminal carbons. Since the latter electron has the same spin as the one in the nonbonding MO, their simultaneous appearance in the same AO is prohibited by the Pauli principle. Spin polarization in the allyl radical reveals itself in the "anomalous" spin density that is observed experimentally.

Triplet cyclobutadiene has a uniform distribution of spin at each atom. Consequently, the triplet cannot benefit energetically from the same type of polarization that is responsible for producing the "anomalous" spin distribution in the allyl radical. Singlet cyclobutadiene has no net spin, but it behaves in CI *as if* it had a nonuniform spin distribution caused by the two electrons of opposite spin, each of which occupies one of the degenerate MO's. Therefore, the singlet can profit from a type of stabilization that is unavailable to the triplet. This effect has been termed "dynamic spin polarization"; its physical description has been refined; and other instances (e.g., in ethylene twisted 90° about the C–C bond) where it is responsible for violations of Hund's rule have been discussed.[17]

Dynamic spin polarization provides a mechanism by which cyclobutadiene would have a singlet ground state, even if the equilibrium geometry of this state were square. Thus, the apparent singlet multiplicity of the ground state[2,8] provides no information as to the preferred geometry of this state.[15] Moreover, despite the orbital degeneracy at square geometries, the lowest singlet state ($^1B_{1g}$), as well as two others that are higher in energy ($^1A_{1g}$ and $^1B_{2g}$), are nondegenerate. Therefore, the Jahn–Teller theorem[18] does not apply to the lowest singlet states of cyclobutadiene, any of which could thus have a square geometry.

Although the $^1B_{1g}$ state of cyclobutadiene is not obliged by the Jahn–Teller theorem to distort from a square geometry, there is still reason to suppose that it might do so. Group theory shows that $^1B_{1g}$ can be mixed with the low-lying $^1A_{1g}$ state by a vibration of b_{1g} symmetry, which distorts square cyclobutadiene to a rectangular geometry. The cyclobutadiene MO's that are shown in Figure 2 are not appropriate for describing the rectangular molecule. However, making the alternative choice of degenerate MO's as the sum and difference of those in Figure 2 provides an acceptable set. The latter MO's, which are shown in Figure 3, will be referred to as the primed set. Rewriting the $^1B_{1g}$ wave function, where one electron occupies each of the unprimed MO's, in terms of the primed set of orbitals, one obtains

$$^1B_{1g} = |\psi_x\psi_y(\alpha\beta - \beta\alpha)\rangle/2^{1/2} = (|\psi_x'^2\rangle - |\psi_y'^2\rangle)/2^{1/2}$$

The $^1A_{1g}$ wavefunction has the same form no matter which set of MO's is used.

$$^1A_{1g} = (|\psi_x^2\rangle + |\psi_y^2\rangle)/2^{1/2} = (|\psi_x'^2\rangle + |\psi_y'^2\rangle)/2^{1/2}$$

These equations show that mixing $^1B_{1g}$ with $^1A_{1g}$ under the influence of a rectangular distortion tends to localize a pair of electrons in one of the primed MO's. In the lowest singlet state the pair of electrons goes into the primed MO that is stabilized by the distortion.

This type of state mixing is termed a "second-order Jahn–Teller effect."[19] Because the states being mixed are nondegenerate, second-order perturbation theory can be used to describe the energy lowering on distortion that is caused by this mixing. Consequently, for small distortions the energy lowering due to mixing is quadratic in the distortion coordinate. The potential that resists molecular deformation is also quadratic for small distortions. Thus, it cannot be predicted a priori whether a second-order Jahn–Teller effect will actually cause a molecular distortion to be favorable or will simply reduce the force constant for that distortion. Nevertheless, since the closer two states are in energy, the greater is the stabilization afforded by their mixing, it is possible to make predictions about the relative ease of different molecular distortions, based on the relative energies of the states that are mixed by them.

