reference polynomial in analyzing aromaticity even in such large conjugated systems as polycyclic benzenoid hydrocarbons. Several energetic relationships found in comparisons with other aromaticity theories have provided a wide basis for further understanding the physical and topological aspect of A-II resonance energies. At the same time, the related theories of aromaticity for benzenoid hydrocarbons have been more strongly supported by these relationships.

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Some Aspects of the Potential Surface for Singlet Trimethylenemethane

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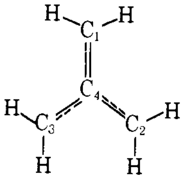
Abstract: The potential surface for bond length variations in singlet trimethylenemethane has been explored by ab initio calculations, employing an STO-3G basis set and including full π space CI. The effects of angle distortions at the central carbon atom, methyl substitution, and twisting of a methylene group by 90° to the orthogonal geometry have also been determined. The design of a trimethylenemethane derivative, in which a planar geometry would be lower in energy than an orthogonal one for the singlet, is discussed.

In previous papers we have discussed the wave functions for the $^1\mathrm{E}'$ state of D_{3h} (planar, all C–C bond lengths and bond angles equal) trimethylenemethane.[1,2] We showed that while the π bonding in the $^3\mathrm{A}_2'$ ground state is necessarily fully delocalized, as represented in **1**, the bonding in the two components of the $^1\mathrm{E}'$ state is more localized,[1,3] as represented in **2** and **3**. The particular choice[4] of $^1\mathrm{E}'$ wave functions implicit in **2** and **3** allows the wave functions to be classified according to their symmetry in the C_{2v} point group, and we will refer to the wave functions by the representation of C_{2v} to which they belong. Thus, the wave function of **2**, which is essentially that of an allyl radical plus an electron localized in a p orbital, we call the $^1\mathrm{B}_2$ wave function. The wave function of **3**, which can be crudely described as an ethylene interacting *weakly*[5] with a diradical, we denote as $^1\mathrm{A}_1$.



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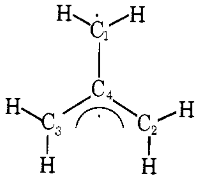

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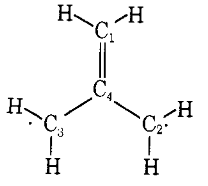

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It is clear from inspection of the bonding in **1–3** that, while the $^3\mathrm{A}_2'$ ground state of trimethylenemethane may prefer a D_{3h} geometry, the two components of the $^1\mathrm{E}'$ state will not. The $^1\mathrm{B}_2$ component will have its energy minimum at a geometry in which the C_1–C_4 bond is longer than the $C_{2(3)}$–C_4 bonds. In contrast, the $^1\mathrm{A}_1$ wave function will prefer a geometry in which the C_1–C_4 bond is shorter than the $C_{2(3)}$–C_4 bonds. In this paper we report the results of ab initio calculations on the optimum geometries and relative energies of the $^1\mathrm{B}_2$ and $^1\mathrm{A}_1$ wave functions, and we discuss pseudorotation in planar singlet trimethylenemethane, the process by which, for instance, C_2 replaces C_1 as the unique peripheral carbon atom. We also report the results of calculations on the effect of substituents on the relative energies of the $^1\mathrm{B}_2$ and $^1\mathrm{A}_1$ wave functions and the consequences of twisting one methylene group 90°, so that its p orbital is orthogonal to the rest of the π system of trimethylenemethane.

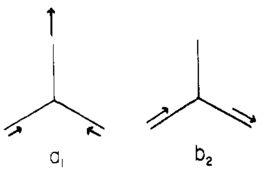


Figure 1. Bond length distortions of e′ symmetry in trimethylenemethane.

Theoretical Considerations

The type of bond length change, described above, which lifts the D_{3h} degeneracy of the $^1B_2$ and $^1A_1$ wave functions, is one of a degenerate pair of e′ nuclear displacements. The phase of this distortion from D_{3h} symmetry that lengthens the C_1-C_4 bond and shortens the $C_{2(3)}$-C_4 bonds is shown in Figure 1. In the other phase of the same distortion the change in the bond lengths is just the opposite. These nuclear displacements have a_1 symmetry in C_{2v}. The second component of the degenerate pair of displacements belongs to b_2 in C_{2v} and shortens one of the $C_{2(3)}$-C_4 bonds while lengthening the other by the same amount. The b_2 component, also shown in Figure 1, does not significantly affect the energy of the $^1B_2$ and $^1A_1$ electronic wave functions. However, it destroys the C_{2v} symmetry, under which the two wave functions belong to different representations, thus allowing them to mix. The two wave functions that result from the mixing are no longer degenerate. The lifting of the degeneracy of the two components of the $^1E'$ electronic state by nuclear displacements of e′ symmetry is, of course, predicted by the Jahn-Teller theorem.[6] Indeed, similar symmetry arguments[7] can be used to show why the a_1 nuclear displacement, without mixing $^1B_2$ and $^1A_1$, causes a first-order lifting of the degeneracy between these components of $^1E'$ trimethylenemethane and why the b_2 displacement, by mixing the $^1B_2$ and $^1A_1$ wave functions, also results in a lifting of the degeneracy that is directly proportional to the amount by which the nuclei are displaced from D_{3h} symmetry.

Mathematically, the two nuclear displacements that are shown in Figure 1 can be expressed as

$$a_1 = \pm \frac{\Delta r}{6^{1/2}} (2\hat{r}_{14} - \hat{r}_{24} - \hat{r}_{34}) \tag{1}$$

$$b_2 = \pm \frac{\Delta r}{2^{1/2}} (\hat{r}_{24} - \hat{r}_{34}) \tag{2}$$

where Δr is the magnitude of the distortion from D_{3h} symmetry and $\hat{r}_{i4}$ is a unit vector pointing from C_4 to C_i. Since these displacements form a degenerate pair in D_{3h}, for a fixed value of Δr they have the same first order effect in lifting the degeneracy of the $^1B_2$ and $^1A_1$ states. Any other e′ distortions can be expressed as linear combinations of eq 1 and 2

$$e_x' = a_1 \cos\theta + b_2 \sin\theta \tag{3}$$

$$e_y' = a_1 \sin\theta - b_2 \cos\theta \tag{4}$$

For a fixed value of Δr, these linear combinations have the same first order effect as a_1 and b_2 on lifting the D_{3h} degeneracy.

