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## A Configuration Interaction Treatment of $^1E'$ Trimethylenemethane

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**Abstract:** Configuration interaction is used to examine the wave function for the  $\pi$  electrons in  $^1E'$  trimethylenemethane from several different perspectives. It is shown that in the planar singlet, repulsion between the nonbonding electrons results in a modification of the MO's appropriate for  $^3A_2'$  trimethylenemethane and that one component of the  $^1E'$  wave function consequently resembles closely that for an allyl radical plus an electron effectively localized in a p orbital. Some problems inherent in the SCF treatment of the  $^1E'$  state of  $D_{3h}$  trimethylenemethane are discussed.

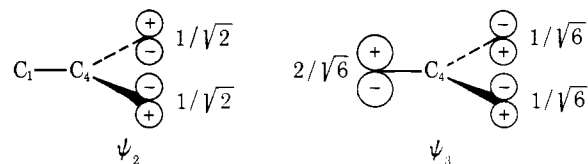
Trimethylenemethane<sup>1</sup> has been of interest to theoreticians for more than a quarter of a century. A number of sophisticated theoretical treatments of triplet trimethylenemethane appeared before Dowd reported the synthesis and characterization of the molecule in this state.<sup>2</sup> Singlet trimethylenemethane, as the presumed intermediate in the rearrangements of methylenecyclopropanes, has an even longer experimental history than the triplet,<sup>1</sup> but only recently has the singlet been the subject of detailed theoretical study. In 1971 Dewar and Wasson<sup>3</sup> reported semiempirical MINDO/2 calculations which showed that, unlike the triplet which adopts a planar geometry, singlet trimethylenemethane prefers a conformation with one methylene group lying in a plane orthogonal to that containing the other two. This finding provided theoretical justification for previous proposals of this geometric preference for the singlet, which had been based on the experimentally observed preservation of optical activity in the rearrangement products of chiral methylenecyclopropanes,<sup>4</sup> the results of detailed stereochemical studies,<sup>5</sup> and the effect of substituents on migrating group selectivity and rate of rearrangement.<sup>5a,6</sup> Subsequent ab initio calculations<sup>7,8</sup> have also found the orthogonal geometry to be lower in energy than the planar one for the singlet, and an explanation of this phenomenon in terms of the effect of electron repulsion in this open-shell  $\pi$  system has been given.<sup>9</sup>

Although both of the ab initio calculations<sup>7,8</sup> agree with the MINDO/2 results in predicting that for the singlet, the orthogonal geometry is favored, the Yarkony and Schaefer<sup>7</sup> calculation found only a small (2.8 kcal/mol) energy difference between it and the planar one. In contrast, like MINDO/2,<sup>3</sup> the other ab initio calculation<sup>8</sup> predicted a substantially larger (>1 eV) energy difference between the two geometries. The Yarkony-Schaefer result is in much better accord with the experimental observation that racemization competes with rearrangement in chiral methylenecyclopropanes.<sup>4,5a</sup> That racemization is probably occurring via the planar singlet, rather than through the intermediacy of the triplet, is strongly indicated both by theoretical considerations and experimental data. If the triplet were

formed, it would not be expected to reclose to methylenecyclopropane,<sup>10</sup> and oxygen, an excellent scavenger of triplet trimethylenemethane,<sup>11</sup> has no effect on the distribution of products or the stereochemical characteristics of the rearrangement of optically active *trans*-2,3-dicyanomethylenecyclopropane.<sup>12</sup>

In a preliminary communication<sup>13</sup> it was argued that the Yarkony-Schaefer result<sup>7</sup> is correct and that, in order to avoid the high energy ionic terms, involving the nonbonding electrons, that appear in the familiar fully delocalized  $D_{3h}$  wave function for singlet trimethylenemethane, the optimum wave function for the planar singlet resembles closely that of an allyl radical plus an electron essentially localized in a p orbital. The overestimation of the energy preference for the orthogonal geometry by the other two calculations<sup>3,8</sup> on singlet trimethylenemethane was attributed to their failure to arrive at the correct wave function for the planar geometry. This failure was seen to result from the use in these calculations of approximate methods for dealing with open-shell systems, which led to the same set of MO's for singlet as for triplet trimethylenemethane.

In this paper configuration interaction is used to examine the wave function for the planar singlet from several different perspectives, in order to amplify and expand upon the points raised in the preliminary communication.<sup>13</sup>



### A Two-Electron Model

The familiar nonbonding MO's of planar ( $D_{3h}$ ) trimethylenemethane are shown above. As has been pointed out previously,<sup>9,13</sup> unlike the case in  $[4n]$ annulenes,<sup>14-16</sup> these nonbonding MO's, or any linear combination of them, have amplitude on at least one common atom. Consequently, in the singlet state in which one electron is placed in each MO,

the wave function contains ionic terms, corresponding to the simultaneous occupancy of an AO common to both MO's by these two electrons. This is easily seen by expanding the singlet wave function,

$$\Psi = [|\psi_2^\alpha\psi_3^\beta\rangle + |\psi_3^\alpha\psi_2^\beta\rangle]/\sqrt{2} \quad (1)$$

in terms of AO's and verifying that it contains terms corresponding to the simultaneous occupancy of  $\phi_2$  and  $\phi_3$  by the two electrons. These ionic terms, which are of high energy because of the large value for the electrostatic repulsion integral for two electrons in the same atomic orbital, are of course absent from the wave function for the triplet (as may be verified by expansion of eq 1 after changing the sign between the Slater determinants to obtain the  $m_s = 0$  component of this state).

