

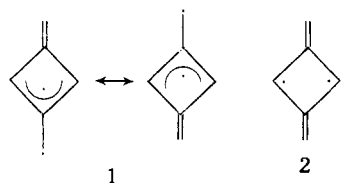
The Potential Surface for 1,3-Dimethylenecyclobutadiene

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Abstract: The potential energy surface for D_{2h} 1,3-dimethylenecyclobutadiene (DMCBD) has been explored by ab initio MO calculations, including full π -space CI. The minimum energy geometries of the lowest triplet ($^3B_{2u}$) and the two lowest singlets (1A_g and $^1B_{2u}$) have been located. The triplet is the ground state, and 1A_g is the lowest singlet. However, near the $^1B_{2u}$ minimum 1A_g and $^1B_{2u}$ are accidentally degenerate. As a result of the proximity of the two singlets in this D_{2h} region, a b_{2u} molecular distortion to C_{2v} symmetry is found to be energetically favorable, not only at points where 1A_g and $^1B_{2u}$ have the same energy but also at the $^1B_{2u}$ minimum. Consequently, this "minimum" is really a saddle point on the 1A_1 potential surface, whose only global minimum is that of 1A_g . The important features of the potential surface can be reproduced by a two-state model that would appear to provide a general description of both first- and second-order Jahn-Teller effects.

The diradical, 1,3-dimethylenecyclobutadiene (DMCBD), is a target for synthesis in several laboratories. In a recent paper¹ we pointed out that this molecule belongs to a class of diradicals in which the two Hückel nonbonding MOs cannot be confined to disjoint sets of atoms. Consequently, the triplet ($^3B_{2u}$) is anticipated to lie below the lowest open-shell singlet ($^1B_{2u}$), and the MOs for the two states are expected to be different.¹ The difference is most pronounced in the b_{1u} manifold of MOs, which contains the nonbonding MO ($2b_{1u}$) whose coefficients are not determined by symmetry. In the $^1B_{2u}$ state the $2b_{1u}$ orbital is much more localized to the two exocyclic carbon atoms than the corresponding Hückel MO. This localization keeps the single electron in $2b_{1u}$ away from the one of opposite spin in b_{3g} , which is confined by symmetry to two ring carbon atoms. As a consequence of the localization of $2b_{1u}$, $1b_{1u}$ is confined largely to the ring carbon atoms; in fact, it resembles closely the lowest MO in cyclobutadiene. In contrast, the b_{1u} MOs in the triplet are much more delocalized. The doubly occupied $1b_{2g}$ MO is almost identical in both states, consisting essentially of an out-of-phase combination of two ethylene bonding MOs. The bonding in the $^1B_{2u}$ state may, therefore, be crudely represented by the two resonance structures in **1**. The bonding in $^3B_{1u}$, being more delocalized, is harder to represent pictorially.



In addition to the $^1B_{2u}$ configuration, in which $2b_{1u}$ and b_{3g} are singly occupied, there exist 1A_g configurations in which each nonbonding MO is doubly occupied. As discussed previously,¹ the two configurations mix to give a low-lying 1A_g state of the form

$$^1A_g = |\dots 1b_{1u}^2 1b_{2g}^2 2b_{1u}^2\rangle - c |\dots 1b_{1u}^2 1b_{2g}^2 b_{3g}^2\rangle \quad (1)$$

This two-configuration wave function largely localizes one electron at each of the two ring atoms not adjacent to an exocyclic methylene group. Thus, the bonding in the 1A_g state may be approximated by **2**.

The similarity between the two lowest singlet states in DM CBD and trimethylenemethane (TMM) is apparent in comparing **1** and **2** with the representations of the bonding in the lowest singlets of TMM.² However, there are some important differences between the molecules. In TMM the Hückel nonbonding MOs are degenerate by symmetry; in DM CBD they are only accidentally degenerate. Indeed, as discussed previously,¹ the degeneracy of the nonbonding MOs

in DM CBD is lifted in going beyond the simplifications of Hückel theory. Consequently, the two configurations in eq 1 have unequal coefficients ($c \neq 1$). Moreover, the absence of degenerate representations from the D_{2h} point group, to which DM CBD belongs, means that there is no fixed set of geometries at which $^1B_{2u}$ and 1A_g must have the same energy. This contrasts, of course, with the situation in TMM where the two lowest singlets are required by symmetry to be degenerate at all D_{3h} geometries, since together they form a basis for the $^1E'$ representation of the D_{3h} point group.