Although the sine and cosine functions of θ are introduced in eq 3 and 4 to preserve orthonormality, we now show that θ, in fact, defines a pseudorotation angle in Jahn-Teller distorted planar trimethylenemethane. If r_0 is the optimum average C-C bond length in the $^1E'$ state, then the lengths of the three C-C bonds for any Jahn-Teller, e_x', distortion can be obtained from eq 1-3 as

$$r_{14} = r_0 + \frac{2}{6^{1/2}} \Delta r \cos\theta \tag{5}$$

$$r_{24} = r_0 + \Delta r \left(\frac{1}{2^{1/2}} \sin\theta - \frac{1}{6^{1/2}} \cos\theta\right) \tag{6}$$

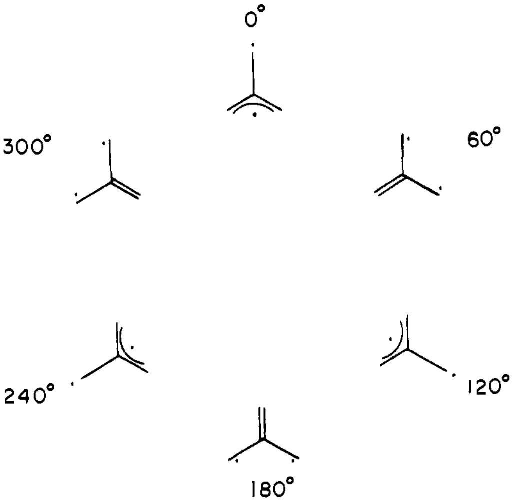


Figure 2. Pseudorotation in singlet trimethylenemethane.

$$r_{34} = r_0 - \Delta r \left(\frac{1}{2^{1/2}} \sin\theta + \frac{1}{6^{1/2}} \cos\theta\right) \tag{7}$$

Note that

$$\sum_{i=1}^{3} (r_{i4} - r_0)^2 = (\Delta r)^2 \tag{8}$$

Equations 6 and 7 can be transformed into cosine functions, which differ from (5) only by phase factors of ±120°. Using the identities

$$\frac{1}{2^{1/2}} \sin\theta = \frac{2}{6^{1/2}} \sin 120° \sin\theta \tag{9}$$

$$\frac{1}{6^{1/2}} \cos\theta = \frac{-2}{6^{1/2}} \cos 120° \cos\theta \tag{10}$$

and the trigonometric products to sums formula, (6) and (7) can be rewritten as

$$r_{24} = r_0 + \frac{2}{6^{1/2}} \Delta r \cos(\theta - 120°) \tag{11}$$

$$r_{34} = r_0 + \frac{2}{6^{1/2}} \Delta r \cos(\theta + 120°) \tag{12}$$

Equations 5, 11, and 12 show that planar singlet trimethylenemethane can travel from one Jahn-Teller distorted geometry to another, without ever passing through a D_{3h} configuration, by varying its C-C bond lengths about r_0 as a function of cos θ, with each bond 120° out of phase from the other two.[8] That, for fixed Δr, this constitutes pseudorotation of trimethylenemethane is apparent in Figure 2, where r_{14}, r_{24}, and r_{34} are shown schematically at 60° intervals of θ.

The relationships, graphically revealed in Figure 2, between various Jahn-Teller distorted geometries of trimethylenemethane, enable one to understand more clearly the nature of the wave function for the planar molecule. Although the $^1B_2$ and $^1A_1$ wave functions are degenerate at D_{3h} geometries, at a pseudorotation angle of 0° $^1B_2$ is expected to lie below $^1A_1$, when $\Delta r \neq 0$, since one bond is lengthened and two are shortened. At $\theta = 60°$, however, a $^1A_1$ wave function with C_3 as the unique peripheral atom is anticipated to lie below the corresponding $^1B_2$, since now one bond is shortened with respect to the other two. The fact that the lowest energy wave function changes symmetry labels on pseudorotation by 60° should not delude one into thinking that there is a crossing between two potential curves somewhere in between, for it must be emphasized that the labeling at 0 and 60° is done with respect to *different* C_{2v} symmetry elements. At angles between 0 and 60° the only element of symmetry is the molecular plane,

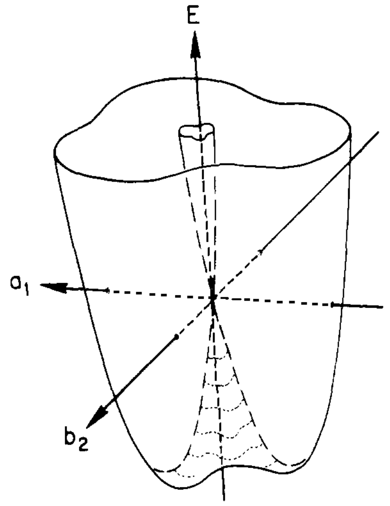


Figure 3. Schematic potential surface for pseudorotation in singlet trimethylenemethane.

with respect to which all the π wave functions remain symmetric. Therefore, there is no crossing of potential curves on pseudorotation;[9] in fact, only at D_{3h} geometries is there a branch cut.[10] This is illustrated in the schematic potential surface shown in Figure 3[8] for Jahn-Teller distortions in trimethylenemethane.

The symmetry manifested in Figure 2 greatly simplifies the actual computation of a potential surface like the one shown in Figure 3. Figure 2 reveals that distorted trimethylenemethane has S_3 permutational symmetry. Except for the special angles 0, 60, 120, 180, 240, and 300°, where two bond lengths are equal, the geometry at each value of θ corresponds to five others, indistinguishable from it except for the numbers arbitrarily assigned to the peripheral carbons. Because of the S_3 permutational symmetry of trimethylenemethane on pseudorotation, the potential surface for this process has the symmetry of the isomorphous C_{3v} point group (see Figure 3). Consequently, calculations need only be carried out for values of θ from 0 to 60°.

Results

In order to define the most interesting part of the potential surface for planar trimethylenemethane, which lies along the trough in the lower energy sheet of Figure 3, we have optimized the geometry for planar trimethylenemethane at three values of the pseudorotation angle, θ = 0, 30, and 60°. C-H bond lengths were held fixed at 1.10 Å, and all bond angles were kept at 120°. The optimizations at 0 and 60° were carried out by finding the two geometries of minimum energy when the molecule was constrained to have C_{2v} symmetry. A similar variation of two bond length parameters was necessary to locate the geometry of minimum energy at θ = 30°. At this angle the distortion has b_1 symmetry with C_2 as the unique atom. Therefore, in this case, one of the parameters optimized was the length of the C_2-C_4 bond, which is not affected by the b_1 displacement. The other parameter optimized was the magnitude of the deviation of the $C_{1(3)}$-C_4 bond lengths from the C_2-C_4 bond length.

Full π space CI calculations, using a basis set of STO-3G orbitals, were carried out as described previously.[1] Molecular orbitals were defined by restricted Hartree-Fock calculations[11] on the triplet state. These MO's were then used to construct the CI matrices for the $^1B_2$ and $^1A_1$ states for the calculations at θ = 0 and 60°. For the calculation at 30°, of course, no symmetry could be employed to partition the CI matrix. The CI matrix for the triplet was also formed and diagonalized. It was found that the triplet has its minimum energy at a D_{3h} geometry[12] with r_{i4} = 1.429 Å. The optimized geometries and energies, relative to that (−153.0294 hartrees) of the D_{3h} $^3A_2'$ state, are shown in Table I. The energies calculated for the corresponding points on the upper singlet potential sheet (see Figure 3) are also shown in Table I.