Two other Slater determinants can be constructed by placing both electrons in the same MO. Neither  $|\psi_2^\alpha\psi_2^\beta\rangle$  nor  $|\psi_3^\alpha\psi_3^\beta\rangle$  by itself is a symmetry-correct wave function, since neither belongs to an irreducible representation of  $D_{3h}$ . The in-phase combination belongs to  $A_1'$  and lies above the out-of-phase combination,

$$\Psi' = [|\psi_2^\alpha\psi_2^\beta\rangle - |\psi_3^\alpha\psi_3^\beta\rangle]/\sqrt{2} \quad (2)$$

which, together with the wave function in eq 1, transforms in  $D_{3h}$  as  $E'$ . Since the wave functions in eq 1 and 2 together form the basis for a degenerate representation, they must have the same energy. In fact, although they appear to be very different,  $\Psi'$  is just a linear combination of the two wave functions with the form of  $\Psi$  that can be created by choosing  $\phi_2$  and  $\phi_3$  as the unique atom in the MO's. A more physical interpretation of  $\Psi'$  is made possible by noting that the wave function can also be written as

$$\Psi' = [(\psi_2 + \psi_3)^\alpha(\psi_2 - \psi_3)^\beta + (\psi_2 - \psi_3)^\alpha(\psi_2 + \psi_3)^\beta]/2\sqrt{2} = [|\psi_2'^\alpha\psi_3'^\beta\rangle + |\psi_3'^\alpha\psi_2'^\beta\rangle]/\sqrt{2} \quad (3)$$

which is the wave function for two electrons occupying two different MO's,  $\psi_2'$  and  $\psi_3'$ , which are respectively the sum and difference of  $\psi_2$  and  $\psi_3$ . It can be verified by expansion that the ionic terms in eq 2 or 3 occur with the same probability as those in eq 1.<sup>17</sup>

The ionic terms in eq 1 can be made to disappear if  $\psi_3$  is altered by confining it to  $\phi_1$ , where  $\psi_2$  has a node, so that the two MO's have no atoms in common. This can be accomplished by adding to  $\psi_3$  the in-phase combination of the three p  $\pi$  AO's of the trimethylenemethane periphery,  $\chi = (\phi_1 + \phi_2 + \phi_3)/\sqrt{3}$  with a coefficient of  $1/\sqrt{2}$ . However, in  $D_{3h}$  symmetry  $\psi_3$  and  $\chi$  belong to different representations, since the former is  $e''$  and the latter  $a_2''$ . Consequently, an SCF calculation, in which the Fock matrix used to find  $\psi_3$  is set up using only a basis set consisting of functions of  $e''$  symmetry, will not mix  $\chi$  into  $\psi_3$ . Should  $\chi$  be mixed into  $\psi_3$ ? Intuitively, we expect the answer to be yes, because we have seen that this mixing eliminates the ionic terms in eq 1. That this mixing does occur, even in  $D_{3h}$  symmetry, can be verified by a CI calculation.

Like  $\Psi$ , the configuration,  $(|\psi_2^\alpha\chi^\beta\rangle + |\chi^\alpha\psi_2^\beta\rangle)/\sqrt{2}$ , is  $^1E'$  in  $D_{3h}$ , since  $e'' \times a_2'' = E'$ . Also, it is, like  $\Psi$ , antisymmetric with respect to the plane that bisects the C<sub>2</sub>-C<sub>4</sub>-C<sub>3</sub> bond angle. Consequently, it can mix with  $\Psi$  via an integral which, ignoring differential overlap, is found to be  $-\sqrt{2}(\gamma_{11} - \gamma_{13})/3$ , where  $\gamma_{11}$  is the repulsion integral between two electrons in the same p orbital and  $\gamma_{13}$  is that between two electrons in p  $\pi$  orbitals on different perimeter atoms. If the small amount of overlap between such AO's is ignored so that  $\chi$  has exactly the same energy as  $\psi_3$ , it is found that the configuration where  $\psi_3$  is replaced by  $\chi$  lies higher in energy than  $\Psi$  by  $(\gamma_{11} - \gamma_{13})/3$ . Mixing between the two configurations is computed to yield a new wave

function,

$$\begin{aligned} & [|\psi_2^\alpha\psi_3^\beta\rangle + |\psi_3^\alpha\psi_2^\beta\rangle + (|\psi_2^\alpha\chi^\beta\rangle + |\chi^\alpha\psi_2^\beta\rangle)/\sqrt{2}]/\sqrt{3} \\ & = [|\psi_2^\alpha(\psi_3 + (1/2^{1/2})\chi)^\beta\rangle \\ & \quad + |(\psi_3 + (1/2^{1/2})\chi)^\alpha\psi_2^\beta\rangle]/\sqrt{3} \quad (4) \end{aligned}$$

with energy equal to  $\gamma_{13}$ , corresponding to the removal by CI of all the ionic terms in  $\Psi$  by mixing  $\chi$  into  $\psi_3$  with coefficient  $1/\sqrt{2}$ .

Although the assumption of  $D_{3h}$  symmetry for the MO's prevents an SCF calculation from arriving at the lowest energy wave function for the two nonbonding electrons, if lower symmetry is assumed in setting up the Fock matrix, an SCF calculation that properly includes the repulsion between the nonbonding electrons (by not making simplifying assumptions that lead to the same set of MO's for both the  $^1E'$  and  $^3A_2'$  states)<sup>3,8,18</sup> will generate the wave function in eq 4. For instance, in  $C_{2v}$  symmetry both  $\psi_3$  and  $\chi$  belong to the same representation and so will be mixed to give the wave function of eq 4. Consequently, in order to arrive at the lowest energy SCF wave function for  $^1E'$  trimethylenemethane in a  $D_{3h}$  geometry, Yarkony and Schaefer<sup>7</sup> had to carry out their SCF calculation with only  $C_{2v}$  symmetry required of the MO's. This is a general problem in SCF calculations on degenerate states of open-shell systems that has been analyzed by Manne.<sup>19</sup> It arises because, as we have seen above, the direct product of two (or more) different representations with a degenerate one may span the same degenerate representation. In the case at hand an  $E'$  wave function can be obtained in  $D_{3h}$  from either  $e'' \times e''$  or  $a_2'' \times e''$ ; consequently, one of the nonbonding MO's can be a mixture of  $e''$  and  $a_2''$  symmetries.