We have made such predictions for singlet and triplet cyclobutadiene, using the state energies computed at a square geometry.[13] Actual calculations of the force constants for various types of distortions correlated well with the predictions based on second-order Jahn–Teller effects. The only negative force constant found was for rectangular distortion in the lowest singlet state. Thus a square geometry represents a minimum for the triplet state and a transition state for the interconversion of two equivalent, rectangular, singlet minima. Our prediction of a rectangular equilibrium geometry for the ground state of cyclobutadiene is in accord not only with the results of other ab initio calculations[11,12,14] but also with subsequent spectroscopic[20] and chemical studies.[21]

The computed energy differences between the rectangular and the square singlet and between the square singlet and the triplet depend somewhat on basis set size and the amount of CI included. Values on the order of 10 kcal/mol represent the best current theoretical estimates for both.[12-14] These predicted values await experimental test.

Despite the fact that theory predicts pronounced alternation of the ring bond lengths at the equilibrium geometry of singlet cyclobutadiene, the X-ray crystal structure of the tetra-*tert*-butyl derivative shows this molecule to be nearly square.[22] Calculations on the

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(16) See, for instance, W. T. Borden, "Modern Molecular Orbital Theory for Organic Chemists", Prentice-Hall, Englewood Clifs, NJ, 1975, pp 265–271.

(17) H. Kollmar and V. Staemmler, *Theor. Chim. Acta*, **48**, 223 (1978).

(18) H. A. Jahn and E. Teller, *Proc. R. Soc. London, Ser. A*, 161, 220 (1937).

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(21) D. W. Whitman and B. K. Carpenter, *J. Am. Chem. Soc.*, **102**, 4272 (1980).

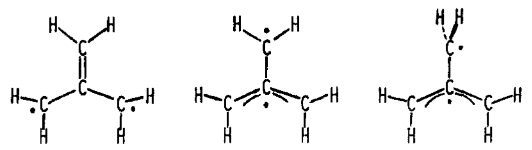

Figure 4. Depiction of the bonding in $^1A_1$, $^1B_2$, and orthogonal trimethylenemethane.

parent reveal that double-bond lengthening in rectangular cyclobutadiene is accompanied by single-bond shortening.[23] The nearly square equilibrium geometry that is found in tetra-*tert*-butylcyclobutadiene can, therefore, be attributed to relief of steric interactions between *tert*-butyl groups by double-bond lengthening, which gives rise to concomitant single-bond shortening. Support for this hypothesis comes from molecular mechanics calculations on tetra-*tert*-butylcyclobutadiene. They indicate that, on going from a rectangular to a square geometry, the relief of strain due to steric interactions between *tert*-butyl groups is very close to the amount, predicted by the best CI calculations, to be required to transform rectangular cyclobutadiene to a square geometry.[24]

Trimethylenemethane

Unlike the case in cyclobutadiene, the degenerate Hückel MO's in trimethylenemethane span common atoms, and, as discussed above, this makes the triplet the ground state. The wave function for the corresponding singlet state, in which one electron occupies each of the degenerate Hückel MO's, contains a large number of high-energy, ionic terms. A Pariser–Parr–Pople type calculation[25] reveals that a π wave function consisting of the MO's for an allyl radical plus an electron localized in the remaining p orbital is, in fact, preferred for this singlet state. Although the Hückel energy of planar trimethylenemethane ($4\alpha + 2(3^{1/2})\beta$) is lower than that of allyl plus p ($4\alpha + 2(2^{1/2})\beta$), the nonbonding MO's in the latter wave function have no atoms in common. Consequently, the Coulombic repulsion energy between the two nonbonding electrons, whose simultaneous occupancy of the same AO is not prohibited by the Pauli principle in a singlet state, is much lower in the allyl plus p wave function. This provides a ready explanation for why a geometry with one methylene group orthogonal to the molecular plane (Figure 4) is found experimentally to be preferred over that for planar trimethylenemethane in thermal methylenecyclopropane rearrangements.[2,26]

Both semiempirical[27] and ab initio[28] calculations found sizable increases in energy on rotating the unique methylene group back into conjugation from the orthogonal geometry in singlet trimethylenemethane. However, in agreement with subsequent experimental results,[29,30] ab initio calculations carried out by Schaefer and Yarkony[31] found only a small increase in energy on methylene group rotation. It was pointed out[32] that the difference between the theoretical estimates of the relative energies of orthogonal and planar singlet trimethylenemethane was caused by the fact that only Schaefer and Yarkony actually solved the open-shell SCF equations for the planar singlet. The other two groups used methods that led to the Hückel MO's. The large Coulombic repulsion between electrons in the nonbonding Hückel orbitals in singlet trimethylenemethane makes the allyl plus p set of orbitals optimum for both orthogonal and planar geometries in this state.