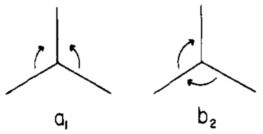


Figure 4. Bond angle distortions of e′ symmetry in trimethylenemethane.

Table I. Optimized Singlet Geometries and Energies in Planar Trimethylenemethane

θ, deg	r_{14}[a]	r_{24}	r_{34}	Energy (1)[b]	Energy (2)[c]
0	1.540	1.402	1.402	22.15[d]	50.39[e]
30	1.530	1.448	1.366	21.71	51.58
60	1.497	1.497	1.355	21.34[e]	53.53[d]
D_{3h}	1.446	1.446	1.446	29.35	29.35

[a] Bond lengths in Å. The last significant figure was extrapolated by fitting to a quadratic potential. [b] Energy of the lowest singlet surface in kcal/mol, relative to that (−153.0294 hartrees) of the optimized D_{3h} triplet (r_{i4} = 1.429 Å). [c] Energy of the upper singlet surface relative to that of the optimized D_{3h} triplet. [d] $^1B_2$ wave function. [e] $^1A_1$ wave function.

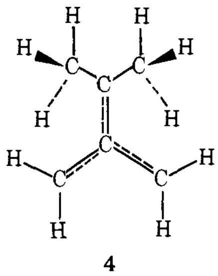
Table II. Effect of Bond Angle Distortions on $^1B_2$ and $^1A_1$ Wave Functions in Planar Trimethylenemethane[a]

C_2-C_4-C_3 angle, deg	C_1-C_4-$C_{2(3)}$ angle, deg	$E(^1B_2)$[b]	$E(^1A_1)$[b]
110	125	3.71	3.31
130	115	3.42	3.15

[a] Bond lengths all fixed at their optimized D_{3h} $^1E'$ value of r_{i4} = 1.446 Å. [b] Energy in kcal/mol relative to optimized D_{3h} singlet.

There are two other nuclear displacements in planar trimethylenemethane, which together also have e′ symmetry, but which effect changes in the bond angles at the central carbon atom (C_4). These are shown in Figure 4. Since, according to the Jahn-Teller theorem, these should also be capable of lifting the degeneracy between the $^1B_2$ and $^1A_1$ wave functions, we carried out calculations on these two states at two geometries in which the bond lengths were held at their optimum D_{3h} value and the C-C-C bond angles were allowed to vary. For computational simplicity and in order that $^1B_2$ and $^1A_1$ remained meaningful designations for the wave functions, two phases of the a_1 component of this e′ mode were examined, so that C_{2v} symmetry was preserved. The results are shown in Table II.

We also carried out calculations on two dimethyl derivatives, **4** and **5**, of planar trimethylenemethane in order to see what effect the substituents would have on the relative energies of the $^1B_2$ and $^1A_1$ wave functions. All the bond angles at the



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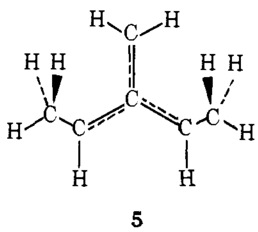

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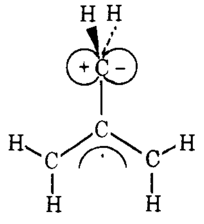
Table III. Energy of Trimethylenemethane and Dimethyl Derivatives

Molecule	r_{14}	$r_{24} = r_{34}$	$E(^1B_2)^b$	$E(^1A_1)^b$
2, 3	1.540	1.402	0.81	29.05
2, 3	1.355	1.497	32.19	0
4	1.540	1.402	0^c	29.49
4	1.355	1.497	33.61	4.57
5	1.540	1.402	3.58	30.06
5	1.355	1.497	33.41	0^d

[a] Bond lengths in Å. [b] Energies in kcal/mol relative to lowest calculated singlet state for each molecule. [c] π space CI energy = −230.1797 hartrees. [d] π space CI energy = −230.1805 hartrees.

methyl carbons were taken as 109.5°, and the methyl C–C and C–H bond lengths were fixed at 1.53 and 1.10 Å, respectively. For each substituted molecule full π space CI (864 and 900 configurations, respectively, for $^1B_2$ and $^1A_1$) calculations were carried out at the lowest energy geometries of the $^1B_2$ and $^1A_1$ states in the unsubstituted molecule. The calculated effect of dimethyl substituents on the relative energies is shown in Table III. To facilitate comparison, the corresponding energy differences for the unsubstituted molecule, computed from the data in Table I, are also shown in Table III.

Finally, we examined the energy gain on twisting one methylene group in planar singlet trimethylenemethane by 90°. Twisting one methylene group from conjugation has been widely discussed[2] as a mode by which the planar singlet might stabilize itself. Unfortunately, in orthogonal trimethylenemethane **6**, it is not at all clear what corresponds to the full π space CI that we carried out for the planar molecule. We considered carrying out CI for the electrons in the allylic π system; however, we found at the SCF level that the lowest and highest MO's of the allyl moiety contained small but not insignificant contributions from the antisymmetric combinations of localized C–H bonding and antibonding MO's of the methylene group. Therefore, because we were unable to define what would constitute the equivalent of full π space CI for orthogonal trimethylenemethane,[13] we had to content ourselves with comparing planar and orthogonal geometries at the SCF level.



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One set of SCF calculations[11] was carried out with all C–C bond lengths equal to 1.43 Å, which we estimate to be very near to the optimum D_{3h} geometry for the $^1B_2$ SCF wave function.[14] The bond lengths for the planar $^1B_2$ and the orthogonal $^1B_1$ state, with which it correlates, should really both be optimized at the SCF level, in order to obtain the most accurate SCF estimate of the energy difference between the two conformations. Nevertheless, because we anticipated that the optimum bond lengths for both planar and orthogonal geometries would be nearly the same and close to the bond lengths at the CI minimum for the planar $^1B_2$ state, we carried out the second calculation using this set of bond lengths for both geometries. The SCF results for singlet and triplet B states are shown in Table IV.[15] For comparison we have also included the CI results for the $^1B_2$ state.

Table IV. Energies of Planar and Orthogonal Trimethylenemethane

Geometry	r_{14}	$r_{24} = r_{34}$	$^1B(SCF)^b$	$^3B(SCF)^b$	$^1B_2(CI)^c$
Planar	1.430	1.430	27.25	1.06	29.80
Orthogonal	1.430	1.430	22.71	20.89	
Planar	1.540	1.402	19.43	5.06	22.15
Orthogonal	1.540	1.402	16.88	15.70	

[a] Bond lengths in Å. [b] Energy relative to that (−152.9670 hartrees) of the D_{3h} $^3A_2'$ state optimized at the SCF level (r_{i4} = 1.408 Å). [c] Energy relative to that (−153.0294 hartrees) of the D_{3h} $^3A_2'$ state optimized at the CI level (r_{i4} = 1.429 Å).