While an SCF calculation that assumes lower than  $D_{3h}$  symmetry for the MO's can lead to the wave function in eq 4, there are two problems with this type of SCF approach. The first is that the total wave function thus obtained may have a contaminant that does not belong to the desired representation in the higher symmetry group to which the molecule actually belongs (vide infra). The second is illustrated by the attempt to obtain an orbital picture for the effect of CI on  $\Psi'$  in eq 3. CI mixes  $(|\psi_3^\alpha\chi^\beta\rangle + |\chi^\alpha\psi_3^\beta\rangle)/\sqrt{2}$  into  $\Psi'$  with a coefficient of  $1/\sqrt{2}$ . However, if the resulting  $^1E'$  wave function is written in terms of just two occupied MO's, a spurious term  $-|\chi^\alpha\chi^\beta\rangle/2\sqrt{3}$  is introduced.

$$\begin{aligned} & [|\psi_2^\alpha\psi_2^\beta\rangle - |\psi_3^\alpha\psi_3^\beta\rangle - (|\psi_3^\alpha\chi^\beta\rangle + |\chi^\alpha\psi_3^\beta\rangle)/\sqrt{2}]/\sqrt{3} \\ & = [(\psi_2 + \psi_3 - (1/2^{1/2})\chi)^\alpha(\psi_2 - \psi_3 + (1/2^{1/2})\chi)^\beta \\ & \quad + |(\psi_2 - \psi_3 + (1/2^{1/2})\chi)^\alpha(\psi_2 + \psi_3 \\ & \quad - (1/2^{1/2})\chi)^\beta\rangle]/2\sqrt{3} + |\chi^\alpha\chi^\beta\rangle/2\sqrt{3} \quad (5) \end{aligned}$$

That this term does not belong in the wave function is apparent from the fact that it has  $A_1'$  symmetry, and it must be eliminated to obtain a wave function with no ionic terms. Since the second component of  $^1E'$  cannot be written simply in terms of just two occupied MO's, it is obvious that no SCF-MO calculation can arrive at the correct wave function for this component. A consequence of this fact is that SCF-MO calculations on the two components of  $^1E'$  will lead to two different energies, despite the fact that the correct wave functions are, of course, degenerate. This lack of equivalence was noted in the SCF calculations on trimethylenemethane carried out by Yarkony and Schaefer.<sup>7</sup>

#### SCF Wave Functions for $^1E'$ Trimethylenemethane

Using a CI approach we have now obtained the lowest energy wave functions for nonbonding electrons in the two components of  $^1E'$  trimethylenemethane and shown that one of them is identical with that which would be generated by an SCF calculation for these electrons, provided that

only  $C_{2v}$  symmetry were imposed on the MO's. However, the energy that must be minimized is that of the wave function for all four  $\pi$  electrons and not just that of the wave function for the two electrons in the NBMO's. In the next section we use CI to obtain the best singlet wave function for the  $\pi$  electrons in trimethylenemethane. First, however, we examine the wave function for the four  $\pi$  electrons in the  $^1E'$  state of trimethylenemethane that is obtained by placing the two bonding electrons in MO's orthogonal to the optimum MO's for the nonbonding electrons. The importance of minimizing the Coulomb repulsion between the nonbonding electrons in determining the optimum wave function for singlet trimethylenemethane has been emphasized;<sup>13</sup> so this procedure might be expected to provide a good approximation to the wave function obtained from an SCF calculation.

The  $\pi$  orbitals that span the peripheral carbons and are orthogonal to  $\psi_2$  and  $(\psi_3 \pm (1/2^{1/2})\chi)\sqrt{2/3}$  are  $((1/2^{1/2})\psi_3 \mp \chi)\sqrt{2/3}$ , where the upper sign corresponds to the orbital to be used with the nonbonding MO's given by eq 4 and the lower to the one for use with those in eq 5. The p  $\pi$  AO,  $\phi_4$ , on the central carbon in trimethylenemethane belongs to  $a_2''$ , so it mixes with  $\chi$ . The resulting bonding orbitals are  $((1/2^{1/2})\psi_3 \mp \chi)/\sqrt{3} \mp (1/2^{1/2})\phi_4$ , both of which have the same energy,  $\alpha + \sqrt{2}\beta$ , in Hückel theory. In fact, the  $\pi$  bonding MO, appropriate for use with the wave function of eq 3, where one of the nonbonding electrons occupies  $\psi_2$  while the other is localized in  $\phi_1$ , is none other than the familiar bonding MO of allyl.

$$\begin{aligned} & \frac{1}{6}(2\phi_1 - \phi_2 - \phi_3) - \frac{1}{3}(\phi_1 + \phi_2 + \phi_3) - (1/2^{1/2})\phi_4 \\ & = - [\frac{1}{2}(\phi_2 + \phi_3) + (1/2^{1/2})\phi_4] \quad (6) \end{aligned}$$

Thus, minimizing the repulsion between the nonbonding electrons in singlet trimethylenemethane, by confining them to different sets of atoms,<sup>9</sup> leads to the wave function for an allyl radical plus a localized electron, even in the planar molecule.<sup>13</sup> This is essentially the wave function that was obtained from the ab initio SCF calculation of Yarkony and Schaefer.<sup>13</sup>

With an allyl plus p wave function the molecule will, of course, be unstable to a distortion from  $D_{3h}$  symmetry that lengthens the bond to  $C_1$ , since the  $\pi$  bond order between  $C_1$  and the central carbon is zero. In contrast, with the bonding MO appropriate for the NBMO's in eq 5,

$$\begin{aligned} & \frac{1}{6}(2\phi_1 - \phi_2 - \phi_3) + \frac{1}{3}(\phi_1 + \phi_2 + \phi_3) + (1/2^{1/2})\phi_4 \\ & = \frac{2}{3}\phi_1 + \frac{1}{6}(\phi_2 + \phi_3) + (1/2^{1/2})\phi_4 \quad (7) \end{aligned}$$

the bond to  $C_1$  will shorten with respect to the other two, because of the larger  $\pi$  bond order between  $C_1$  and the central carbon. There is a vibration of  $e'$  symmetry which effects changes in the length of this bond with respect to that of the other two and thus can lift the degeneracy of the two components of the  $^1E'$  state, as predicted by the Jahn-Teller theorem.<sup>20</sup> It is perhaps worth noting that neither component of  $^1E'$ , when constructed from the MO's appropriate for triplet trimethylenemethane, confers on the molecule a propensity to undergo a first-order Jahn-Teller distortion.<sup>21</sup> Consequently, such  $^1E'$  wave functions violate the Jahn-Teller theorem, and this fact provides a clue that such  $^1E'$  wave functions for planar trimethylenemethane are not the correct ones.

