

(i.e., the benzidine rearrangement^{33,40,41}), *N,O*-diarylhydroxylamines,⁴² substituted triphenylmethylhydroxylamines,⁴³ hydroxyimines (i.e., oximes, cf. Beckmann rearrangement⁴⁴), oxaziridines,⁴⁵ and alkyl and α -hydroxylalkyl hydroperoxides (cf. the Baeyer–Villiger reaction⁴⁶). One can also consider syn–anti isomerization⁴⁴ and even hydrolysis of oximes.⁴⁷

Let us now briefly consider reactions of HOF and F₂ and their protonated species. For HOF we calculated a 12-kcal/mol difference between O and F protonation favoring the former. HOF is one of the most thoroughly investigated triatomic molecules with regard to physical properties.⁴⁸ However, few chemical reactions have been performed most probably due in large part to the inherent instability of aqueous HOF solutions. In base, HOF decomposition yields O₂ while in acid it yields H₂O₂.⁴⁸ The latter may be explained in terms of either F protonation or O–F bond polarization³⁰ and a subsequent SN2 attack on the oxygen by a water molecule to form H₂OOH⁺, i.e., protonated H₂O₂. Analogous O–F bond polarization has been invoked³⁰ in a discussion of the reaction of OF₂ with primary amines to form the corresponding

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nitroso compound.⁴⁹ To the best of the authors' knowledge, protonated F₂ has not been proposed in the literature. We note, however, that protonated Cl₂ and Br₂ have recently been invoked in aromatic halogenations⁵⁰ and proton-polarized F₂ in low-temperature olefin–fluorine reactions (ref 30 discussing the results in ref 51).

Conclusion

In general, the theoretically calculated proton affinities here are in reasonable agreement with experimental values and give us some confidence in the predictions of proton affinities for NH₂OH, NH₂F, HOOH, HOF, and F₂. CH₃F is a molecule where a more precise calculation of the proton affinity would be of interest. When a plus charge is placed on a molecule (as in substituted carbonium ions RCH₂⁺ or in protonated species such as RNH₃⁺), R = CH₃ and NH₂ appear to be inductively stabilizing and R = OH and F destabilizing relative to R = H.

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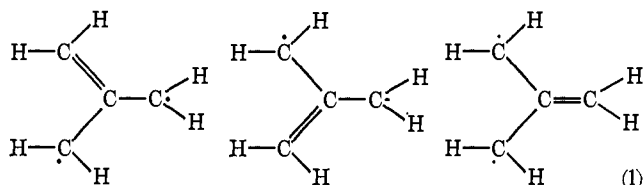
Triplet Electronic Ground State of Trimethylenemethane^{1a}

David R. Yarkony^{1b} and Henry F. Schaefer III*^{1c}

Contribution from the Department of Chemistry and Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720. Received January 16, 1974

Abstract: A nonempirical quantum mechanical study of the electronic structure of C(CH₂)₃ has been carried out. A double ζ basis set of contracted Gaussian functions was employed, and self-consistent-field wave functions were obtained for the triplet ground state. The planar (*D_{3h}*) configuration is predicted to lie 17 kcal/mol below the orthogonal (*C_{2v}*) form. The electronic structure is discussed in terms of Mulliken populations and orbital perspective plots. Some preliminary results for the lowest singlet states are reported.

There is a long history of interest among theoretical organic chemists in the trimethylenemethane radical, traditionally represented by the three structures



(1) (a) Work performed under the auspices of the U. S. Atomic Energy Commission; (b) Charles Fish Fellow; (c) Alfred P. Sloan Fellow.

Interest in C(CH₂)₃ began in 1948 with the work of Moffitt, who was cited in a paper by Coulson² as having shown the central atom in trimethylenemethane to have the greatest π bond order attainable by a carbon atom. In a related paper appearing 4 years later, Greenwood³ discussed the critical role of C(CH₂)₃ in the notion of "free valence," defined by Coulson²

$$FV = N_{\max} - N \quad (2)$$

(2) C. A. Coulson, *J. Chim. Phys. Physicochim. Biol.*, **45**, 243 (1948). For an interesting review, see C. A. Coulson, "Wave Mechanics: The First Fifty Years," W. C. Price, S. S. Chissick, and T. Ravensdale, Ed., Wiley, New York, N. Y., 1973, p 255.