Table V. Values of Pseudorotation Parameters at Optimized Geometries

θ, deg	$r_0{}^a$	$2\Delta r/6^{1/2}$
0	1.448	0.092
30	1.448	0.095
60	1.450	0.095
D_{3h}	1.446	

[a] Bond lengths in Å.

Discussion

From the data reported in Table I it is apparent that a Jahn-Teller distortion has a significant effect on lowering the energy of $^1E'$ trimethylenemethane. By dropping the energy of the singlet by 8.0 kcal/mol, the distortion decreases the singlet-triplet energy gap in the planar molecule from 29.35[16] to 21.34 kcal/mol. It is also clear that in the lowest singlet state the molecule will find it much easier to pseudorotate from one distorted geometry to another than to pass through D_{3h} symmetry. The minima in the trough of the lower potential sheet of Figure 3, which occur at θ = 60, 180, and 300°, lie only 0.8 kcal/mol below the maxima at θ = 0, 120, and 240°. Circumambulation around the trough is therefore predicted to be a facile process in singlet trimethylenemethane.

This, perhaps, might have been expected; since, as noted in the second section, the energy decrease on distortion away from D_{3h} symmetry is, to first order, independent of θ. If the energy lowering on distortion were totally independent of θ, not only would the bottom of the trough be completely flat, but the optimized distortion parameters, r_0 and Δr, would also be independent of θ. The extent to which this latter consequence actually obtains is shown in Table V.

If, to first order, the $^1B_2$ and $^1A_1$ wave functions should have exactly the same energy and optimized values for r_0 and Δr, then the fact that they do not must be due to a higher order effect. There exists in D_{3h} trimethylenemethane a relatively low-lying $^1A_1'$ state,[13,17] which can be mixed into the $^1E'$ state by a nuclear displacement of e′ symmetry. This is not, however, a first-order Jahn-Teller effect. Since $^1A_1'$ lies above $^1E'$ the energy lowering caused by their mixing occurs in second order.[18] As we have seen, there are two components of an e′ nuclear displacement, a_1 and b_2 in C_{2v} symmetry. The a_1 component of an e′ displacement can mix the $^1A_1$ but not the $^1B_2$ component of the E′ state with the excited $^1A_1'$ state.[19] The a_1 displacement that alters bond lengths distorts the molecule to θ = 0, 60, . . . , 300°. The fact that this distortion has not only a first but also a second order effect on lowering the energy of the $^1A_1$ wave function is probably the reason that this wave function at its optimized geometry at θ = 60, 180, 300° lies below $^1B_2$ at its optimized geometry at θ = 0, 120, 240°. Consistent with this explanation is the fact that the data in Table I also show the $^1A_1$ wave function on the upper potential sheet at 0, 120, 240° to lie below the $^1B_2$ wave function on this sheet at 60, 180, 300°. In this latter case the first order Jahn-Teller effect raises the energies of both these wave functions, which is, of course, why they lie on the upper sheet in Figure 3. However, the second order effect stabilizes $^1A_1$, causing it to lie lower than $^1B_2$ on this sheet. The observation that $^1A_1$ lies farther below $^1B_2$ on the upper than on the lower sheet is also consistent with an explanation in terms of a second order stabilization of $^1A_1$. Since the first order effect of the distortion moves $^1A_1$ on the upper sheet closer in energy to the excited $^1A_1'$ state, these two wave functions mix more strongly, and the energy lowering due to their mixing is greater.[18]

The $^1B_2$ wave function also undergoes a second order energy lowering on mixing with the same $^1A_1'$ excited state. In this case, however, the mixing is brought about by the b_2 component of the e′ nuclear displacement.[19] This component distorts the molecule to $\theta = 30, 90, \ldots, 330°$. At these angles the first order effect of this displacement is to mix $^1A_1$ and $^1B_2$ equally, so that the resulting wave function consists of only 50% of $^1B_2$. Thus, at these angles the energy lowering due to the second order effect is expected only to be approximately half as great as it is at the angles $\theta = 60, 180, 300°$. The data in Table I are again consistent with this interpretation.

The entries in the third column of Table V can similarly be understood on the basis of this second order effect, which enhances the a_1 distortion when the wave function is $^1A_1$ and the b_2 when the wave function contains $^1B_2$. The differences in the second column are also explicable in terms of higher order effects, involving, however, interaction terms between e′ nuclear displacements and an a_1' mode, which stretches all the C–C bonds by the same amount.

The results given in Table II appear to violate the Jahn-Teller theorem. Nevertheless, they too can be explained in terms of the operation of a second order effect that, in this case, dominates the first order one. It should be made clear, however, that the fact that the energies of both the $^1B_2$ and $^1A_1$ wave functions increase on angle distortion is not a violation of the theorem. The theorem only guarantees that an e′ distortion will cause a first order lifting of the degeneracy of the two wave functions in an E′ state, not that the energy of one will necessarily go down. If the average energy of the two wave functions increases faster on distortion than the rate at which the two split apart, the energy of the lower can actually increase, as is demonstrated by the data in Table II. The average energy of the singlet wave functions in trimethylenemethane increases on bond angle distortion because of the resulting angle strain at the central carbon and because nonbonded hydrogens move closer than the sum of their van der Waals radii. The latter problem is especially serious for two of the hydrogens when the unique bond angle drops to 110°, which is almost certainly why the average energy on line one of Table II is greater than that on line two.

The data in Table II appear to violate the Jahn-Teller theorem, because the theorem predicts a *first order* lifting of the degeneracy, so that the splitting in energy should be linear in the displacement. Since we have examined two phases of the same displacement, the splitting of $^1B_2$ and $^1A_1$ should reverse in sign in going from line one to line two of Table II, just the way it does in going from $\theta = 0$ to 180° for bond length distortions. The reason the expected reversal does not occur in the a_1 component of the e′ bond angle distortion that we have studied is that the second order effect of mixing $^1A_1'$ into the $^1A_1$ component of $^1E'$ dominates the first order Jahn-Teller effect. Since, in the a_1 component of the e′ distortion, the second order effect only occurs for the $^1A_1$ wave function, and since the second order energy lowering goes as the square of the displacement, $^1A_1$ lies below $^1B_2$ for both phases of the distortion.

The dominance of the second over the first order Jahn-Teller effect is not due to the large magnitude of the former. Indeed, the second order decrease in energy is swamped by the increase due to angle strain and van der Waals repulsions. Rather, it is the fact that the first order Jahn-Teller effect for e′ angle distortions is very small which results in the second order's dominance. The reason for the small magnitude of the first order effect is readily understood when it is realized that at the Hückel level the π bond orders between the peripheral carbons for an allyl plus p type wave function are identically zero. The same is true at the Hückel level for the $^1A_1$ wave function. At the ab initio CI level the π bond orders remain small,[20] although for the $^1A_1$ wave function they now favor decreasing the C_2–C_4–C_3 bond angle while for $^1B_2$ they favor increasing this angle. Thus, there is a first order Jahn-Teller effect for bond angle distortions, which is probably responsible for the change in the energy gap between the wave functions from 0.40 kcal/mol, when the angle is decreased from 120° by 10°, to 0.27 kcal/mol on a 10° increase. For this 20° bond angle change, however, the first order effect apparently results in a net change in energy of only about 0.1 kcal/mol.