One last point that should be raised regarding the allyl plus p wave function for the planar singlet is whether it, or the SCF wave function to which it is a close approximation, is actually a pure  $^1E'$  state in  $D_{3h}$ . It will be recalled that to arrive at an optimum singlet wave function by an SCF calculation, only  $C_{2v}$  symmetry can be demanded of the MO's. Since both  $E'$  and  $A_2'$  in  $D_{3h}$  correspond to  $B_2$  in  $C_{2v}$  sym-

metry, it is possible that the total wave function, constructed from SCF MO's belonging to the  $B_2$  representation in  $C_{2v}$ , will have a  $^1A_2'$  as well as the desired  $^1E'$  component. In order to investigate whether this is indeed the case, we begin by noting that in the singlet, if one of the nonbonding MO's of symmetry  $e_x''$  contains an  $a_2''$  component as in eq 4, then to ensure orthogonality, the bonding orbital, which in the triplet is pure  $\bar{a}_2''$ , must mix in some  $e_x''$ . [The bar over the  $a_2''$  component of the bonding MO merely indicates that it is different from the  $a_2''$  component of the nonbonding MO; compare, for instance, the MO's given by eq 4 and 6.] The symmetry of the total wave function may then be deduced from the representations spanned by the direct product

$$\begin{aligned} & |(\bar{a}_2'' + e_x'')^\alpha(\bar{a}_2'' + e_x'')^\beta e_y''^\alpha(e_x'' + a_2'')^\beta\rangle \\ & + |(\bar{a}_2'' + e_x'')^\alpha(\bar{a}_2'' + e_x'')^\beta(e_x'' + a_2'')^\alpha e_y''^\beta\rangle \\ & = |\bar{a}_2''^\alpha \bar{a}_2''^\beta e_y''^\alpha e_x''^\beta\rangle + |\bar{a}_2''^\alpha \bar{a}_2''^\beta e_x''^\alpha e_y''^\beta\rangle \\ & + |e_x''^\alpha \bar{a}_2''^\beta e_y''^\alpha e_x''^\beta\rangle + |\bar{a}_2''^\alpha e_x''^\beta e_x''^\alpha e_y''^\beta\rangle \\ & + |\bar{a}_2''^\alpha \bar{a}_2''^\beta e_y''^\alpha a_2''^\beta\rangle + |\bar{a}_2''^\alpha \bar{a}_2''^\beta a_2''^\alpha e_y''^\beta\rangle \\ & + |e_x''^\alpha \bar{a}_2''^\beta e_y''^\alpha a_2''^\beta\rangle + |\bar{a}_2''^\alpha e_x''^\beta a_2''^\alpha e_y''^\beta\rangle + \dots \quad (8) \end{aligned}$$

The terms not shown have the same symmetry as those on lines three and four. Together the first two terms in the expansion transform as  $E_y'$ , while the next four transform individually as  $E_y'$ . The last two terms in (8), however, constitute part of a  $^1A_2'$  state (note that the electrons in  $e_x''$  and  $e_y''$  have the same spin, as in the  $^3A_2'$  state), which is much higher in energy than  $^1E'$ . Therefore, to the extent that  $a_2''$  and  $\bar{a}_2''$  are different orbitals, so that the terms on the last line do not vanish, the SCF wave function for the  $^1E'$  state of  $D_{3h}$  trimethylenemethane contains a  $^1A_2'$  component which raises its energy. This contaminant can be annihilated using a projection operator<sup>23</sup> to yield a wave function that is pure  $^1E'$ . However, projection requires determining how the SCF-MO's transform into each other for each of the operations of  $D_{3h}$  and applying this information to the tedious transformation of the determinantal wave function for the singlet. Moreover, although projection results in a multiconfigurational wave function of  $^1E'$  symmetry, this wave function is by no means the  $^1E'$  multiconfigurational wave function of lowest energy.<sup>24</sup> The latter can be obtained for the  $\pi$  electrons of trimethylenemethane with far less effort than is required to generate the former, and it is to obtaining such a wave function by a CI calculation that we turn in the following section.

### CI Calculations on $^1E'$ Trimethylenemethane

Although, as noted above, SCF calculations on the two components of the  $^1E'$  state will not in general give the same energy, this equivalence problem does not arise in CI; so we are free to choose either component for our calculation. Because of the difficulty in interpreting physically the wave function for the nonbonding electrons in eq 2 and the less familiar nature of the MO's in eq 3, we elect to work with the  $^1E'$  component in which the starting wave function for the nonbonding electrons is given by eq 1. The remaining two electrons are placed in the familiar Hückel bonding MO for trimethylenemethane,  $\psi_1 = (\phi_4 + \chi)/\sqrt{2}$ , which has energy  $\alpha + \sqrt{3}\beta$ . The starting wave function for our CI calculation is then

$$\Psi_1 = (|\psi_1^\alpha \psi_1^\beta \psi_2^\alpha \psi_3^\beta\rangle + |\psi_1^\alpha \psi_1^\beta \psi_3^\alpha \psi_2^\beta\rangle)/\sqrt{2} \quad (9)$$

Since this configuration has one electron in  $\psi_2$ , and all the other MO's are symmetric with respect to the plane that bisects the  $C_1$ - $C_4$ - $C_2$  angle, this configuration will only mix with others of  $E'$  symmetry that also have one and only one electron in  $\psi_2$ . There are two low-lying configurations that

can mix with  $\Psi_1$ . One of these results from substituting  $\psi_4 = (\chi - \phi_4)/\sqrt{2}$  for  $\psi_3$  in eq 9, the other from removing one of the electrons in  $\psi_1$  and placing it in  $\psi_3$ , so that the latter MO is doubly occupied. Excited triplet configurations with the same MO occupancy can be constructed, but they do not mix with the  ${}^3A_2'$  ground state, since, like the singlets, they have  $E'$  symmetry. We can immediately conclude that the triplet wave function corresponding to (9) is a much better one than the singlet,  $\Psi_1$ , since there are no low-lying excited configurations that mix in to improve the triplet, while there are two,

$$\Psi_2 = (|\psi_1^\alpha\psi_1^\beta\psi_2^\alpha\psi_4^\beta\rangle + |\psi_1^\alpha\psi_1^\beta\psi_4^\alpha\psi_2^\beta\rangle)/\sqrt{2} \quad (10)$$