(3) H. H. Greenwood, *Trans. Faraday Soc.*, **48**, 677 (1952).

where N is the total bond order of the atom in question and N_{\max} is the maximum possible bond order, $3 + \sqrt{3}$, the value taken on by the central atom of trimethylenemethane. Hence the free valence of the central carbon of $C(CH_2)_3$ is identically zero and serves as a frame of reference.

The role of trimethylenemethane as one of the simplest hydrocarbon molecules possessing no normal Kekulé-type structure was first discussed by Longuet-Higgins⁴ in 1950. The general question he addressed was "why are there relatively few stable molecules for which it is impossible to write some classical valence bond structure?" At the time, of course, $C(CH_2)_3$ was no more than a gleam in the eyes of several theoreticians. Using qualitative molecular orbital theory, Longuet-Higgins was able to show that such non-Kekulé molecules should have paramagnetic ground states, react extremely easily with oxygen, and hence be very difficult to prepare in the presence of air.

Trimethylenemethane has also played an important role in the development of the theory of zero field splittings in organic triplet states. The first paper in this area was that of McConnell,⁵ who predicted a negative spin density at the central carbon atom and suggested that the spin-spin parameter D might be close to zero. A longer paper⁶ by McLachlan on the same problem appeared shortly thereafter and considered, but ultimately discounted, the possibility that D for $C(CH_2)_3$ might take on a negative value. More detailed calculations of the zero field splittings have recently been reported by Gold^{7a} and by Gondo and Maki.^{7b}

Among the most sophisticated of the semirigorous calculations performed on $C(CH_2)_3$ are those of Chong and Linnett, who compared the methods of alternate molecular orbitals⁸ and nonpaired spatial orbitals.⁹

In light of the above theoretical background, the importance of the first preparation of trimethylenemethane by Dowd¹⁰ is obvious. The original synthesis was by irradiation of the pyrazoline system

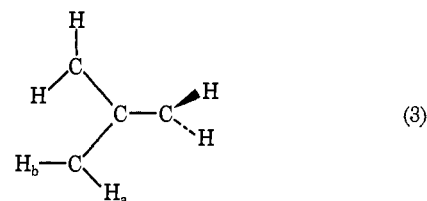


Experimental work following this initial breakthrough has been nicely summarized in a recent review article by Dowd.¹¹ Of particular importance to us is the electron diffraction study¹² of the related compound $C(CH_2)_3Fe(CO)_3$. The C-C bond distance was found to be 1.437 Å and the C-H distance 1.111 Å. Also noteworthy is the photoelectron spectrum of the same compound, obtained by Dewar and Worley.¹³

The recent semiempirical study of Dewar and Wasson¹⁴ differs in scope from earlier theoretical work, in that the potential energy surfaces of the three lowest

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- (5) H. M. McConnell, *J. Chem. Phys.*, **35**, 1520 (1961).
- (6) A. D. McLachlan, *Mol. Phys.*, **5**, 51 (1962).
- (7) (a) A. Gold, *J. Chem. Phys.*, **51**, 4961 (1969); (b) Y. Gondo and A. H. Maki, *ibid.*, **50**, 3638 (1969).
- (8) D. P. Chong and J. W. Linnett, *Mol. Phys.*, **8**, 541 (1964).
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electronic states were explored. As expected, the planar triplet state is predicted to be the electronic ground state. However, the first excited state is an open-shell singlet, predicted to have one methylene group orthogonal to the other two.



This result appears to be consistent with the conclusions of Doering and Roth,¹⁵ based on the stereochemistry of the methylenecyclopropane rearrangement.

A final index of the impact of trimethylenemethane is the significant number of texts in which it is used as an example.¹⁶

In the present paper we present the first *a priori* study of the electronic structure of $C(CH_2)_3$. A primary goal is to discuss the electronic structure of the planar triplet state in terms of population analyses and perspective plots. We also discuss the lowest planar singlet state, as well as the triplet ground state in its orthogonal configuration.

Theoretical Aspects

For planar D_{3h} geometries, the lowest electron configuration of trimethylenemethane is

$$1a_1'^2 1e'^4 2a_1'^2 3a_1'^2 2e'^4 4a_1'^2 3e'^4 1a_2'' 2e_2''^4 1a_2''^2 1e''^2 \quad (4)$$

Hence we expect the ground state to be $^3A_2'$, the first excited state to be $^1E'$, and the second excited state to be of $^1A_1'$ symmetry.