While it is clear that e′ bond angle distortions have little effect on lifting the degeneracy between the $^1B_2$ and $^1A_1$ states, in a different sense the same could be said of the e′ bond length distortions. It is true that the latter distortions do strongly lift the D_{3h} degeneracy of these wave functions, but comparing the energy of each wave function at its optimum geometry ($\theta = 0, 120, 240°$ for the former and $\theta = 60, 180, 300°$ for the latter) they differ by only 0.8 kcal/mol.

The reasonable expectation that the wave functions in the unsubstituted molecule would respond differently to selective substitution of methyl for hydrogen motivated the CI calculations, the results of which are reported in Table III. Indeed, placement of two methyl groups on C_1 reverses the relative energies of the $^1B_2$ and $^1A_1$ wave functions at their optimum geometries, causing the former to lie below the latter by about 4.6 kcal/mol. In contrast, placement of one methyl on C_2 and the other on C_3 enhances the preference for the $^1A_1$ wave function in the unsubstituted molecule to 3.6 kcal/mol.

The explanation of the effects of methyl substituents is most easily couched, not in the language of theoreticians, but in terms familiar to students of organic chemistry. The well known ability of methyl groups to stabilize radicals and the pictoral representations of the bonding in the $^1B_2$ (**2**) and $^1A_1$ (**3**) wave functions make rationalizing the results in Table III a trivial exercise. If two methyls are placed at C_1, they both serve to stabilize the radical localized there in **2** but have no radical stabilizing effect in **3**. In contrast, when the methyls are placed on C_2 and C_3, in **2** they can each stabilize the half-odd electron at each terminus of the allylic radical. However, in **3** the methyls each stabilize the full-odd electron that is localized on each of these carbons.

When it is recalled that in unsubstituted trimethylenemethane $^1A_1$ lies 0.8 kcal/mol below $^1B_2$, it becomes possible to calculate from the data in Table III a stabilization energy for each methyl group attached to a carbon bearing an odd electron in trimethylenemethane. For instance, each methyl group in **4** stabilizes an odd electron in the $^1B_2$ wave function but provides no stabilization to the odd electrons in the $^1A_1$ wave function. The resulting change in the relative energies of the two wave functions in going from the unsubstituted molecule to **4** is 5.4 kcal/mol, giving a stabilization energy per methyl group of 2.7 kcal/mol for the unpaired electron stabilized. In going from the unsubstituted molecule to **5**, the change in the relative energies of the two wave functions is 2.8 kcal/mol, with the methyl groups each stabilizing one-half more odd electron in the $^1A_1$ wave function than in the $^1B_2$. Thus, 2.8 kcal/mol is obtained as the stabilization energy per methyl per odd electron. The surprisingly good agreement between two independent values for this number

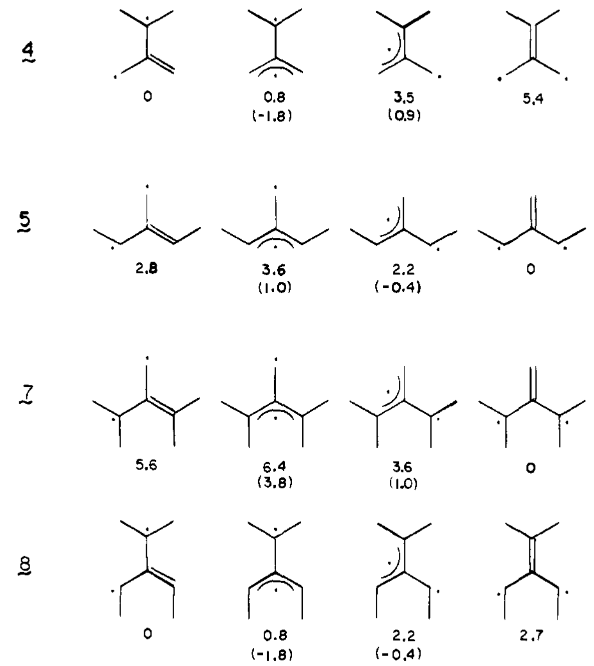


Figure 5. Relative energies (kcal/mol) of wave functions of types **2** and **3** in methylated derivatives (**4**, **5**, **7**, **8**) of trimethylenemethane. The numbers in parentheses are the relative energies of the orthogonal geometries, estimated using the value for the decrease in energy on methylene twisting in the unsubstituted molecule.

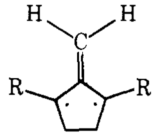
has led us to use it to estimate relative energies in some additional substituted derivatives of trimethylenemethane. In each case comparisons were only made between different forms of the same molecule.[21] In carrying out these computations additivity of methyl stabilization has been assumed, as has the 0.8 kcal/mol preference in the unsubstituted molecule for **3** over **2**. Possible steric effects have been ignored. The results are shown in Figure 5. Needless to say, we do not attribute to them anything more than semiquantitative significance.

From Figure 5 it would appear that no matter what the substitution pattern in trimethylenemethane, a $^1A_1$ type wave function at its optimum geometry will always lie below a $^1B_2$ type at its best planar geometry. However, by restricting ourselves to comparisons at planar geometries, we ignore the fact, noted in the previous section, that a $^1B_2$ wave function can be stabilized by twisting about the unique C–C bond, while a $^1A_1$ wave function cannot.[15] Twisting about one of the two equivalent bonds in a $^1A_1$ wave function is not expected to lower the energy either, for it should be recalled that there is a weak π bond between these carbons and the central one. If such twisting were to occur with all bond lengths frozen, the resulting species could be described as a distorted allyl radical plus an electron localized in an orthogonal p orbital. The energy of this species would decrease were the bond lengths allowed to relax to those in the species obtained by twisting out of conjugation the unique carbon in a $^1B_2$ wave function. Thus, in assessing the effect of twisting on the relative energies of the species in Figure 5, we can assume that only a wave function of the allyl plus p type can be stabilized by such a motion.

Previous theoretical estimates of the change in energy on rotating one carbon out of conjugation in trimethylenemethane have assumed a geometry with all bond lengths held equal in both the planar and orthogonal forms.[13,17] This leads to an overestimation of the energy gain on twisting in the singlet, as shown by the data in Table IV.[22] The larger drop in energy at r_{i4} = 1.43 Å is probably due to the fact that the π bond order to the unique carbon is negative. Replacing a destabilizing π interaction in the planar molecule with a stabilizing hyperconjugative one in the orthogonal form leads to a decrease in energy. The shorter the bond to the unique carbon, the larger both these interactions will be and the larger will be the drop in energy on twisting. Thus, the calculated stabilization on twisting is 4.54 kcal/mol at r_{i4} = 1.43 Å but only 2.55 kcal/mol with the optimized $\theta = 0°$ bond lengths. It should also be noted that going from the D_{3h} geometry to the optimized $\theta = 0°$ distorted one for the planar molecule is calculated to lower the energy of the $^1B_2$ state by 7.82 kcal/mol at the SCF and by 7.65 kcal/mol at the CI level. The similarity between the former number and the latter gives us some faith that our SCF results for twisting also correspond closely to those that would be obtained by a complete CI treatment.