$$\Psi_3 = (|\psi_3^\alpha\psi_1^\beta\psi_2^\alpha\psi_3^\beta\rangle + |\psi_1^\alpha\psi_3^\beta\psi_3^\alpha\psi_2^\beta\rangle)/\sqrt{2}$$

that mix into  $\Psi_1$ . A corollary is that singlet and triplet planar trimethylenemethane must use different sets of MO's. For instance, mixing  $\Psi_2$  into  $\Psi_1$  has the effect of altering the wave function for the electron in  $\psi_3$  by mixing into it  $\psi_4$ . Consequently, since this mixing does take place,  $\psi_3$  cannot be the best possible orbital with which to construct a  ${}^1E'$  wave function; therefore  $\Psi_1$  cannot be the correct SCF wave function for this state. This is the physical equivalent of the more mathematical statement that  $\Psi_1$  is not a true SCF wave function, since it can be improved by mixing with configurations that differ from it by one-electron excitations,<sup>25</sup> so that it does not satisfy Brillouin's theorem for open-shell systems.<sup>19</sup>

Since  $\Psi_1$  differs from both  $\Psi_2$  and  $\Psi_3$  in the orbital assignment of just one electron, the Hamiltonian matrix elements between  $\Psi_1$  and the latter two configurations consist of several integrals over MO's. Some of these are zero by symmetry; the rest can be easily evaluated, using the approximations previously employed in a model calculation on the trimethylenemethane  $\pi$  system.<sup>9</sup> The result is

$$\langle\Psi_1|\mathcal{H}|\Psi_2\rangle = -\langle\Psi_1|\mathcal{H}|\Psi_3\rangle = -(\gamma_{11} - \gamma_{13})/3 = -2 \text{ eV} \quad (11)$$

Since both  $\Psi_2$  and  $\Psi_3$  lie  $-\sqrt{3}\beta + (\gamma_{11} - \gamma_{13})/6$  above  $\Psi_1$ , they mix equally into it. From eq 11 it is clear that it is the combination  $(\Psi_2 - \Psi_3)/\sqrt{2}$  that is mixed into  $\Psi_1$ . This combination lies  $-\sqrt{3}\beta$  above  $\Psi_1$ , since  $\langle\Psi_2|\mathcal{H}|\Psi_3\rangle = (\gamma_{11} - \gamma_{13})/6$ . The physical reason for the drop in energy is that both  $\Psi_2$  and  $\Psi_3$  separate charge, since  $\Psi_2$  has more than one  $\pi$  electron in  $\phi_4$  and  $\Psi_3$  has an identical amount of excess  $\pi$  electron density in  $\phi_1$ . Rewriting the wave function  $(\Psi_2 - \Psi_3)/\sqrt{2}$  as in eq 3, it is easy to show that this combination has the same net  $\pi$  electron distribution (one electron in each p  $\pi$  AO) as  $\Psi_1$ .

The energy lowering obtained by mixing  $(\Psi_2 - \Psi_3)/\sqrt{2}$  into  $\Psi_1$  depends on the value of  $\beta$  that one assumes. With  $\beta = -1.5$  eV, the energy lowering is 1.8 eV and the resulting unnormalized wave function is  $\Psi_1 + 0.45(\Psi_2 - \Psi_3)$ . As indicated above, mixing  $\Psi_2$  into  $\Psi_1$  with a plus sign is equivalent to altering  $\psi_3$  by adding a little of  $\psi_4$ . The effect is to increase the coefficient of the resulting MO at  $\phi_1$ , decrease the coefficients at  $\phi_2$  and  $\phi_3$ , and give the MO some electron density at  $\phi_4$ . The coefficient at  $\phi_4$  is such that the resulting MO is  $\pi$  antibonding between carbons 1 and 4 and bonding between  $C_2$  and  $C_4$  and between  $C_3$  and  $C_4$ . Similarly, mixing  $\Psi_3$  into  $\Psi_1$  with a minus sign is equivalent to altering  $\psi_1$ , for the electron of spin opposite to that in  $\psi_3$ , by subtracting a little of  $\psi_3$ . The changes in the magnitudes of the coefficients on subtracting  $\psi_3$  from  $\psi_1$  are equal and opposite to those that take place on adding  $\psi_4$  into  $\psi_3$ , while the changes in the  $\pi$  bond orders are identical. In fact, in the normalized wave function obtained using  $\beta = -1.5$  eV, the  $\pi$  bond order between carbons 1 and 4 drops to less than

20% of that between  $C_2$  or  $C_3$  and  $C_4$ . Clearly, the wave function that results from CI<sup>26</sup> resembles that for allyl plus an unconjugated p orbital more closely than it does the wave function given by  $\Psi_1$  and comprised of the MO's appropriate for the triplet.

Physically, the mixing of  $\Psi_2$  into  $\Psi_1$  moves the electron in  $\psi_3$  away from the one in  $\psi_2$ , in a manner very similar to that discussed above when just the nonbonding electrons were considered. The mixing of  $\Psi_3$  into  $\Psi_1$  with a minus sign moves the electron in  $\psi_1$  with spin opposite to that in  $\psi_3$  away from the latter electron. Since their appearing in the same AO is not forbidden by the Pauli principle, confining these two electrons to different regions of space reduces the size of the ionic terms in the wave function. It should be noted that although the modified  $\psi_1$  has larger coefficients at those atoms spanned by  $\psi_2$ , this fact causes no increase in electron repulsion. The reason is that in the singlet the electrons in these two MO's have the same spin, so they cannot simultaneously appear in the same AO. The physical explanation of why the triplets corresponding to  $\Psi_2$  and  $\Psi_3$  do not mix into the triplet corresponding to  $\Psi_1$  should now be apparent, in the triplet both nonbonding electrons have the same spin, so neither of the changes brought about by mixing  $\Psi_2$  and  $\Psi_3$  into  $\Psi_1$  causes any energy lowering.<sup>27</sup>

If the singlet trimethylenemethane wave function, obtained by mixing  $\Psi_2$  and  $\Psi_3$  into  $\Psi_1$ , resembles that of allyl plus p, the energies of these wave functions should be comparable. Before CI, the difference in energy between  $\Psi_1$  and the wave function for an allyl radical plus an unconjugated p orbital is<sup>9</sup>

$$\Delta E = 2(\sqrt{3} - \sqrt{2})\beta + \frac{3}{8}(\gamma_{11} - \gamma_{13}) \quad (12)$$