If we retain the D_{3h} nuclear geometry, but require the individual orbitals to transform according to the lower symmetry point group C_{2v} , we now have three electron configurations.

$$1a_1^2 2a_1^2 1b_2^2 3a_1^2 4a_1^2 5a_1^2 2b_2^2 6a_1^2 7a_1^2 3b_2^2 4b_2^2 8a_1^2 \quad 5b_2^2 1b_1^2 1a_2 2b_1 \quad ^3B_2, ^1B_2 \quad (5)$$

$$(2)^{-1/2}(1a_1^2 2a_1^2 1b_2^2 3a_1^2 4a_1^2 5a_1^2 2b_2^2 6a_1^2 7a_1^2 3b_2^2 4b_2^2 8a_1^2 5b_2^2 1b_1^2 1a_2) \pm (2)^{-1/2}(1a_1^2 2a_1^2 1b_2^2 3a_1^2 4a_1^2 5a_1^2 2b_2^2 6a_1^2 7a_1^2 3b_2^2 4b_2^2 8a_1^2 5b_2^2 1b_1^2 2b_1) \quad ^1A_1 \quad (6)$$

The correspondence between D_{3h} and C_{2v} electronic states is¹⁷

$$\begin{aligned} ^3A_2' &\longrightarrow ^3B_2 \\ ^1E' &\longrightarrow ^1B_2 + ^1A_1 \\ ^1A_1' &\longrightarrow ^1A_1 \end{aligned} \quad (7)$$

For D_{3h} geometries, the symmetric combination of configurations 6 will be of $^1A_1'$ irreducible representation, while the antisymmetric combination will be a $^1E'$ state.

One might think that the total self-consistent-field (SCF) energy of the $^1E'$ state should be the same whether it is obtained using configuration 4, configuration 5, or the antisymmetric combination of configura-

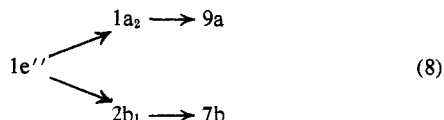
(15) W. von E. Doering and H. D. Roth, *Tetrahedron*, **26**, 2825 (1970).

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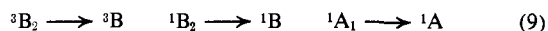
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tions 6. However, this is not the case.¹⁸ In fact, the imposition of full D_{3h} symmetry upon the orbitals represents a significant constraint on the SCF wave function of this open-shell system. Furthermore, even when the calculations are carried out for C_{2v} orbitals, the 1B_2 and 1A_1 components of the ${}^1E'$ state are not precisely degenerate. This latter inconsistency illustrates the equivalence restrictions problem discussed by Julienne, Krauss, and Wahl¹⁹ with reference to the asymptotic degeneracy of the ${}^2\Pi$ and ${}^2\Sigma^+$ states of HF^+ . Finally it should be noted that semiempirical methods suffer from similar inconsistencies. For example, the MINDO calculations of Dewar and Wasson¹⁴ predict, in the limit of D_{3h} geometry, the 1B_2 state to lie a full 20 kcal/mol below the 1A_1 state. In fact, of course, these two states are the degenerate components of the ${}^1E'$ state.

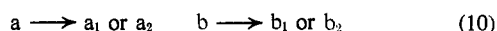
Our next problem is to correlate the D_{3h} electronic states with those for the nonplanar orthogonal geometry 3. As the nonequivalent methylene group is twisted out of the plane, only a single twofold rotation remains, and hence the new point group is C_2 . The over-all state symmetries of twisted trimethylenemethane are determined by the symmetries of the open-shell orbitals, which resolve as



Therefore the $C_{2v} \rightarrow C_2$ state correlation is

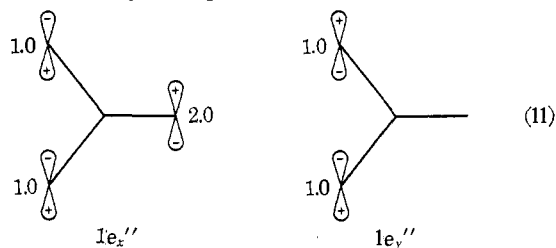


When we proceed from the twisted form to the orthogonal geometry 3, the point group changes from C_2 to C_{2v} . Unfortunately, we then have the ambiguous correlation