Because of the lifting of the Hückel degeneracy of the two nonbonding MOs in DM CBD, we expected that 1A_g would lie below $^1B_{2u}$. However, at the assumed geometry (all C-C bond lengths set equal to 1.41 Å) where we carried out our initial calculations,¹ we found the reverse to be true. This suggested that at some set of points intermediate between this geometry and the 1A_g minimum, a crossing of the $^1B_{1u}$ and 1A_g states would be encountered. Our interest in the behavior of potential surfaces around such points of intersection,²⁻⁴ coupled with a desire to locate the $^3B_{2u}$, $^1B_{2u}$, and 1A_g minima and to establish their relative energies, led to this study.

Results and Discussion

D_{2h} Geometries. SCF calculations were carried out with D_{2h} symmetry constraints, using an STO-3G basis set,⁵ for the lowest $^3B_{2u}$ and $^1B_{2u}$ configurations, as well as for the two 1A_g configurations in eq 1. The resulting MOs were used to form matrices for complete π -space CI calculations. The results of such calculations should be independent of the set of π MOs used; however, the results will depend on the electron distribution in the σ core, which is established at the SCF level. It was found that SCF calculations on either 1A_g configuration gave the worst CI energies, even for the lowest 1A_g state. This was not surprising since an adequate 1A_g wave function requires two Slater determinants (eq 1), and it was anticipated that a single determinantal 1A_g SCF wave function would probably contain a severely distorted σ core. The MOs from the $^3B_{2u}$ and $^1B_{2u}$ SCF calculations gave the same CI energies to within 0.0001 hartree for the $^3B_{2u}$ state and also for the $^1B_{2u}$ state. Nevertheless, the MOs from the $^3B_{2u}$ SCF calculation gave a slightly better CI energy for the 1A_g state than those from the $^1B_{2u}$ SCF. Consequently, only the CI results using the MOs from the triplet SCF calculations are reported here.

In order to find the minimum energy geometry for each state, the C-C bond lengths internal and external to the ring were varied. A standard geometry about the methylene groups was assumed with the C-H bond lengths fixed at 1.10 Å and the H-C-H angles at 120°. The four-membered ring was kept planar, but the effect of changing the ring angles from 90° was

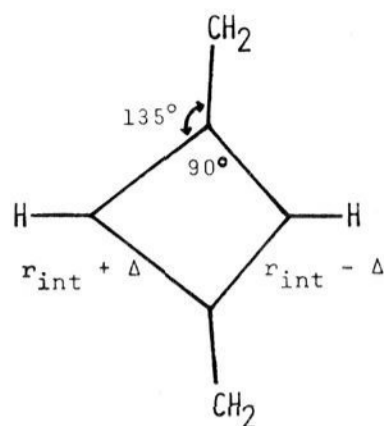


Figure 1. Effect of a b_{2u} distortion on DMCBD.

Table I. Optimized D_{2h} Geometries and CI Energies

State	r_{int} , Å	r_{ext} , Å	Energy, kcal/mol ^a
$^3B_{2u}$	1.471	1.374	0
$^1B_{2u}$	1.451	1.427	35.2
1A_g	1.506	1.342	23.6

^a Relative to $^3B_{2u}$, $E = -227.8257$ hartrees.