Since by mixing  $\Psi_3$  into  $\Psi_1$  we have allowed for correlation between the electron in  $\psi_3$  and the one of opposite spin in  $\psi_1$ , we must include the same type of correlation in the wave function for the allyl radical in order to make the comparison a fair one. The appropriate configuration in the allyl radical lies  $-2\sqrt{2}\beta + (\gamma_{11} + 4\gamma_{14} - 5\gamma_{13})/8$  above the lowest one, and the Hamiltonian matrix element between them is  $\sqrt{6}(\gamma_{11} - \gamma_{13})/8$ .<sup>28</sup> Taking  $\gamma_{11} = 11.1$  eV,  $\gamma_{14} = 7.5$  eV, and  $\gamma_{13} = 5.1$  eV,<sup>9</sup> a value of  $\beta = -1.5$  eV gives  $\Delta E$  in eq 12 as 1.3 eV. CI stabilizes trimethylenemethane by  $-1.8$  eV and allyl by  $-0.5$  eV; thus, for this choice of  $\beta$  the two wave functions have the same energy. A smaller magnitude for  $\beta$  diminishes the importance of the lower one-electron energy of trimethylenemethane, but it also increases the stabilization by CI of trimethylenemethane relative to allyl plus p, since it decreases the energy gap between  $\Psi_1$  and  $(\Psi_2 - \Psi_3)/\sqrt{2}$ . Consequently, the relative energies of the two wave functions are not very dependent on the value of  $\beta$  chosen. For  $\beta = -1.0$  eV, allyl plus p lies lower by 0.1 eV; for  $\beta = -2.0$  eV, trimethylenemethane is lower in energy by 0.2 eV. A larger magnitude for  $\beta$  favors trimethylenemethane, since in the limit  $\beta \rightarrow -\infty$ , one-electron energies outweigh electron repulsion effects, and the first term in eq 12 dominates all the others. In fact, when complete CI is carried out for both systems, the trimethylenemethane wave function lies lower than that for allyl plus p for all values of  $\beta$ . Mathematically, this results from the fact that two other more highly excited configurations mix into  $\Psi_2$  and  $\Psi_3$ , though not into  $\Psi_1$ . Consequently, the energy gap between  $(\Psi_2 - \Psi_3)/\sqrt{2}$  and  $\Psi_1$  is effectively lowered, so that full CI results in a somewhat greater stabilization of singlet trimethylenemethane than that which we have calculated by mixing in only the lowest two excited configurations. Physically, the fact that the  $\pi$  system of trimethylenemethane has lower energy than that of an allyl radical plus an unconjugated p orbital is a consequence of the fact that

even in the limit where  $\beta \rightarrow 0$ , so that electron repulsion effects dominate, trimethylenemethane can always adopt the allyl plus p wave function by mixing into  $\Psi_1$  sufficient amounts of the appropriate excited configurations.

This fact is made obvious by a CI calculation on singlet trimethylenemethane that starts with a configuration which is comprised of the filled MO's for allyl plus p.

$$\Psi_1' = (|\psi_1'\alpha\psi_1'\beta\psi_2'\alpha p^\beta\rangle + |\psi_1'\alpha\psi_1'\beta p^\alpha\psi_2'\beta\rangle)/\sqrt{2} \quad (13)$$

In eq 13  $\psi_1' = \frac{1}{2}(\phi_2 + \sqrt{2}\phi_4 + \phi_3)$ ,  $\psi_2'$  is the same as before, and  $p = \phi_1$ . There are again two configurations involving one-electron excitations that can mix with  $\Psi_1'$

$$\Psi_2' = (|p^\alpha\psi_1'\beta\psi_2'\alpha p^\beta\rangle + |\psi_1'\alpha p^\beta\psi_2'\beta\rangle)/\sqrt{2}$$

$$\Psi_3' = (|\psi_1'\alpha\psi_1'\beta\psi_2'\alpha\psi_3'\beta\rangle + |\psi_1'\alpha\psi_1'\beta\psi_3'\alpha\psi_2'\beta\rangle)/\sqrt{2} \quad (14)$$

Mixing of these configurations with  $\Psi_1'$  creates bonding between  $\phi_1$  and  $\phi_4$ ; in fact, the matrix element of the Hamiltonian between  $\Psi_1'$  and  $\Psi_2'$  reduces to the one-electron interaction between p and  $\psi_1'$ , which is equal to  $\beta/\sqrt{2}$ . Similarly, the matrix element between  $\Psi_1'$  and  $\Psi_3'$  is equal to the interaction of  $\psi_3' = (\phi_2 - \sqrt{2}\phi_4 + \phi_3)/2$  with p, which is  $-\beta/\sqrt{2}$ . The two excited configurations do not mix with each other, but they do have the same energy, which is  $-\sqrt{2}\beta + 7(\gamma_{11} - \gamma_{13})/8$  above that of  $\Psi_1'$ . The reason why the excited configurations have so much higher electron repulsion energy than  $\Psi_1'$  is twofold. First, unlike  $\Psi_1'$  they represent very polar electron distributions.  $\Psi_2'$  places two electrons in  $\phi_1$ , while  $\Psi_3'$  removes all the electron density from this AO, leaving a full positive charge at  $C_1$ . Second, both configurations are open-shell singlets in which, unlike the case in  $\Psi_1'$ , the two singly occupied MO's have atoms in common. Thus, the wave functions  $\Psi_2'$  and  $\Psi_3'$  both contain high energy ionic terms corresponding to the simultaneous occupancy of the same AO by the electrons in these MO's. Such ionic terms are, of course, absent from the wave functions for the triplets corresponding to  $\Psi_2'$  and  $\Psi_3'$ . Consequently, the triplets are  $(\gamma_{11} - \gamma_{13})/2$  lower in energy than the singlets, and so they mix more strongly into the triplet configuration corresponding to  $\Psi_1'$ , which is accidentally degenerate with  $\Psi_1'$  itself when differential overlap is neglected. Therefore, we are again led to the inescapable conclusion that the wave functions for singlet and triplet trimethylenemethane will differ and that the  $\pi$  bonding between  $\phi_1$  and  $\phi_4$  will be much stronger in the latter than in the former.