There is a second, low-energy wave function for the planar singlet.[33,34] It consists of essentially a double bond between the central carbon and unique methylene group and rather weak π bonds to the remaining two methylenes, where the two nonbonding electrons are largely localized, one on each carbon. The bonding in this wave function ($^1A_1$ in C_{2v} symmetry) and in the allyl plus p type ($^1B_2$ in planar trimethylenemethane) is depicted in Figure 4.

Group theory shows that at D_{3h} geometries $^1A_1$ and $^1B_2$ become the degenerate components of a $^1E'$ state. However, even at D_{3h} geometries, the optimal π MO's for these singlets are not D_{3h} symmetry orbitals like those shown in Figure 2. D_{3h} symmetry MO's give singlet SCF energies that are more than 70 kcal/mol higher than those obtained when only C_{2v} symmetry is imposed on the MO's.[34] It is generally the case in carrying out SCF calculations on spatially degenerate states that the full molecular symmetry must not be imposed on the MO's.[35]

The fact that only C_{2v} symmetry can be imposed on the optimal SCF MO's for singlet trimethylenemethane at D_{3h} geometries causes a serious problem, because there is no guarantee that either the $^1A_1$ or $^1B_2$ SCF wave function will have pure $^1E'$ symmetry. In fact, it can be demonstrated that neither will.[33] As a result the $^1A_1$ and $^1B_2$ SCF wave functions are nondegenerate at D_{3h} geometries, where pure $^1E'$ wave functions would have equal energies. This nondegeneracy amounts to almost 8 kcal/mol in a calculation at the equilibrium geometry of the triplet, carried out with an STO-3G basis set.[36]

Since the $^1A_1$ SCF wave function lies well below that for $^1B_2$ at a point on the potential surface where the two should be degenerate, it is likely that the relative SCF energies will also be in error at other points on the surface. Thus, calculations on D_{3h} trimethylenemethane alert one to an important fact about geometries of lower symmetry in this diradical and, by inference, about related diradicals of intrinsically lower symmetry. SCF wave functions for the two lowest singlets will not, in general, give the correct relative energies. Full CI in

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(30) J. J. Gajewski and S. K. Chou, *J. Am. Chem. Soc.*, **99**, 5696 (1977).

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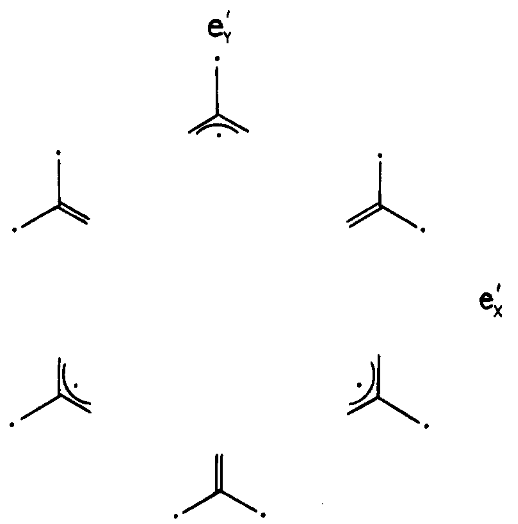

Figure 5. Pseudorotation in singlet trimethylenemethane.

the π space is necessary,[33] and in the case of trimethylenemethane sufficient,[34] for generating singlet wave functions with the correct relative energies.

Obtaining correct relative energies for the $^1A_1$ and $^1B_2$ wave functions in trimethylenemethane is very important because, despite the difference in their symmetry, both wave functions lie on the potential surface for the lowest singlet state of the planar diradical.[37] This is illustrated by the diagram for pseudorotation in this state, shown in Figure 5. The relative energies of $^1A_1$ and $^1B_2$ at their equilibrium geometries determine the location of the maxima and minima along the lowest energy pathway for pseudorotation on this surface.