With the consideration of twisting one methylene group as a mode of stabilization of $^1B_2$ wave functions, it is clear from the data in Tables I and IV that the minima for singlet trimethylenemethane are shifted from planar geometries at θ = 60, 180, 300° to orthogonal geometries at θ = 0, 120, 240°. The planar minima at the former angles now lie 1.75 kcal/mol above the orthogonal minima at the latter.[23] The relative energies, after methylene twisting, in methyl substituted derivatives of trimethylenemethane are given by the numbers in parentheses in Figure 5. They are crude estimates, since they were obtained using the stabilization energy computed for the parent molecule.[24]

Davis and Goddard[13] have suggested that appropriate substituents might stabilize a planar $^1A_1$ state relative to a twisted $^1B_1$. In molecule **7** of Figure 5 a planar $^1A_1$ state is estimated to lie lowest, but an orthogonal geometry is only 1 kcal/mol higher in energy. Moreover in the lowest energy orthogonal geometry one of the disubstituted carbons is twisted, and twisting of one of these carbons would relieve considerable steric compression, a fact not reflected by the numbers in Figure 5.[24] Consequently, it is very likely that in **7** an orthogonal geometry would actually be lowest in energy. However, if the two disubstituted carbons in **7** were tied into a small enough ring so that their twisting became impossible, Figure 5 shows that a planar molecule with a $^1A_1$ wave function would lie 3.8 kcal/mol below the only possible orthogonal form. Thus, **9** or, perhaps even better, **10** are candidates for trimethylenemethane derivatives that would preferentially exist in a planar geometry in both the triplet and the singlet state.[25]



9, R = CH_3
10, R = Ph
11, R = H

Whether in a molecule such as **9** the lowest singlet state will actually prefer a planar geometry to an orthogonal one depends on whether the value for the stabilization energy on methylene twisting in **9** is greater than that calculated for unsubstituted trimethylenemethane and used in Figure 5. Since to assume these numbers are the same is certainly questionable,[24] we carried out SCF calculations on **5**, where the steric compression relieved by methylene twisting is expected to be similar to that in **9**. With r_{14} = 1.540 Å and $r_{2(3)4}$ = 1.402 Å, the energy difference between the planar and orthogonal geometries of **5** was calculated to be 5.2 kcal/mol, so that the planar form of **9** is expected to lie, not 3.8, but only 1.2 kcal/mol below the orthogonal one. Therefore, it would appear that a planar geometry would be only marginally more favored in **9** than in the parent methylenecyclopentanediyl (**11**),[26] since the effect of the additional two methyl groups in **9** on electronically stabilizing a $^1A_1$ wave function is apparently canceled by their steric destabilization of the planar conformation. Thus, if a derivative of **11**, with a preference for the planar geometry large enough to be experimentally detectable,[25] is to be prepared, the substituents chosen for the 1,3 positions of the ring must be more radical stabilizing than methyl, without being proportionately greater in their steric demand.

Conclusions

The potential surface for singlet trimethylenemethane that emerges from our calculations on the parent molecule is one with three minima, corresponding to orthogonal geometries at pseudorotation angles of $\theta = 0$, 120, and 240°. The molecule can travel from one minimum to another by methylene twisting coupled with pseudorotation. The barrier between orthogonal minima is estimated at between 1.8 and 2.6 kcal/mol, with the former value obtaining if there is no barrier between the orthogonal minima that is higher than the planar minima at $\theta =$ 60, 180, and 300°.[23] At all geometries investigated the singlet lies well above the energy of the D_{3h} triplet.[22,27]

We find that methyl substituents have an appreciable effect on destroying the C_{3v} symmetry of the potential surface for the unsubstituted molecule. The influence of methyl groups can be understood on the basis of their radical stabilizing ability, but the steric compression engendered in the planar molecule by introduction of these groups is probably sufficient to make an orthogonal geometry accessible, if not preferred, for alkyl substituted derivatives of trimethylenemethane. Nevertheless, it should be possible, at least in principle, to prepare a 1,3-disubstituted derivative of **11**, in which, by suitable choice of radical stabilizing substituents, a planar geometry for the singlet would be favored over an orthogonal one.

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References and Notes

(1) W. T. Borden, *J. Am. Chem. Soc.*, **98**, 2695 (1976); E. R. Davidson and W. T. Borden, *J. Chem. Phys.*, **64**, 663 (1976).

(2) Leading references to other theoretical and experimental studies of trimethylenemethane are contained in ref 1.

(3) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2906 (1975).

(4) Any orthonormal linear combination of these two wave functions is also an acceptable set of $^1E'$ wave functions.

(5) Since the wave functions represented by **2** and **3** are degenerate, the total π bond order of **2** must equal that of **3**. Further, for each bond the sum of the bond orders in **2** and **3** must be the same. The Hückel π bond orders in an allyl plus p wave function are $P_{14} = 0$ and $P_{2(3)4} = 0.707$. Thus, those in **3** must be $P_{14} = 0.943$ and $P_{2(3)4} = 0.236$. However, the π bond orders in **3**, obtained from an ab initio CI calculation,[1] are in a ratio of 7.5 to 1, instead of the 4.0 to 1 predicted from the argument given above. This argument underestimates the π bond order ratio in the $^1A_1$ wave function because the CI calculation on the $^1B_2$ wave function of **2** finds the π bond order between C_1 and C_4 to be neeative rather than zero.

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

(7) Let $(\partial H/\partial Q_1)dQ_1$ be the first order perturbation to the Hamiltonian due to the a_1 displacement from D_{3h} symmetry and $(\partial H/\partial Q_2)dQ_2$ the corresponding term for the b_2 nuclear displacement. The quantities dQ_1 and dQ_2 are the nuclear displacements and therefore have respectively a_1 and b_2 symmetry. Since the Hamiltonian is invariant to every symmetry operation of C_{2v}, all the terms in the Hamiltonian must belong to the A_1 representation of this group. Therefore $(\partial H/\partial Q_1)$ and $(\partial H/\partial Q_2)$ must also transform respectively as a_1 and b_2. The first order energy change, due to the a_1 nuclear displacement, is $\langle \Psi_{B_2} | \partial H/\partial Q_1 | \Psi_{B_2} \rangle dQ_1$ for the $^1B_2$ wave function. The expression for the $^1A_1$ wave function is identical. Similar terms for the b_2 displacement are zero, because the functions that correspond to the one in brackets above transform as B_2, while the one above transforms as A_1. Only functions that transform as the totally symmetric representation give nonzero integrals. For this reason the term $\langle \Psi_{B_2} | \partial H/\partial Q_2 | \Psi_{A_1} \rangle dQ_2$ is nonzero, since the symmetry of the function in brackets is $B_2 \times b_2 \times A_1 = A_i$. Because the $^1B_2$ and $^1A_1$ wave functions are degenerate at a D_{3h} geometry, twice this latter term represents the difference in energy between the two new wave functions that result from the mixing of $^1B_2$ and $^1A_1$. Therefore, the lifting of the degeneracy by a b_2 nuclear displacement is also linear in the displacement coordinate.