Nevertheless, in singlet trimethylenemethane  $\Psi_2'$  and  $\Psi_3'$  do mix into  $\Psi_1'$ , unless  $\beta_{14} \rightarrow 0$ . Since  $\Psi_2'$  and  $\Psi_3'$  each differ from  $\Psi_1'$  by a one-electron excitation, it is clear that, like  $\Psi_1$ ,  $\Psi_1'$  cannot be the true SCF wave function for planar trimethylenemethane. That  $\Psi_1'$  is a closer approximation than  $\Psi_1$  to the SCF wave function can be inferred from the relative weights of these configurations in the CI wave function and the size of the energy lowering that results from CI, starting with each. Recalling that a value for  $\beta$  of  $-1.5$  eV leads to a calculated energy lowering of 1.8 eV on mixing  $0.45(\Psi_2 - \Psi_3)$  into  $\Psi_1$ , with the same value of  $\beta$  the energy of  $\Psi_1'$  is lowered by only 0.3 eV on mixing in  $0.14(\Psi_2' - \Psi_3')$ . Since at this level of CI for the two different approaches to the wave function for singlet trimethylenemethane  $\Psi_1'$  represents 96% of the wave function, while  $\Psi_1$  represents only 71%, it is clear that the description of the planar singlet as allyl plus p is by far the more accurate one.<sup>29</sup>

In fact, partial CI *overestimates* the mixing of  $\Psi_2' - \Psi_3'$  into  $\Psi_1'$ . The reason is that the configuration,  $\Psi_4'$ , which is responsible for correlating the motions of the electrons in  $\psi_1$ , with that of the electron in  $\psi_2$ , lies  $-2\sqrt{2}\beta + (\gamma_{11} + 4\gamma_{14} - 5\gamma_{13})/8$  above  $\Psi_1'$ , and the matrix element for the

interaction of  $\Psi_4'$  with  $\Psi_1'$  is  $\sqrt{6}(\gamma_{11} - \gamma_{13})/8$ .<sup>28</sup> Thus, for reasonable values of  $\beta$ ,  $\Psi_4'$  lies below  $\Psi_2'$  and  $\Psi_3'$  and interacts more strongly with  $\Psi_1'$  than they do. Moreover,  $\Psi_4'$  interacts with  $\Psi_2'$  and  $\Psi_3'$  in such a way that when  $\Psi_4'$  is mixed into  $\Psi_1'$  in a stabilizing fashion, the addition of  $\Psi_2' - \Psi_3'$  to the wave function does not result in as large an energy lowering as when  $\Psi_4'$  is absent.<sup>30</sup> With  $\beta = -1.5$  eV, the addition of  $\Psi_2' - \Psi_3'$  to the wave function containing  $\Psi_4'$  results in an energy lowering of less than half of the 0.3 eV calculated when  $\Psi_4'$  is not included. Concomitantly, there is a reduction in the mixing coefficient for these two configurations in the resulting unnormalized wave function from 0.14 to 0.10.<sup>31</sup>

At the equilibrium geometry of this component of  ${}^1E'$  planar trimethylenemethane, the mixing of  $\Psi_2' - \Psi_3'$  into the wave function causes an even smaller energy lowering and occurs with a correspondingly lower coefficient. Since the  $\pi$  bond order between  $\phi_1$  and  $\phi_4$  is much smaller than that between the  $\pi$  AO's of the allylic moiety, the molecule will distort from  $D_{3h}$  symmetry by lengthening the bond to the unique peripheral carbon atom. Using the wave function derived for  $\beta = -1.5$  eV, the  $\pi$  bond order between carbons 1 and 4 is computed from the mixing between  $\Psi_1'$  and  $\Psi_2' - \Psi_3'$  to be 0.14, compared to the value of 0.70 for the  $\pi$  bonds in the allylic moiety. Actually the  $\pi$  bond order between  $C_1$  and  $C_4$  is even smaller than this value, since the mixing between  $\Psi_2' - \Psi_3'$  and  $\Psi_4'$  contributes negatively to it. Using a standard relationship between  $\pi$  bond order and bond length,<sup>32</sup> the bond to the unique peripheral carbon atom is calculated to be  $>0.1$  Å longer than those in the allylic moiety. Thus, if a value of  $\beta = -1.5$  eV is used for these two  $\pi$  bonds, a  $\beta$  of smaller magnitude should be used for the unique one. A reduction in the magnitude of  $\beta_{14}$  to 1.2 eV decreases the contribution of  $\Psi_2'$  and  $\Psi_3'$  to the CI energy lowering to less than 0.1 eV, and the mixing coefficient for these two configurations of course also drops correspondingly.

## Conclusions

It is obvious from the results of this semiempirical CI study<sup>33</sup> that the description of the wave function for planar singlet trimethylenemethane as being that of an allyl radical plus a p orbital is a quite accurate one. From these  $\pi$  electron calculations it seems quite probable that the preferred geometry for singlet trimethylenemethane is the orthogonal one, since the energy lowering on hyperconjugation of the p orbital with the  $\sigma$  bonds is quite likely to exceed the small stabilization gained by its conjugation with the  $\pi$  system of the allylic moiety. It is clear, however, that the energy difference between orthogonal and planar trimethylenemethane must be small in the singlet, a consequence of the fact that electron repulsion in this open-shell system causes the optimum singlet wave function to be essentially that for an allyl radical plus an electron localized in a p orbital,<sup>35</sup> independent of the geometry of trimethylenemethane.<sup>38</sup>