It might be argued that there should be no maxima or minima along this pseudorotation pathway since at a D_{3h} geometry $^1A_1$ and $^1B_2$ become the two components of $^1E'$. The first-order Jahn–Teller effect expected for this state should lower the energy of both $^1A_1$ and $^1B_2$, or any linear combination of the two, equally. Thus, to first order, pseudorotation should be unimpeded by an energy barrier.

CI calculations on trimethylenemethane show, however, that the three equivalent $^1A_1$ wave functions represent minima on the pseudorotation pathway and the three equivalent $^1B_2$ wave functions maxima.[37] The topography of the potential surface is predictable from consideration of how second-order Jahn–Teller mixing of $^1A_1$ and $^1B_2$ with the third low-lying singlet state modifies the first-order Jahn–Teller effect.[37]

The potential curve for pseudorotation in planar trimethylenemethane is computed to be relatively flat since the first-order effect dominates the second-order one. The influence of bond angle distortions and substituents on the energies of the $^1A_1$ and $^1B_2$ wave functions has been determined, and it has been found that the calculated difference in energy between planar and orthogonal singlet trimethylenemethane is in good agreement with experiment.[37] However, the calculated energy difference between the orthogonal singlet and the D_{3h} triplet is significantly larger than experimental determinations of the size of the singlet–triplet energy separation in trimethylenemethane and derivatives.[2,26] The reasons for this discrepancy are not clear.

Cyclopentadienyl Cation

Like planar trimethylenemethane, the degenerate Hückel MO's for cyclopentadienyl cation have atoms in common. Thus, one might expect that the ground state of the cation will be a triplet and that, in order to reduce the ionic terms in the two lowest energy singlet wave functions, the optimal MO's for these singlets will differ from each other and from those of the triplet. The resulting deviation of the bonding from D_{5h} symmetry in both components of the lowest $^1E_2'$ state should give rise to the first-order molecular distortion that is anticipated from the Jahn–Teller theorem. In addition, a second-order effect should be caused by mixing of $^1E_2'$ with $^1A_1'$, the third low-lying singlet.

Unlike the case in trimethylenemethane, the first- and second-order Jahn–Teller effects in cyclopentadienyl cation occur along different distortion coordinates, respectively e_1' and e_2'. CI calculations on the cation find a negligibly small first-order effect and a large second-order one,[38] the reverse of the situation in trimethylenemethane.

Since the degenerate MO's in cyclopentadienyl cation span five instead of just three atoms, there are fewer ionic terms in the singlet wave functions constructed from symmetry MO's in cyclopentadienyl cation than in trimethylenemethane. Moreover, modification of the degenerate Hückel MO's is energetically more costly in cyclopentadienyl cation than in trimethylenemethane, because all the pπ AO's in the cation have two nearest neighbors. Since the deviation from full molecular symmetry of the bonding in the two, lowest energy, singlet wave functions is, therefore, smaller in cyclopentadienyl cation than in trimethylenemethane, the first-order Jahn–Teller effect is also smaller in the former than in the latter diradical.

The second-order effect is large in cyclopentadienyl cation because, as in cyclobutadiene, the state mixing tends to localize two electrons in the degenerate MO that is strongly stabilized by distortion. In contrast, in trimethylenemethane the second-order mixing results in but a small modification of the lowest singlet wave function and a correspondingly small stabilization energy.[37]

The second-order effect in singlet cyclopentadienyl cation is calculated to result in a stabilization of 13.4 kcal/mol on distortion,[38] an amount of energy more than an order of magnitude greater than that found in trimethylenemethane and roughly three times larger than that predicted for cyclobutadiene when CI is carried out in just the π space.[13] The $^1E_2'$–$^1A_1'$ energy gap in D_{5h} cyclopentadienyl cation is only about a third that calculated for $^1B_{1g}$–$^1A_{1g}$ in D_{4h} cyclobutadiene. Other things being equal, a smaller energy gap between the states being mixed by distortion should result in a proportionately larger stabilization upon distortion.