investigated at a point near the 1A_g minimum. For distortions of the ring angles by $\pm 5^\circ$, the energies of all the states increased. However, some asymmetry was noted in the energy changes, the increases being largest when the bond angles at C-1 and C-3 were widened to 95° , moving these two carbons closer together. This asymmetry is probably due to the fact that the doubly occupied $1b_{2g}$ MO is strongly antibonding between these two carbons. The 1A_g state showed the largest asymmetry. Cross-ring π bonding between C-2 and C-4, which are moved apart on opening the angles of C-1 and C-3 to 95° and brought closer on decreasing these angles to 85° , would be expected to be strongest in this state. The asymmetry in the energy increases on ring bond angle changes of $\pm 5^\circ$ indicated that the optimal angles were not exactly 90° and, moreover, were different for different states. Nevertheless, it was also clear that the C-1 and C-3 ring bond angles for all the states were within the range $91 \pm 1^\circ$, so that it seemed pointless to carry out the rest of the geometry optimization with different angles for each state. Keeping all the bond angles at 90° for each state allowed a single SCF calculation on $^3B_{2u}$ to be used to generate the CI matrices for all three states. From the CI energies the optimal internal and external C-C bond lengths were found for each state, assuming quadratic potentials to obtain the last significant figure. The results are shown in Table I.

The optimized geometries for the two singlet states are consistent with the depiction in **1** and **2** of the bonding in them. The internal and external C-C bonds in $^1B_{2u}$ are nearly the same length and about halfway between the lengths of double and single bonds. The external bonds in 1A_g are about the length of double bonds, although the internal ring bonds are slightly shorter than expected for pure single bonds. This shortening suggests that in 1A_g there is actually some weak π bonding between the ring carbon atoms, analogous to that found between the central and the symmetry equivalent pair of carbons in the 1A_g state of TMM.² The bond lengths in the $^3B_{2u}$ state are intermediate between the corresponding ones in the two lowest singlets, but slightly shorter than the numerical average of those in the singlets. In this respect a parallel with TMM is again noted.

Inspection of Table I shows that $^3B_{2u}$ is the ground state of DMCBD and that the energy of the 1A_g minimum is, indeed, lower than that of the $^1B_{2u}$. However, at the $^1B_{2u}$ minimum the 1A_g state lies 3.8 kcal/mol above $^1B_{2u}$. Therefore, these two states must have the same energy at some set of D_{2h} geometries

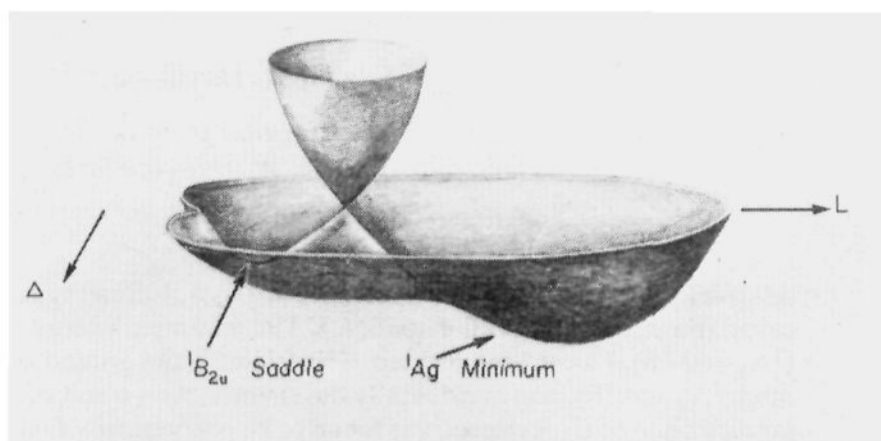


Figure 2. Schematic potential surface for 1A_1 DMCBD as a function of Δ and L .

between the 1A_g and $^1B_{2u}$ minima. By varying the internal and external C-C bond lengths, the points were located at which the two states are accidentally degenerate. The points were found to lie approximately on a straight line passing through the geometries (internal, external) = (1.450, 1.408 Å) and (1.460, 1.418 Å). Calculation of the energy of points along this line showed that the minimum energy occurred at (1.458, 1.416 Å). This point also lies on the straight line joining the 1A_g and $^1B_{2u}$ minima. At this point the energy of the two states is only 0.3 kcal/mol above that at the $^1B_{2u}$ minimum, but a pathway through this point is not the lowest energy route from the $^1B_{2u}$ to the 1A_g minimum.