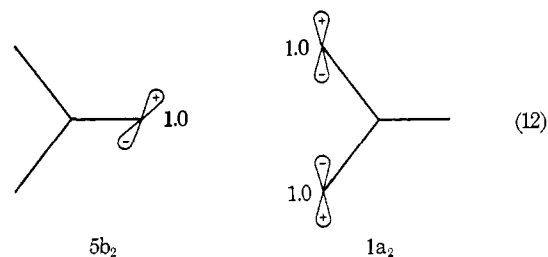


Hence there are four acceptable (from symmetry considerations only) sets of electron configurations: $a_1^2, b_1^2, a_1b_1; a_1^2, b_2^2, a_1b_2; a_2^2, b_1^2, a_2b_1$; or, finally, a_2^2, b_2^2, a_2b_2 , where only the outer two electrons have been indicated. Which of these four sets of configurations will correlate with the $1e''^2$ configuration of D_{3h} trimethylenemethane cannot be determined by symmetry arguments alone. In fact, the correct adiabatic correlation can only be made by knowing the relative positions of the various electronic states in the orthogonal configuration.

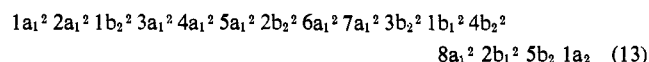
However, simple orbital considerations can guide us to a reasonable prediction of the correct state correlation. For the planar triplet, the two components of the $1e''$ orbital may be depicted as



In these sketches, the lobes of the $p\pi$ orbitals are meant to lie above and below the plane of this page. When the molecule is twisted into the orthogonal geometry form, the $1e_y''$ remains intact but is now the $1a_2$ orbital. The $1e_x''$ combination is no longer a symmetry orbital but is likely to be converted (during the adiabatic twisting motion) to a distorted atomic p function perpendicular to the function with coefficient 2.0 in the $1e_x''$ orbital of eq 11. That is the orbitals of eq 11 are likely to correlate with the orbitals



Hence the electron configuration for orthogonal trimethylenemethane should be



In the present study we have carried out *ab initio* SCF calculations on the planar ${}^3A_2'$, ${}^1E'$, and ${}^1A_1'$ states arising from electron configuration 4. To test the effects of the spatial symmetry restrictions implicit in (4), the same electronic states have been studied with orbitals constrained only to be of C_{2v} symmetry. That is, SCF wave functions have been obtained for the 3B_2 and 1B_2 states, which arise from electron configuration 5. For the orthogonal geometry 3, an SCF wave function was obtained for the 3B_2 ground state arising from configuration 13. The computations were carried out using the SCF methods of Hunt, Hay, and Goddard.²⁰

A contracted Gaussian basis set of double ζ quality was used. For carbon, Huzinaga's (9s 5p) basis²¹ was contracted to (4s 2p) following Dunning.²² A comparable (4s/2s) contraction was adopted for hydrogen, with each Gaussian exponent α multiplied by $(1.2)^2 = 1.44$.

The geometries chosen were based on a C-C distance of 1.43 Å and a C-H distance of 1.10 Å. The C-C-C and H-C-H angles were taken to be 120° .

Results and Discussion

The SCF energy for the ${}^3A_2'$ ground state was -154.8252 hartrees. An identical energy was obtained when the same state was described as 3B_2 . For the ${}^1E'$ state the restricted SCF energy was -154.7159 hartrees. However, in this case, as expected,¹⁸ the C_{2v} symmetry calculation gave a significantly lower energy. The 1B_2 energy was -154.7914 hartrees, or a full 0.0755 hartree = 47 kcal/mol lower than the result obtained constraining the molecular orbitals to have full D_{3h} symmetry.

The ambiguity of the ${}^1E'$ energy creates something of a dilemma for the prediction of the ${}^3A_2' - {}^1E'$ energy separation. The symmetry and equivalence restriction do not affect the ${}^3A_2'$ energy but have a profound

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(19) P. S. Julienne, M. Krauss, and A. C. Wahl, *Chem. Phys. Lett.*, **11**, 16 (1971).

(20) W. J. Hunt, P. J. Hay, and W. A. Goddard, *J. Chem. Phys.*, **57**, 738 (1972).

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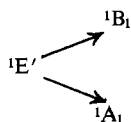
(22) T. H. Dunning, *J. Chem. Phys.*, **53**, 2823 (1970).

effect on the ${}^1E'$ energy. Our contention is that the calculated ${}^1E'$ energy is artificially high, due to the symmetry and equivalence restrictions, and that either the 1B_2 or 1A_1 energy should be used to obtain the separation. Hence we predict the ${}^3A_2' - {}^1E'$ separation to be 0.0338 hartree or 21 kcal/mol. The MINDO/2 calculations of Dewar and Wasson¹⁴ predict this energy difference to be ~ 35 kcal/mol.