(8) The analysis is similar for other open-shell systems whose most symmetrical geometry has D_{3h} symmetry (e.g., cyclopropenyl radical and anion). See, for instance, A. Liehr, *J. Phys. Chem.*, **67**, 389 (1963).

(9) This fact can be used to help understand the physical reason for the mathematical relationships between $^1B_2$ and $^1A_1$ wave functions in D_{3h} trimethylenemethane. For instance, as we have previously pointed out,[1] the $^1A_1$ wave function with C_1 as the unique peripheral atom can be expressed as an equal combination of the two $^1B_2$ wave functions in which C_2 and C_3 are the unique atoms. Consider how, in the limit $\Delta r \rightarrow 0$, the $^1B_2$ wave function with C_2 as the unique atom ($\theta = 120°$) is transformed into the $^1B_2$ wave function with C_3 as the unique atom ($\theta = 240°$) by a pseudorotation of 120°. Clearly, at the midway point ($\theta = 180°$) the wave function will be an equal mixture of the two $^1B_2$ wave functions, but this, the lowest energy wave function at $\theta = 180°$, is precisely the $^1A_1$ wave function with C_1 as the unique peripheral atom.

(10) For a discussion of branch cuts in triatomic potential surfaces, see E. R. Davidson, *J. Am. Chem. Soc.*, **99**, 397 (1977).

(11) The spin-restricted open-shell method of E. R. Davidson, *Chem. Phys. Lett.*, **21**, 565 (1973), was used for the SCF calculations on the triplet and open-shell singlets.

(12) It was noted that at the spin-restricted SCF level the D_{3h} minimum for the triplet occurred at $r_{i4} = 1.408$ Å. This is not unexpected, since bond lengths calculated at the SCF level are almost always increased upon inclusion of CI. What was somewhat surprising, however, was the fact that the D_{3h} geometry for the triplet did not prove to be a global minimum at the SCF level. Instead, the energy decreased as one bond was shortened and two were lengthened. No attempt was made to locate the SCF minimum, since at the CI level the D_{3h} geometry was a global minimum for planar trimethylenemethane. Around the CI minimum the energy increase for small displacements was quadratic, and force constants for a_1' and e' (a_1 component) nuclear displacements were calculated as 8.8 and 5.6 mdyn/Å, respectively. It should also be noted that the optimum bond length in the triplet state is less than that in the D_{3h} singlet state. This fact is understandable, since the Hückel bond order for the triplet is 1.732, compared to 1.414 for the singlet.[5]

(13) J. H. Davis and W. A. Goddard III, *J. Am. Chem. Soc.*, **98**, 303 (1976), claim to have carried out calculations on orthogonal trimethylenemethane that correspond to full π space CI on the planar molecule. They do not state in their communication, however, exactly what configurations were used in the calculations at the orthogonal geometry.

(14) For the triplet state, the D_{3h} SCF minimum occurs at a geometry with C–C bond lengths 0.021 Å shorter than at the CI minimum.[12] The SCF D_{3h} singlet minimum is also expected to occur at shorter bond lengths than the CI minimum of 1.446 Å. In addition, at the CI level the C–C bond lengths in the optimized D_{3h} singlet are 0.017 Å longer than those in the triplet. Since the D_{3h} triplet at the CI level has C–C bonds 1.408 Å long, this also suggests an optimized D_{3h} geometry for the singlet with C–C bond lengths of 1.425 Å at the SCF level.

(15) Calculations were not carried out for the ^1A states, since in orthogonal trimethylenemethane the $^1A_2$ state, which correlates with $^1A_1$ in the planar molecule, lies at quite high energy.[13]

(16) This value for the singlet–triplet splitting in D_{3h} trimethylenemethane is in good agreement with the CI value of 26.4 kcal/mol, computed by Davis and Goddard,[13] using a higher quality basis set than ours and an assumed D_{3h} geometry with $r_{i4} = 1.40$ Å for both states. However, at the same geometry we calculate a splitting of 31.6 kcal/mol. Using the same Dunning basis set as Davis and Goddard and an assumed D_{3h} geometry with $r_{i4} =$ 1.43 Å, SCF calculations[17] yield a value of 21 kcal/mol for the splitting, compared with our SCF results (Table IV, line 1) of 26.2 kcal/mol at the same geometry. It is apparent that at both the SCF and CI levels the STO-3G basis set gives a value for the singlet–triplet splitting about 5 kcal/mol higher than the Dunning basis set near the triplet's optimum geometry.

(17) D. R. Yarkony and H. F. Schaefer III, *J. Am. Chem. Soc.*, **96**, 3754 (1974).

(18) The energy lowering is given by second order perturbation theory as $\langle \Psi_{E'} | \partial H/\partial Q_{e'} | \Psi_{A_1'} \rangle^2 dQ_{e'}^2/(E_{E'} - E_{A_1'})$. Note that the energy lowering is quadratic in the distortion, $dQ_{e'}$, rather than linear, as in the first order Jahn-Teller effect. Thus, in molecules where a second order Jahn-Teller effect is operative, the mixing of the ground state with an excited state under the influence of a vibration has the effect of reducing the quadratic force constant for that vibration. A relevant example of this effect occurs in $^3A_2'$ trimethylenemethane. There is a low-lying $^3E'$ excited state that can be mixed with the ground state by an e' vibration. It is this second order Jahn-Teller effect that causes the e' vibration in $^3A_2'$ trimethylenemethane to have a substantially smaller force constant than the a_1' vibration.[12] For a lucid discussion of second order Jahn-Teller effects, see R. G. Pearson, *J. Am. Chem. Soc.*, **91**, 4947 (1969).

(19) The group theoretical argument is essentially that given in ref 7.

(20) The important quantities in determining the first order energy change on distortion are not the bond orders but the overlap populations, which are the products of the bond orders and the overlap integrals. Not only are the π bond orders between the peripheral carbons small, but the π overlap integrals are small as well. Therefore, the corresponding overlap populations are minute.

(21) The accuracy with which different isomers can be compared is indicated by comparing the energies of 4 and **5** at their optimum geometries. Each has two methyl groups stabilizing an odd electron, but **5** has a $^1A_1$ wave function at its optimum geometry, while that of 4 is $^1B_2$. Consequently the energy of **5** at its optimum geometry would be expected to be 0.8 kcal/mol lower than that of 4. The actual difference, obtained by comparing the energies given in footnotes c and d of Table III, is 0.5 kcal/mol.