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- (18) Note that the NBMO's,  $\psi_2$  and  $\psi_3$ , for the  ${}^3A_2'$  state differ from the optimum NBMO's for the singlet in eq 4, where  $\psi_3$  is replaced by  $(\psi_3 + (1/2^{1/2})\chi)/\sqrt{2/3} = \phi_1$ .
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- (24) The situation is analogous to that which obtains after projection of an unrestricted Hartree–Fock wave function for a radical. For a discussion see ref 16, pp 263–265.
- (25) For a lucid discussion, see H. C. Longuet-Higgins and J. A. Pople, *Proc. Phys. Soc., London, Sect. A*, **68**, 591 (1955).
- (26) The CI wave function is not quite equivalent to  $[(\psi_1 - 0.45\psi_3)^\alpha\psi_1^\beta\psi_2^\alpha(\psi_2 + 0.45\psi_4)^\beta + |\psi_1^\alpha(\psi_1 - 0.45\psi_3)^\beta(\psi_3 + 0.45\psi_4)^\alpha\psi_2^\beta|]/\sqrt{2}$  since the latter wave function is equal to  $\Psi_1 + 0.45(\Psi_2 - \Psi_3) - (0.45)^2(|\psi_3^\alpha\psi_1^\beta\psi_2^\alpha\psi_4^\beta| + |\psi_1^\alpha\psi_3^\beta\psi_4^\alpha\psi_2^\beta|)$ . The last two terms are, in fact, of  $A_2'$  symmetry and so do not belong in the  ${}^1E'$  wave function. Since the latter wave function has the form of that which would be obtained from an unrestricted Hartree–Fock calculation, it is clear that this type of SCF method will also introduce foreign symmetry contaminants into the total wave function for  $D_{3h}$  trimethylenemethane.
- (27) Triplet trimethylenemethane can profit from CI with a configuration that mixes  $\psi_4$  into  $\psi_1$  with a plus sign for the electron of the same spin as those in the NBMO's and with a minus sign for the electron of opposite spin. This mixing is responsible for the negative spin density at the central carbon in triplet trimethylenemethane.<sup>1</sup> For another example of the differences in CI possible for singlet and triplet configurations with the same MO occupancy, see ref 15.
- (28) See ref 16, pp 265–271.
- (29) This fact can also be inferred from the relative energies of  $\Psi_1$  and  $\Psi_1'$ . From eq 12  $\Psi_1'$  lies below  $\Psi_1$  by 1.3 eV with  $\beta = -1.5$  eV.
- (30) One effect of mixing  $\Psi_4'$  into  $\Psi_1'$  is to introduce a net spin in  $\phi_4$ , opposite to that of the electron in  $\psi_2$ .<sup>28</sup> Dewar<sup>3</sup> has suggested that in the singlet; since the net spin at  $\phi_4$  is the same as that in p, the bonding between these two AO's is reduced. This appears to be a satisfactory explanation of the reduction of bonding between  $\phi_4$  and p when  $\Psi_4'$  is included in the wave function. Further support for the intuitive argument given by Dewar for the effect of negative spin density on the bonding in trimethylenemethane is the enhancement of bonding between  $\phi_4$  and p, when the configuration corresponding to  $\Psi_4'$  is included in the wave function for the triplet. However, as noted previously,<sup>9</sup> spin polarization effects are irrelevant in explaining the difference in energy between  $\Psi_1$  and  $\Psi_1'$ .
- (31) Mixing in of other more highly excited configurations effectively lowers the energy of  $\Psi_2' - \Psi_3'$  relative to  $\Psi_1'$  by about 0.5 eV and that of  $\Psi_4'$  by roughly twice this amount. The net effect is to reduce very slightly the energy lowering due to the presence of  $\Psi_2'$  and  $\Psi_3'$  in the wave function, while leaving the mixing coefficient for these two configurations essentially unchanged in the unnormalized wave function.
- (32) See, for instance, ref 16, p 47.
- (33) These semi-empirical results have been confirmed by ab initio calculations carried out in collaboration with Professor E. R. Davidson, *J. Chem. Phys.*, **64**, 663 (1976). One difference found in the ab initio study is that the interaction between  $\phi_1$  and  $\phi_4$  is net antibonding, both at the SCF and CI levels. The principal reason for this difference is the inclusion of overlap in the ab initio calculations. For instance, if  $S$  is the overlap integral between  $\phi_1$  and  $\phi_4$ ,  $\Psi_1'$  is not properly normalized, since  $\langle\Psi_1'|\Psi_1'\rangle = \langle\psi_1^\alpha|\psi_1^\alpha\rangle\langle\psi_2^\beta/\psi_2^\beta\rangle\langle\psi_3^\beta|\psi_3^\beta\rangle\langle\rho^\beta|\rho^\beta\rangle - \langle\psi_1^\beta|\rho^\beta\rangle^2 = 1 - \frac{1}{2}S^2$ . More important, if  $h$  is the one-electron part of the Hamiltonian and  $\Psi_1'$  is correctly normalized,  $\langle\Psi_1'|h|\Psi_1'\rangle = \langle\psi_1^\alpha|h|\psi_1^\alpha\rangle + \langle\psi_2^\beta|h|\psi_2^\beta\rangle + \langle\psi_3^\beta|h|\psi_3^\beta\rangle + \langle\rho|h|\rho\rangle - 2\langle\psi_1^\beta|\rho\rangle\langle\psi_1^\beta|h|\rho\rangle/(1 - \frac{1}{2}S^2)$ , and the last term gives  $-S\beta/(1 - S^2/2)$  for the interaction between  $\phi_1$  and  $\phi_4$ . This term represents the net antibonding that results from the electrons of the same spin that are effectively localized in these AO's. Since this effect manifests itself only when the overlap between orbitals is included in a calculation, it has been called "overlap repulsion".<sup>34</sup>
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- (35) Electron repulsion in the  ${}^1E'$  state of open-shell annulene ions must also result in optimum MO's for this state that differ from those appropriate for the triplet ground state.<sup>14,16</sup> In these systems. From the results of this study on trimethylenemethane it can also be inferred that the optimum wave function for the lowest singlet state of tetramethylenemethane must be approximately that for two isolated allyl radicals,<sup>36</sup> so that repulsion between the nonbonding electrons cannot be invoked<sup>37</sup> to explain the anomalously high activation energy for the degenerate rearrangement of 1,2-dimethylenecyclobutane.
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- (38) NOTE ADDED IN PROOF. The precise magnitude of the energy difference between planar and orthogonal singlet trimethylenemethane has been the subject of further research while this paper was in press. The experimental work of W. R. Roth and G. H. Wegener, *Angew. Chem. Int. Ed. Engl.*, **14**, 758 (1975), and the theoretical study of J. H. Davis and W. A. Goddard III, *J. Am. Chem. Soc.*, **98**, 303 (1976), have both found the energetic preference for the orthogonal geometry to be small.