The planar ${}^1A_1'$ state was also studied, with configuration 4 yielding an SCF energy of -154.6200 hartrees. The same state was also studied with no constraints being put on the spatial form of the molecular orbitals. That is, there were 14 doubly occupied orbitals and 2 singly occupied orbitals in this two-determinant wave function. Interestingly enough, the SCF energy was the same as that obtained with the full D_{3h} symmetry. Actually, this result is predicted by Manne's analysis,¹⁸ since the ${}^1A_1'$ representation is totally symmetric. Thus we predict the ${}^1A_1'$ state, which was not studied by Dewar and Wasson, to lie 0.2052 hartree or 128 kcal/mol above the ground state. However, the correlation energy of the ${}^1A_1'$ state should be significantly greater²³ (perhaps 10 kcal/mol) than that of the ${}^3A_2'$ state, and thus a somewhat smaller separation is expected.

For the orthogonal geometry 3, the 3B_1 ground state energy, corresponding to electron configuration 13, was -154.7982 . Thus the twisted molecule is predicted to lie 17 kcal/mol above the planar geometry. In a valence bond picture, of course, this preference for planarity can be rationalized in terms of a loss of "resonance" energy at the orthogonal geometry. We should point out that this 17 kcal/mol might be reduced if the bond between the central and orthogonal carbons was permitted to relax.

Due to the ambiguity in correlating the two lowest orthogonal singlets with the planar ${}^1E'$ state, and the resulting difficulty encountered by Dewar and Wasson in their semiempirical study, it was decided not to attempt to follow the



paths for the twisting of trimethylenemethane. However, a single SCF calculation was carried out for the open-shell singlet, 1B_1 state, at the orthogonal geometry. The energy obtained was -154.7958 hartrees, only 1.5 kcal/mol above the 3B_1 ground state energy at this geometry. This same separation appears to be ~ 3 kcal/mol in the calculations of Dewar and Wasson.¹⁴ Finally, we predict that at the orthogonal geometry the open-shell singlet lies 2.8 kcal/mol below the planar 1B_2 component of the ${}^1E'$ state.

The electronic structure of the triplet ground state may be discussed further in terms of the orbital energies and Mulliken populations, given in Table I (planar geometry) and in Table II (orthogonal geometry). Perhaps the first point to be made is that the σ and π orbital energies are well separated. For the planar geometry, Table I shows the highest σ orbital ($4e'$) to have $\epsilon = -0.5236$ hartree, whereas the lowest π orbital ($1a_2''$) has $\epsilon = -0.4383$ hartree. Thus it may

be reasonable to discuss the excited states of $C(CH_2)_3$ without reference to the σ orbitals.

The correspondence between the orbitals of planar and orthogonal trimethylenemethane is greatly simplified by comparison of the orbital energies. The planar $1a_1'$ orbital is a $1s$ orbital on the central carbon and is essentially identical with the orthogonal $1a_1$ orbital. The nearly degenerate $1e'$ and $2a_1'$ orbitals correlate with the $1b_2$, $2a_1$, and $3a_1$ orbitals. These are $1s$ orbitals on the terminal carbon atoms. Note that for the orthogonal geometry, the orbital ($3a_1$) corresponding to the twisted methylene group has a noticeably higher orbital energy. The $3a_1'$ and $4a_1$ orbitals have very close ϵ 's and similar composition, a symmetric combination of carbon $2s$ orbitals, with a central carbon contribution of $\sim 43\%$. The $2e'$ orbital decomposes into the $5a_1$ and $2b_2$ orbitals upon twisting. These orbitals are primarily terminal carbon $2s$ in nature, with a significant contribution ($\sim 18\%$) from hydrogen $1s$. The $4a_1'$ orbital becomes $6a_1$ upon twisting and is a conglomeration of all the atomic orbitals except the central carbon p functions. The $3e'$ orbital is clearly related to the $7a_1$ orbital; they have nearly identical orbital energies and have their greatest contribution from the outer carbon p orbitals, with, in addition, $\sim 27\%$ hydrogen $1s$ character.