(22) It is also clear from these data that calculations on the triplet, carried out at $r_{i4} = 1.43$ Å, will overestimate the energy required to twist one methylene from conjugation. On allowing the orthogonal form to distort to a geometry more appropriate for a molecule consisting of an allyl radical plus an electron localized in an orthogonal p orbital, the calculated energy required for twisting the triplet state drops from 19.8 to 14.8 kcal/mol. The energy requirement for twisting, starting from the optimized SCF D_{3h} geometry for the triplet, is slightly greater, 15./ kcal/mol. At the orthogonal geometry the singlet lies only 2.2 kcal/mol above the triplet; so we calculate that

roughly 17 kcal/mol would have to be supplied to the planar triplet in order for it to cross to the singlet at the orthogonal geometry. However, there may be a lower energy pathway for intersystem crossing from the triplet to the singlet (for instance, rotating two methylene groups) than twisting to the orthogonal geometry.

(23) It is almost certain that methylene rotation *coupled* with bond length changes would provide the lowest energy pathway from a planar to an orthogonal minimum. It should also be noted that an orthogonal minimum is not a global one, since rotation of a second methylene group leads to methylenecyclopropane.

(24) Because of relief of steric compression on methylene twisting in substituted derivatives of trimethylenemethane, the stabilization energy on twisting will be greater in these molecules than in the unsubstituted parent. Therefore, the numbers in parentheses in Figure 5 most certainly represent algebraic upper limits.

(25) J. A. Berson, L. R. Corwin, and J. H. Davis, *J. Am. Chem. Soc.*, **96,** 6177 (1974), have shown that in an isomer of **9**, in which the two methyl groups are both attached to the unique carbon, the singlet is trapped by diylophiles to give, preferentially, fused rather than bridged adducts. They have interpreted this finding as evidence for the orthogonal geometry, expected in such a derivative of **8**. It is conceivable that **9** or **10** would preferentially give, instead, bridged adducts; since, electronically, if planar, the lowest singlet might be expected to react most readily at the ring carbon atoms. Thus, an alteration in regioselectivity would be indicative of a planar singlet in these molecules. However, steric effects would tend to favor attack at the least substituted, exocyclic carbon, and so fused adducts might again be obtained, even if the lowest singlet preferred a planar geometry. A better probe for a planar singlet in **9** and **10** would be a stereochemical one, in which preservation of geometrical integrity about the double bond in these molecules was examined by substituting deuterium for one of the hydrogens in the methylene group and labeling the ring with a stereochemical point of reference.

(26) The relative energy of the orthogonal geometry of **11** is probably represented adequately by the number in parentheses for the appropriate form of **5** in Figure 5, since the energy gain on methylene rotation in **11** should be comparable to that in unsubstituted trimethylenemethane.

(27) These conclusions are in good agreement with the known experimental facts about trimethylenemethane and its derivatives.[2]

Internal Rotation in the Ground Electronic State of Allene[1]

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Abstract: The internal rotation potential of allene has been studied with ab initio self-consistent field (SCF) methods using a double-ζ basis set of 38 contracted Gaussian functions and an extended set of 65 functions including polarization functions, and with the method self-consistent electron pairs (SCEP) using the double-ζ set. The ground state of allene is a closed shell $^1A_1$ state in D_{2d} symmetry. In the D_2 symmetry of the twisted form, this closed shell state mixes with a $2b_3 \rightarrow 3b_3$ open shell $^1A_1$ state which correlates with a ^1A_u state in the D_{2h} symmetry of the planar form of the molecule. The planar closed shell state, ^1A_g, is higher in energy than the ^1A_u state. Examination of pair correlation energies indicates that correlation effects will not reverse this order. The internal rotation barrier is predicted to be about 49 kcal, after geometry optimization, and there is little effect on relative energies from including polarization functions.

Allene is the simplest molecule containing two carbon-carbon double bonds and like ethylene, the effects of internal rotation on electronic structure have been of theoretical interest. The lowest energy structure of the ground state of allene is with the two CH_2 groups in perpendicular planes. A detailed molecular orbital comparison of the planar ground state (D_{2h}) structure of ethylene and the out-of-plane (D_{2d}) structure of allene has been given by Buenker.[2a] Experimental studies of allene include the UV spectrum taken by Sutcliffe and Walsh[2b] who identified several Rydberg series at short wavelengths. Maki and Toth[3] used high-resolution infrared spectra to determine the structure of allene: $R_{C=C}$ = 1.308 Å, R_{C-H} = 1.087 Å, and $\angle HCH$ = 118.2°.

There have been several ab initio theoretical studies of allene. The largest basis set allene calculation appears to be that of Hariharan and Pople[4] who showed that polarization functions were important in comparing energetics of C_3H_4 isomers. FSGO calculations include those of Talaty, Schwartz, and Simons[5] who found a C=C length 0.03 Å longer than experiment and a rather large H-C-H angle of 126° in the nonplanar structure. Weimann and Christoffersen[6] used FSGO to predict a barrier to rotation (to the planar ^1A_g state) of 75.1 kcal. Earlier calculations on a large number of molecules by Preuss and Janoschek[7] gave a 65 kcal difference between planar and nonplanar closed shell states. A partial geometry optimization determined the C=C bond length to be 1.310 Å in the D_{2d} form, quite close to experiment, and 1.323 in the planar form. A geometry optimization of the D_{2d} form by Radom, Lathan, Hehre, and Pople[8] used a minimum STO-3G basis and gave the C=C length as 1.288 Å and the bond angle as 116.2°. In another STO-3G study, by Radom and Pople,[9] a separation of 92 kcal for the closed shell states was given from calculations performed without optimization of the geometry.

Schaad, Burnelle, and Dressler[10] studied the excited states of allene in the D_{2d} and D_{2h} structures and confirmed Buenker's[2a] result that the lowest planar allene electronic state is a ^3A_u state ($1b_{2g} \rightarrow 2b_{2u}$) and that the lowest singlet is a ^1A_u state arising from the same occupancy. (The convention for distinguishing b_2 and b_3 symmetry species of the D_{2h} point group used by Buenker and Schaad et al. is opposite that used here.) Buenker[2a] determined that the open shell singlet was about 6 kcal lower than the closed shell singlet and estimated that the real difference could be five times that. The separation between the ^3A_u and ^1A_u states was estimated to be less than 0.1 eV (2.3 kcal). Furthermore, it was suggested that the singlet might have a relative minimum in the planar form. The SCF calculations of Schaad and co-workers[10] yield a smaller value for the energy difference of the closed shell states, 3.15 eV (73 kcal), a ^3A_u-^1A_u separation of 0.09 eV and a very small separation for the ^1A_u and ^1A_g states of 0.03 eV (0.7 kcal). The open shell energies were calculated using the virtual orbitals from a closed shell calculation. Correlated wave functions were not used in any of the studies.

The closeness of the two lowest planar singlet states of allene determined in these two SCF calculations suggests that even small correlation effects or the inclusion of polarization functions could reverse the relative ordering of these states and