The large second-order Jahn–Teller effect in the lowest singlet state of cyclopentadienyl cation is computed to make up about two-thirds of the singlet–triplet energy difference calculated at the optimal D_{5h} geometry of each state. In accord with experiment,[5] the triplet is the ground state. However, at the equilibrium geometry of the singlet, the energy of the triplet is found to be higher than that of the singlet, so that the singlet

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(37) E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, **99**, 2053 (1977).

(38) W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **101**, 3771 (1979).

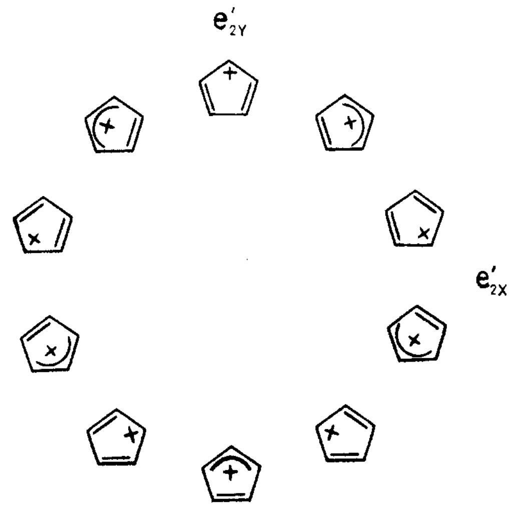

Figure 6. Pseudorotation in singlet cyclopentadienyl cation.

is predicted to be metastable. There is some evidence[39] that the adiabatic singlet–triplet energy difference of 7.3 kcal/mol, computed with the STO-3G basis set and π CI,[38] may be somewhat too large. However, it is considerably smaller than the energy separation found at the SCF level with the same basis set[40] and much more in keeping with the ability of substituents to reverse the singlet–triplet ordering.[41]

Despite the fact that the second-order effect in cyclopentadienyl cation is larger than in cyclobutadiene, as a consequence of molecular symmetry it should be much easier for the former than for the latter to pass from one distorted geometry to the other. Since a degenerate e_2' vibration produces the second-order effect in cyclopentadienyl cation, pseudorotation about the D_{5h} energy maximum, shown in Figure 6, is essentially free. In cyclobutadiene, however, the b_{1g} distortion is nondegenerate. Consequently, as discussed above, in going from one equivalent rectangular geometry to the other, cyclobutadiene must pass through a square transition state.

Cyclopropenyl Anion

Although Breslow and co-workers have generated and measured the pK_a of the parent cyclopropenyl anion and derivatives electrochemically,[42] little is known about the relative energies of the low-lying states or their preferred geometries. Thus, calculations on the anion are particularly useful.

Because cyclopropenyl anion in its most symmetrical geometry belongs to the same D_{3h} point group as trimethylenemethane, there are a number of predictions that one can make about the planar anion without recourse to computations. At a D_{3h} geometry the ${}^3A_2'$ state should lie well below ${}^1E'$. The optimal MO's for ${}^1E'$ should not be the D_{3h} symmetry orbitals, and the resulting deviation of the bonding in each component of ${}^1E'$ from D_{3h} symmetry should give rise to the first-ordering energy lowering on e′ distortion that is expected from the Jahn–Teller theorem. In addition, second-order mixing of ${}^1E'$ with ${}^1A_1'$ should also occur on e′ distortion, giving rise to maxima and minima along the pathway for pseudorotation in the lowest singlet state. From these considerations it is possible to predict that the three equivalent minima on the energy surface for the lowest singlet state of planar cyclopropenyl anion should occur for positive e_y' distortions, with one lengthened C–C bond and two shortened ones.[43]

Figure 7. Depiction of the bonding of lowest ${}^1A_1$ wave function for both positively and negatively e_y' distorted cyclopropenyl anion and in the ${}^1B_2$ wave function for this diradical.