For the orthogonal geometry, the orbital energies of $3b_2$ and $1b_1$ differ by only 0.003 hartree and hence it is not immediately obvious which of these correlates with the second component of the planar $3e'$ orbital. In this regard, note also that the next planar orbital, the $1a_2'$, has no obvious counterpart among the orthogonal orbitals. We conclude that, as a pair, the b component of the $3e'$ orbital and the $1a_2'$ orbital correlate with the ($3b_2$, $1b_1$) pair but that some mixing of orbitals occurs during the twisting motion. The $4e'$ orbital decomposes into $4b_2$ and $8a_1$ upon twisting and is a combination of carbon $2p$ and hydrogen $1s$ functions.

With the exception of the $1e''$ orbital, the orbital energies for the excited ${}^1E'$ and ${}^1A_1'$ states are within 0.02 hartree of those for the ${}^3A_2'$ ground state. For the ${}^3A_2'$, ${}^1E'$, and ${}^1A_1'$ states, the $1e''$ orbital energies are respectively -0.3211 , -0.2088 , and -0.1142 hartree. This result is by no means unreasonable, since the positive ion for all three of the electronic states is the same ${}^2E'$ state. Further, the differences in orbital energies are quite similar to the total energy differences.

In light of the history behind trimethylenemethane, the π orbitals are of greatest interest. We have already noted that the π orbital energies are significantly higher than those of the 14σ orbitals. In the case of D_{3h} symmetry, the $1a_2''$ and $1e''$ orbitals are restricted to be composed only of π functions, $2p$ functions pointing out of the plane of the molecule. Thus the $1a_2''$ orbital is $\sim 50\%$ central carbon $2p\pi$, with a $\sim 17\%$ contribution from each terminal $2p\pi$. This orbital is depicted in Figure 1 of ref 24, a perspective plot of the orbital in a plane 0.7 Å above the plane of the molecule. In going to the orthogonal geometry, $1a_2''$ becomes a $2b_1$ orbital. The b_1 irreducible representation is not strictly limited to $2p\pi$ functions. In fact there is a finite contribution to the $2b_1$ orbital from

(24) Figures 1-5 are not included here but may be found in our complete report of this work: D. R. Yarkony and H. F. Schaefer, Lawrence Berkeley Laboratory Report, LBL-2345, Jan 1974.

(23) P. O. Löwdin, *Advan. Chem. Phys.*, **2**, 207 (1959).

Table I. Orbital Energies and Mulliken Populations for the Triplet Ground State of Planar Trimethylenemethane^a

Orbital	ϵ , hartrees	Central C		Terminal C		Hydrogen s
		s	p	s	p	
1a ₁ '	-11.2690	2.00	0.00	0.00	0.00	0.00
1e'	-11.2447	0.00	0.00	4.00	0.00	0.00
2a ₁ '	-11.2446	0.00	0.00	2.00	0.00	0.00
3a ₁ '	-1.0956	0.84	0.00	0.96	0.13	0.08
2e'	-0.9082	0.00	0.09	3.00	0.09	0.72
4a ₁ '	-0.7189	0.29	0.00	0.35	0.71	0.65
3e'	-0.6327	0.00	0.41	0.05	2.35	1.19
1a ₂ '	-0.5437	0.00	0.00	0.00	1.03	0.97
4e'	-0.5236	0.00	0.77	-0.01	1.99	1.25
1a ₂ ''	-0.4383	0.00	0.99	0.00	1.01	0.00
1e''	-0.3211	0.00	0.00	0.00	2.00	0.00
Totals		3.12	2.26	3.45	3.13	0.81
Atom totals		5.38		6.58		0.81

^a The totals take into account the equivalence of the terminal carbon atoms and of the hydrogens.

causes the twisted form to lie ~ 17 kcal/mol above the planar molecule.

The singly occupied orbitals follow our qualitative discussion of the previous section. That is, Figures 3 and 4 of ref 24 demonstrate the essential correctness of our qualitative picture (eq 11). As suggested earlier, the detailed calculations show the 1e_y'' orbital to become the 1a₂ orbital as the methylene group is twisted. In fact, a perspective plot of the 1a₂ orbital is virtually indistinguishable from Figure 4 in ref 24, the 1e_y'' orbital. We have not plotted the 5b₂ orbital, since it has little magnitude in the plane 0.7 Å above the molecule. However, inspection of the expansion coefficients shows the 5b₂ orbital to be as in (12), a 2p orbital in the plane of the four carbon atoms. Finally, the total π electron density for the ³A₂' ground state is seen in Figure 5 of ref 24.