Distortions to C_{2v} Geometries. Group theory shows that a distortion of b_{2u} symmetry is capable of mixing states of A_g and B_{2u} symmetry. The effect of this distortion is to lengthen both C-C bonds to C₂ and to shorten those to C₄ by the same amount, as shown in Figure 1. This reduces the symmetry to C_{2v} , with the twofold axis passing through C-2 and C-4. Both A_g and B_{2u} in the D_{2h} point group correlate with A_1 of C_{2v} , which is why mixing can occur between them. Since at (1.458, 1.416 Å) 1A_g and $^1B_{2u}$ are degenerate, mixing between these states should be linear in a b_{2u} distortion coordinate and provide a lower energy pathway from the $^1B_{2u}$ to the 1A_g minimum than one that preserves D_{2h} symmetry. This is illustrated schematically in Figure 2. A parallel is noted with the Jahn-Teller effect,⁶ which in TMM lifts the symmetry enforced degeneracy of the 1A_1 and 1B_2 components of $^1E'$ by allowing them to mix.² In fact, the b_{2u} distortion that lifts the accidental degeneracy of $^1B_{2u}$ and 1A_g in DMCBD may also be considered a first-order Jahn-Teller effect.

In order to investigate the Jahn-Teller effect in DMCBD, we studied b_{2u} distortions as a function of two parameters. One of these, Δ , is the magnitude of the b_{2u} distortion (Figure 1). The other, L , defines the D_{2h} geometry along the line joining the 1A_g and $^1B_{2u}$ minima.

Some care had to be taken in relaxing the D_{2h} symmetry constraints on the wave functions for it sometimes happens that, on reducing the symmetry required of an SCF wave function, solutions of broken symmetry appear at undistorted geometries.^{2,4} This can introduce discontinuities into the calculated energies. For example, when only C_{2v} symmetry is required of the DMCBD wave function, the $^1B_{2u}$ SCF solution might be expected to be unstable at D_{2h} geometries where 1A_g is lower in energy. The 1A_g wave function in eq 1 can be factored¹ as

$$^1A_g = |\dots 1b_{1u}^2 1b_{2g}^2 (2b_{1u} + \sqrt{c} b_{3g}) \times (2b_{1u} - \sqrt{c} b_{3g})(\alpha\beta - \beta\alpha)\rangle \quad (2)$$

In C_{2v} symmetry this becomes an open-shell 1A_1 wave function

$$^1A_1 = |\dots 1b_{1u}^2 1a_2^2 2b_1 3b_1(\alpha\beta - \beta\alpha)\rangle \quad (3)$$

Table II. Effect of C_{2v} Distortions on the Lowest Singlet State

r_{int}	r_{ext}	Δ (Å) = 0	0.01	0.02	0.03	0.04
1.458	1.416 ^a	-227.7691 ^d	-227.7719	-227.7738	-227.7747	-227.7747
1.451	1.427 ^b	-227.7696	-227.7705	-227.7718	-227.7725	-227.7723
1.506	1.342 ^c	-227.7881	-227.7878			

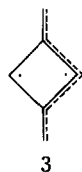
^a Crossing of 1A_g and ${}^1B_{2u}$. ^b ${}^1B_{2u}$ minimum. ^c 1A_g minimum. ^d Energies in hartrees.

which has the same form as that assumed by the ${}^1B_{2u}$ SCF wave function when the symmetry imposed on the MOs is reduced to C_{2v} . Therefore, in regions where 1A_g lies below ${}^1B_{2u}$ a C_{2v} constrained open-shell SCF calculation would probably converge to the 1A_g SCF wave function. Since this SCF wave function has a different σ core than that for ${}^1B_{2u}$, the CI energy for the ${}^1B_{2u}$ state would not be the same as that computed with a D_{2h} symmetry constrained SCF calculation on ${}^1B_{2u}$.