The bonding in the corresponding allylic anion wave function is depicted in Figure 7. Also shown is the bonding in two wave functions that might represent the three equivalent maxima on the pseudorotation pathway, which are expected to occur for negative e_y' distortions. The ${}^1B_2$ wave function is stabilized by a first-order Jahn–Teller effect for this type of distortion, and the ${}^1A_1$ is destabilized by it. However, ${}^1A_1$ is stabilized along e_y' by a second-order effect, which is expected to be large in cyclopropenyl anion. Thus, although for small distortions along negative e_y' the first-order effect must dominate, causing ${}^1B_2$ to lie below ${}^1A_1$, one cannot be certain that for sufficiently large distortions along this coordinate a ${}^1A_1$ minimum might not be found that would be lower in energy than that for ${}^1B_2$.

π CI calculations on planar cyclopropenyl anion[43] failed to reveal an energy minimum for ${}^1A_1$ on negative e_y' distortions. A wave function consisting of a double bond between two carbons and a pair of electrons localized in a pπ orbital at the third merely represents an arbitrary point on the surface for the first excited singlet state of the planar anion. The minimum on this upper surface occurs at a D_{3h} geometry, where it joins that for the lowest singlet state at a cusp.

Our π CI calculations confirmed the expectation that ${}^3A_2'$ would be the ground state of the planar molecule and that an allylic anion type ${}^1A_1$ wave function would represent the planar singlet minima. However, the calculations also revealed several disquieting facts. First, they showed that planar cyclopropenyl anion would almost certainly not be bound in the gas phase, even in the triplet state. Thus, if a complete basis set were used, one π electron would be found at infinity. Consequently, calculations with a small basis set might be indicative of the behavior of the planar anion in solution, but certainly not in the gas phase.

A second problem, more intriguing than the first, was that even with full π space CI, the ${}^1A_1$ and ${}^1B_2$ components of ${}^1E'$ were nondegenerate by about 6 kcal/mol at D_{3h} geometries. Although the D_{3h} symmetry MO's did, of course, give degenerate π CI energies for the two components of ${}^1E'$, these energies were higher than those obtained with orbitals from either ${}^1A_1$ or ${}^1B_2$ calculations. In contrast, in trimethylenemethane all three types of SCF orbitals give the same π CI energies.[34]

The difference in cyclopropenyl anion is that there is a non-D_{3h} distribution of negative charge in the π

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(39) E. Wasserman and R. S. Hutton, *Acc. Chem. Res.*, **10**, 27 (1977).

(40) W. J. Hehre and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5837 (1973).

(41) R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *J. Am. Chem. Soc.*, **89**, 1112 (1967).

(42) M. R. Wasielewski and R. Breslow, *J. Am. Chem. Soc.*, **98**, 4222 (1976).

(43) E. R. Davidson and W. T. Borden, *J. Chem. Phys.*, **67**, 2191 (1977).

system in each of the two lowest singlet states, which causes the σ MO's to deviate from D_{3h} symmetry orbitals. A theoretical analysis[44] revealed that, even with a π wave function that is $^1E'$ in D_{3h}, deviation of the σ core from $^1A_1'$ symmetry gives a total wave function that is not pure $^1E'$. It was further shown that when the σ core is distorted by π charge, CI in the σ space must accompany π CI in order to obtain acceptable wave functions.

Calculations were carried out on $(NH)_3^{2+}$ in order to test this conclusion.[44] The choice of this molecule was based on our finding that planar cyclopropenyl anion is almost certainly unbound in the gas phase. The triaziridenyl dication is isoelectronic with cyclopropenyl anion, but the additional proton in each heavy atom nucleus guarantees that small basis set calculations are relevant for the species to which they are supposed to refer, the unsolvated molecule in the gas phase.

The potential surfaces for planar $(NH)_3^{2+}$ that emerged from our σ–π CI calculations were qualitatively similar to the π CI surfaces for planar cyclopropenyl anion that were obtained using the triplet MO's for the CI. Unlike π CI calculations on either the anion or $(NH)_3^{2+}$, however, the σ–π CI results for $(NH)_3^{2+}$ showed that the triplet MO's yielded slightly lower, instead of higher, energies than CI's based on $^1A_1$ or $^1B_2$ MO's. Moreover, all three sets of orbitals gave nearly the same σ–π CI energies.