Table II. Orbital Energies and Mulliken Populations for Triplet Trimethylenemethane in Its Orthogonal Configuration 3

Orbital	ϵ , hartrees	Central C		Terminal C		Orthogonal C		Hydrogen a s	Hydrogen b s	Orthogonal hydrogen s
		s	p	s	p	s	p			
1a ₁	-11.2697	2.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1b ₂	-11.2467	0.00	0.00	2.00	0.00	0.00	0.00	0.00	0.00	0.00
2a ₁	-11.2467	0.00	0.00	2.00	0.00	0.00	0.00	0.00	0.00	0.00
3a ₁	-11.2335	0.00	0.00	0.00	0.00	2.00	0.00	0.00	0.00	0.00
4a ₁	-1.0944	0.86	0.00	0.66	0.08	0.30	0.04	0.01	0.03	0.02
5a ₁	-0.9081	0.00	0.08	0.49	0.07	0.97	-0.01	0.08	0.05	0.27
2b ₂	-0.9049	0.00	0.13	1.45	0.03	0.00	0.02	0.19	0.19	0.00
6a ₁	-0.7158	0.28	0.00	0.24	0.47	0.13	0.45	0.21	0.21	0.21
7a ₁	-0.6334	0.00	0.20	0.01	0.95	0.01	0.25	0.07	0.39	0.11
3b ₂	-0.6002	0.00	0.36	0.01	1.08	0.00	0.04	0.52	0.00	0.00
1b ₁	-0.5972	0.00	0.15	0.00	0.05	0.00	1.05	0.00	0.00	0.76
4b ₂	-0.5297	0.00	0.25	0.00	1.00	0.00	0.00	0.10	0.64	0.00
8a ₁	-0.5204	0.00	0.37	0.00	0.56	0.00	0.45	0.42	0.09	0.11
2b ₁	-0.3867	0.00	0.87	0.00	0.97	0.00	0.05	0.00	0.00	0.13
5b ₂	-0.3750	0.00	0.01	0.00	0.00	0.00	0.98	0.01	0.00	0.00
1a ₂	-0.2895	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Totals		3.14	2.41	3.42	3.14	3.40	3.08	0.808	0.806	0.805
Atom totals		5.55		6.56		6.48		0.808	0.806	0.805

s and p functions on each of the four carbons and from all but the orthogonal hydrogen s functions. The latter atomic functions are of a₁ irreducible representation. Nevertheless, the 2b₁ orbital remains primarily π -like in character, being $\sim 43\%$ central carbon 2p π , with $\sim 24\%$ 2p π contribution coming from each of the two methylene groups remaining in the plane of the D_{3h} molecule. These characteristics are seen qualitatively in Figure 2 of ref 24, a perspective plot analogous to Figure 1 of ref 24. Comparison of Figures 1 and 2 in ref 24 shows that in going to the orthogonal geometry the contribution of the twisted methylene carbon essentially disappears, with contributions from the other three 2p π orbitals becoming appropriately larger. Thus it is easy to imagine the 1a₂'' orbital growing²⁵ into the 2b₁ orbital in a smooth and continuous manner. In addition, the absence of a significant contribution of the orthogonal methylene carbon to the 2b₁ orbital may be associated with the loss of resonance energy, which

(25) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

To conclude, we note the total atomic populations in Tables I and II. In both the planar and twisted configurations, the central carbon has a large positive charge, if discussions of atomic charges are meaningful. In fact, the charge of +0.62 on the planar central carbon is one of the largest we have encountered on any carbon atom study by *ab initio* methods with comparable basis sets. In hydrocarbons, the carbon atoms usually have populations greater than 6.0, while for CF₂ and C₂F₄ the carbon charges obtained^{26,27} are 0.36 and 0.53. The only positive charges larger than +0.62 with which we are familiar are those obtained by Snyder and Basch for CHF₃ (+0.67) and CF₄ (0.96). Thus, it is quite conceivable that as well as having the lowest possible free valence² the central carbon in trimethylenemethane may have the largest positive "atomic charge" attainable in a hydrocarbon molecule.

(26) S. Rothenberg and H. F. Schaefer, *J. Amer. Chem. Soc.*, **95**, 2095 (1973).

(27) L. C. Snyder and H. Basch, "Molecular Wave Functions and Properties," Wiley, New York, N. Y., 1972.