The occurrence of this phenomenon was verified at the D_{2h} geometry (internal, external) = (1.460, 1.370 Å). Unless $c = 1$, the factorization in eq 2 requires that $2b_1$ and $3b_1$ in eq 3 be allowed to be nonorthogonal. Therefore, a nonorthogonal SCF program was used, with only C_{2v} symmetry imposed on the open-shell 1A_1 wave function. The resulting MOs are shown in Figure 3. As can be seen, the $2b_1$ and $3b_1$ MOs are mirror images of each other; so the SCF wave function does, in fact, have 1A_g symmetry in D_{2h} . The SCF energy was -227.6960 hartrees, lower by 0.0656 hartree than the D_{2h} symmetry constrained ${}^1B_{2u}$ solution.⁷

When the MOs from the nonorthogonal open-shell SCF calculation were used to carry out full π -space CI, as expected, ${}^1B_{2u}$ was found to be significantly higher in energy than when the MOs from D_{2h} symmetry constrained ${}^1B_{2u}$ or ${}^3B_{2u}$ SCF calculations were employed. Surprisingly, however, the CI energy of 1A_g was also found to be slightly higher than when ${}^3B_{2u}$ SCF MOs were used. Obviously, the set of σ MOs from the D_{2h} constrained ${}^3B_{2u}$ SCF calculation must be more appropriate for the 1A_g CI wave function than those from the nonorthogonal, C_{2v} constrained, SCF calculation on the open-shell 1A_1 state. Since it was also found that triplet SCF calculations gave the same set of MOs, whether the calculations were carried out with D_{2h} or C_{2v} symmetry constraints, the lowest triplet was the obvious configuration to use to define SCF MOs for CI calculations at C_{2v} geometries.

Table II lists some of the CI results for DMCBD at C_{2v} geometries. For the series that begins at the minimum energy D_{2h} geometry where 1A_g and ${}^1B_{2u}$ are degenerate (1.458, 1.416 Å), for small Δ (<0.01) the drop in energy appears linear in Δ , as expected. At larger Δ a second-order term with positive coefficient is evident, leading to a minimum at $\Delta = 0.035$ Å and a net energy lowering of 3.6 kcal/mol upon distortion. The optimized distorted geometry suggests that the wave function here may be roughly described as that for a pentadienyl radical plus an electron localized in a p orbital (3).



At the ${}^1B_{2u}$ minimum (1.451, 1.427 Å) the two D_{2h} states are not degenerate. Therefore, the initial drop on distortion to C_{2v} symmetry appears quadratic in Δ , as expected of a second-order Jahn-Teller effect.⁸ The energy drop on distortion is 1.8 kcal/mol at an optimum $\Delta = 0.033$ Å. Although the optimized ${}^1B_{2u}D_{2h}$ geometry is a relative minimum in the coordinate L , it is obviously not a minimum in Δ . Thus, the ${}^1B_{2u}$ "minimum" is actually a saddle point on the lowest 1A_1 (C_{2v}) potential surface. This is illustrated in Figure 2. The 1A_g

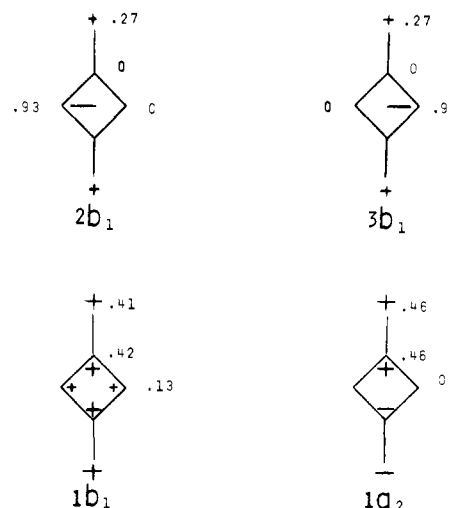


Figure 3. The four lowest π MOs of 1A_1 (1A_g in D_{2h} symmetry) DMCBD, obtained from an SCF calculation in which $2b_1$ and $3b_1$ were allowed to be nonorthogonal.

minimum does, however, represent a true global minimum, as indicated by the third line of Table II, which shows an energy increase on distortion from (1.506, 1.342 Å).