Although these findings were anticipated on the basis of our theoretical analysis, completely unanticipated was the discovery that the MCSCF wave function for $^1A_1$ showed completely the wrong behavior on distortions from D_{3h} symmetry. Instead of increasing in energy on negative e_y' distortions and decreasing on positive ones, $^1A_1$ did exactly the reverse. This was also true when π CI was carried out with the MCSCF MO's for $^1A_1$. The correct Jahn–Teller behavior was obtained with the MCSCF MO's for $^1A_1$ only when CI was carried out in both the σ and the π space. Of course, an indication that MCSCF or π CI wave functions for $^1A_1$ are unacceptable is given by their pronounced lack of D_{3h} degeneracy with those for $^1B_2$. It is still noteworthy, however, that wave functions at this level of theory predict a completely incorrect $^1A_1$ potential surface for planar cyclopropenyl anion and $(NH)_3^{2+}$. Since it is currently standard theoretical practice to locate mimima on potential surfaces with little or no CI included in wave functions, the behavior of the $^1A_1$ state in these two molecules should serve as a cautionary tale.

Nonplanar Geometries

As in the case of trimethylenemethane, in cyclopropenyl anion and $(NH)_3^{2+}$ it is also important to consider nonplanar geometries. For instance, calculations on the $^1A_1$ wave function for cyclopropenyl anion that places a double bond between two carbons and an electron pair at the third reveal a strong preference for pyramidalization at the unique carbon.[45] Such a distortion from planarity could change the role of this type of wave function from being merely that for an arbitrary point on the upper singlet surface for the planar molecule to representing a stationary point on the global surface for the lowest singlet state.

To investigate this possibility we devised a CI protocol suitable for use at nonplanar geometries, where σ–π separability cannot be employed to partition the orbitals for CI.[44] By use of this prescription, CI calculations on $(NH)_3^{2+}$ find that a singlet wave function, consisting of a π bond between two nitrogens and a lone pair of electrons localized at the third, highly pyramidalized, nitrogen atom, does indeed lie on the lowest global singlet surface and, in fact, corresponds to the symmetry-equivalent minima on this surface. The energy at these minima is computed to be significantly lower than that at the optimal geometry for an allyl anion type wave function. Pyramidalization of the two equivalent nitrogens in the latter type of singlet wave function is calculated to be favorable but considerably less stabilizing than pyramidalization of the unique nitrogen in the former. Pseudorotation from one singlet minimum to another, with an allyl anion type wave function at the transition state, is predicted to require more than 20 kcal/mol of energy.

The triplet was found to prefer to have all three nitrogens moderately pyramidalized. Because of the sacrifice in π bonding required, however, nitrogen pyramidalization on the triplet surface produces a relatively modest energy lowering. Consequently, despite the fact that for the planar molecule the D_{3h} triplet lies well below the singlet minima, on the global surfaces the energy of the singlet minima is below that of the triplet.

The driving force for pyramidalization, which determines not only the topography of the lowest singlet surface but also the ground state of $(NH)_3^{2+}$ (and, by inference, that of cyclopropenyl anion too), is not relief of strain in the σ bonds of the three-membered ring. Instead, pyramidalization has its origin in the increased occupancy of the nitrogen 2s orbitals on molecular distortion from planarity.[44] This type of distortion can also be regarded as a second-order Jahn–Teller effect.