A Generalized Treatment of Jahn-Teller Effects. We have found that the complicated behavior of the energy as a function of Δ and L in DMCBD can be reproduced by a simple, parametrized, two-state interaction model. Consider two states, A and B, with energies given by

$$H_{AA}(\Delta, L) = E_A(0, L) + k_A \Delta^2 \quad (4)$$

$$H_{BB}(\Delta, L) = E_B(0, L) + k_B \Delta^2 \quad (5)$$

In DMCBD $E_A(0, L)$ and $E_B(0, L)$ correspond to the energies of the D_{2h} 1A_g and ${}^1B_{2u}$ states. The energies of the unmixed states, A and B, are assumed to increase quadratically with Δ , since their energies must, by symmetry, be even functions of Δ . The off-diagonal element that mixes A and B is, as required by the Jahn-Teller theorem,⁶ assumed to be linear in Δ .

$$H_{AB}(\Delta) = k_{AB} \Delta \quad (6)$$

For the sake of simplicity we have assumed H_{AB} to be independent of L , although this certainly need not be the case. Diagonalizing the two-state interaction matrix gives

$$E = (E_A + E_B)/2 + (k_A + k_B)\Delta^2/2 \pm \{[(E_A - E_B) + (k_A - k_B)\Delta^2]^2/4 + k_{AB}^2\Delta^2\}^{1/2} \quad (7)$$

Immediately one can see that the sum of the roots will increase with Δ in exactly the same manner as the average of diagonal elements. Therefore, if the lowest root decreases in energy with Δ , the upper root will increase much more rapidly. This is shown in Figure 2 and was evident in our calculations on not only DMCBD, but also a variety of other molecules.^{2,4}

Further discussion of eq 7 is simplified by assuming that $k_A = k_B$. At a point in L where states A and B are degenerate, whether by symmetry (TMM) or by accident (DMCBD), $E_A = E_B = E_0$, and the lowest root of eq 7 is

$$E = E_0 + k_A \Delta^2 - k_{AB} \Delta \quad (8)$$

For small Δ the linear term will dominate, but at large Δ the quadratic term will. A minimum will occur at

$$\Delta = k_{AB}/2k_A \quad (9)$$

If k_A is much larger than k_{AB} , then the minimum will occur very close to the undistorted geometry. We encountered such a case in TMM where for very modest e' distortions of the bond angles from D_{3h} symmetry, the energy of both components of $^1E'$ was found to increase.²

Even if for some value of L the two states, A and B, are degenerate, at other undistorted geometries E_A will not equal E_B . Then, assuming $E_A < E_B$, for small Δ the lowest root of eq 7 may be written

$$\begin{aligned} E &= (E_A + E_B)/2 + k_A \Delta^2 - \frac{1}{2} (E_B - E_A) \\ &\quad \times (1 + 4k_{AB}^2 \Delta^2 / (E_A - E_B)^2)^{1/2} \\ &= E_A + [k_A - k_{AB}^2 / (E_B - E_A)] \Delta^2 + \dots \quad (10) \end{aligned}$$

A similar expression has previously been derived for the second-order Jahn-Teller effect.⁸ Equation 10 shows that whether distortion lowers the energy of E_A depends on the sign of the term in brackets. Obviously, the closer E_B is to E_A , the greater the likelihood that distortion will be energetically favorable. When distortion is favorable, the energy lowering will initially be quadratic in Δ . The value of Δ at the energy minimum, assuming that this does not occur at $\Delta = 0$, may be obtained by differentiation of eq 7. This gives

$$\Delta = \pm \frac{1}{2} \left(\frac{k_{AB}^2}{k_A^2} - \frac{(E_A - E_B)^2}{k_{AB}^2} \right)^{1/2} \quad (11)$$

In the specific case of DM CBD a satisfactory fit to the calculated potential surface near the D_{2h} crossing was obtained with the parameters $k_A = 4.0$ hartrees/ \AA^2 , $k_B = 5.2$ hartrees/ \AA^2 , and $k_{AB} = 0.34$ hartrees/ \AA . It is not surprising that the quadratic force constant for b_{2u} ring bond distortion in the 1A_g state is smaller than that in $^1B_{2u}$; for, as indicated by **1** and **2**, the ring bonds in the former state are weaker than those in the latter. In a molecule like DM CBD, where $k_A \neq k_B$, eq 9 and 11 become rather more complicated. However, for small Δ eq 8 changes only in the replacement of k_A by $(k_A + k_B)/2$, and eq 10 remains the same. Equation 10 shows that in the region where $E_A < E_B$ distortion will lower the energy only if

$$(E_B - E_A) < k_{AB}^2/k_A \quad (12)$$

Using the above values of k_{AB} and k_A , distortion is predicted to result in energy lowering for values of $(E_B - E_A) < 0.029$ hartree. At the D_{2h} geometry (1.465, 1.405 \AA) $^1B_{2u}$ lies 0.0066 hartree above 1A_g . Therefore distortion is expected to be en-

ergetically favorable; and, in fact, the energy drops 1.7 kcal/mol at an optimum value of $\Delta = 0.34$ \AA . However, at the 1A_g minimum, $^1B_{2u}$ lies 0.0456 hartree above 1A_g ; so distortion is predicted to be energetically costly, as the last line of Table II shows it to be.

Conclusions

There are three reasonable ways to confine two electrons of opposite spin to disjoint sets of atoms in DM CBD.⁹ These modes are crudely portrayed in structures **1-3**. The wave functions whose bonding is represented in **1-3** all lie on the same singlet potential surface. The D_{2h} $^1B_{2u}$ wave function corresponding to **1** is a saddle point, while the 1A_g state corresponding to **2** is the only minimum. Wave functions with bonding of the pentadienyl plus p type (**3**) provide pathways of lower energy from the saddle point to the minimum than routes that preserve D_{2h} symmetry. The important features of the potential surface can be reproduced by a two-state model that should provide a generally valid description of Jahn-Teller effects engendered by crossings (first-order effects)⁶ and near crossings (second-order effects)⁸ of potential curves.

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References and Notes

- (1) W. T. Borden and E. R. Davidson, *J. Am. Chem. Soc.*, **99**, 4587 (1977).
- (2) E. R. Davidson and W. T. Borden, *J. Am. Chem. Soc.*, **99**, 2053 (1977), and references cited therein.
- (3) E. R. Davidson, *J. Am. Chem. Soc.*, **99**, 397 (1977).
- (4) C. F. Jackels and E. R. Davidson, *J. Chem. Phys.*, **64**, 2908 (1976); **65**, 2941 (1976); E. R. Davidson and W. T. Borden, *ibid.*, **67**, 2191 (1977).
- (5) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).
- (6) H. A. Jahn and E. Teller, *Proc. R. Soc. London, Ser. A*, **161**, 220 (1937).
- (7) When the $2b_1$ and $3b_1$ MOs were required to be orthogonal, the open-shell 1A_1 SCF calculation failed to converge. Nevertheless, the small overlap of 0.16 between the $2b_1$ and $3b_1$ MOs obtained from the nonorthogonal SCF calculation suggests that the energy of the orthogonal SCF solution might be similar to that of the nonorthogonal one.
- (8) R. G. Pearson, *J. Am. Chem. Soc.* **91**, 4947 (1969), and references cited therein.
- (9) Since the π system of DM CBD can be constructed by union of those of two allyl radicals,¹ this suggests another possible localization. The required distortion is b_{1g} in D_{2h} symmetry. It mixes 1A_g with a state of $^1B_{1g}$ symmetry. The lowest such state differs from $^1B_{2u}$ only by the replacement of the singly occupied $2b_{1u}$ MO by $2b_{2g}$. Although $2b_{2g}$ is an out-of-phase combination of two antibonding ethylene π MOs, $^1B_{1g}$ is, nevertheless, relatively low in energy, lying about 45 kcal/mol above 1A_g at the equilibrium geometry of the latter. The reason for the energetic proximity is that, by symmetry, $2b_{2g}$ is zero at the two ring carbons to which the unpaired electron that occupies b_{3g} is confined. We have found some geometries quite far from the 1A_g minimum at which 1A_g approaches $^1B_{1g}$ in energy. However, at these D_{2h} geometries the lowest energy wave function is $^1B_{2u}$; therefore, we have not bothered to investigate the possible b_{1g} distortion that would mix 1A_g with $^1B_{1g}$ and lead to a wave function resembling that for two allyl radicals.