Concluding Remarks

In both trimethylenemethane and cyclopropenyl anion, the lowest singlet state is not expected to prefer a planar geometry, much less one of D_{3h} symmetry. Nevertheless, calculations at D_{3h} geometries are very useful for indicating the type of wave function that is minimally necessary for the satisfactory description of the global surface for the lowest singlet state. For diradicals like trimethylenemethane that are neutral alternant hydrocarbons, CI in just the π space suffices; but for those like cyclopropenyl anion that have a nonsymmetric distribution of π charge, CI in both the π and σ space is required.[46]

The high symmetry of trimethylenemethane and of antiaromatic annulenes like cyclopropenyl anion, cyclobutadiene, and cyclopentadienyl cation also allows the prediction of the location of the equivalent minima on the lowest singlet surfaces for the planar diradicals, without recourse to calculations. These predictions, based on Jahn–Teller effects, have been confirmed

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(46) We discussed the need for CI in both the σ and the π space in our calculations on cyclopentadienyl cation,[38] but since the first- and second-order Jahn–Teller effects occur along different distortion coordinates and since the latter totally dominates the former, the correct relative energies of $^1A_1$ and $^1B_2$ are not essential for describing pseudorotation on the lowest singlet surface. σ–π CI might, however, further reduce the singlet–triplet gap.

computationally, and in cyclobutadiene the qualitative predictions and quantitative calculations appear to be in good agreement with the available experimental evidence.

Our work on defining the minimally acceptable wave functions for diradicals whose high symmetry allows a test of the adequacy of different types of calculations should be a useful guide for theoretical studies of systems with lower symmetry. For instance, one would anticipate that π CI will still be essential for obtaining the correct relative energies of $^1A_1$ and $^1B_2$ in trimethylenemethane derivatives where substituents reduce the maximum molecular symmetry from D_{3h} to C_{2v}. Similarly, the Jahn–Teller effects that can be anticipated to occur in the highly symmetrical diradicals discussed here are also useful for understanding the potential surfaces for diradicals in which two states are degenerate by "accident" instead of by symmetry.[47]

In addition to being of methodological use to theoreticians, we hope that our work on diradicals will stimulate experimental attempts to test our computational predictions. The expectation of a short-lived triplet state in cyclobutadiene, the possibility that substitution in singlet trimethylenemethane can result in a planar geometry being lower in energy than an orthogonal one, the prediction of facile pseudorotation in singlet cyclopentadienyl cation, and the suggestion of a singlet ground state for cyclopropenyl anion are but a few of the qualitative results that await experimental verification.

Although we do not claim to have come close to solving the Schrödinger equation for any of the diradicals discussed here, some of the calculations carried out by us and by others on these molecules have been near or at "state of the art" for systems of this size. Consequently, experimental tests of some of our more quantitative predictions, for instance, those regarding the size of the barrier to pseudorotation in cyclobutadiene and in $(NH)_3^{2+}$, should provide information regarding the numerical reliability of results at this level of theory.

Experiments on diradicals are by no means easy to carry out, and those necessary to test some of our predictions may even require the development of new techniques. Nevertheless, given the healthy skepticism of most experimental chemists regarding the relability of calculations, one of the strongest prods to experimental work is to make specific theoretical predictions that can, at least in principle, be tested.

Although the predictive ability of our calculations on diradicals certainly requires further experimental verification, we have established that theory can furnish simple explanations of apparently anomalous experimental results in this area of chemistry. The difference in ground states between cyclobutadiene and cyclopentadienyl cation, two antiaromatic annulenes with isoelectronic π systems, can be understood on the basis of orbital pictures and minimization of electron repulsion. Minimization of Coulombic repulsion between electrons is also responsible for the fact that singlet trimethylenemethane, in contrast to the triplet, prefers an orthogonal geometry. The qualitative importance of the effects of electron repulsion in diradicals is what makes the theoretical study of this type of molecule rich in both interest and challenge.

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Valence Bond Isomers of Aromatic Compounds Stabilized by Trifluoromethyl Groups

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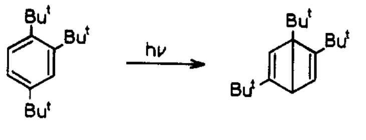
The first synthesis of valence bond isomers of aromatic compounds was carried out in 1962 by van Tamelen and his group,[1] through the isolation of a stable Dewar-type benzene by irradiation of tri-*tert*-butylbenzene (eq 1). Their idea was that the bulkiness of the *tert*-butyl groups would destabilize the flat structure of benzene; if it were converted to the nonplanar Dewar structure, the repulsion between *tert*-butyl groups would be relieved.



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