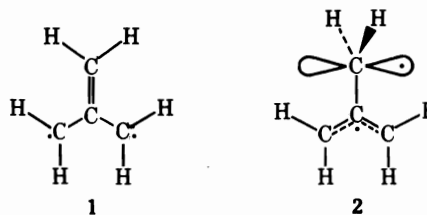


Figure 1

let state; however, calculations of the lowest planar singlet state lead to energies of 21,¹ 68,¹ and 88 kcal/mol² from ab initio Hartree-Fock (HF) wave functions and 35 kcal/mol³ from semiempirical Hartree-Fock wave functions. Part of the problem here is a special difficulty with spatial symmetry for the Hartree-Fock wave function of the lowest singlet state.⁴ We report here the results of ab initio configuration interaction (CI) calculations based on generalized valence bond⁵ (GVB) wave functions which eliminate this difficulty and provide a description of the other excited states, including the transition oscillator strengths.

We carried out ab initio calculations on several excited states of both the planar (1) and the bisected (2) geome-



tries⁶ of trimethylenemethane using HF, GVB, and CI wave functions. For all calculations, Dunning's⁷ "double zeta" contracted Gaussian basis set was used. In the GVB calculations, the orbitals corresponding to the CC and CH σ bonds and the carbon 1s core orbitals were not correlated. In the planar case the CI calculations utilized the full π -space but without excitations involving the GVB σ orbitals. The corresponding calculations were carried out for the bisected geometry. The excitation energies⁸ from the CI calculations are listed in Figure 1.

The first five states in Figure 1 for the planar geometry correspond to the two singlets and three triplets expected for a system with four singly-occupied orbitals (i.e., these are covalent states). The other state ($1A_1$) is of ionic character. The calculated (vertical) ionization potential is 8.3 eV so that transitions to 3p Rydberg-like states are expected at ~ 5.6 eV (220 nm).

Carrying out a CI based on the GVB orbitals of the triplet state we encountered no spatial symmetry problems (correctly obtaining two degenerate components for the $1E'$ state). Since we use the full self-consistent field equations for open-shell systems,⁹ we have avoided the difficulties in-

The Ground and Excited States of Trimethylenemethane

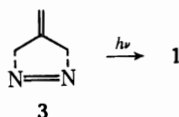
Sir:

Previous theoretical studies on trimethylenemethane diradical 1 have led to contradictory results. Most workers agree that for the planar geometry the lowest state is a trip-

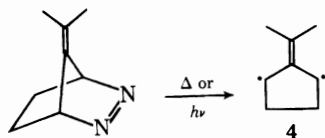
herent in other calculations,^{2,3} which utilized either the "half-electron model"³ or the Nesbet method of symmetry and equivalence restrictions.² Both these methods can lead to spurious results for open-shell molecules.⁴

The two lowest states for the bisected geometry correspond to the resonant state of allyl coupled in a triplet way (³B₂) or in a singlet way (¹B₁) to the rotated p orbital. The next two states correspond to the antiresonant state of allyl (coupled both ways to the p orbital). As expected, the excitation energies for bisected trimethylenemethane, 80 and 81 kcal, are comparable with the separation (74 kcal) of the resonant and antiresonant states of allyl.¹⁰

These results indicate that the ground state of **1** is a planar triplet state while the lowest singlet state of **1** should twist to a bisected form. Both the singlet and triplet states should be reactive species, although their chemistry could be different. These results agree well with experimental work¹¹ by Dowd and by Berson and with the theoretical studies of Yarkony and Schaefer.¹ Dowd has shown by ESR experiments that trimethylenemethane, prepared from the photolysis of 4-methylene-Δ¹-pyrazoline (**3**), probably has a



triplet ground state.¹² In 1974, Berson and co-workers¹³ showed that the trimethylenemethane analogue **4** has at



least two reactive electronic states, only one of which is a triplet. In fact, Berson suggests that the reactive singlet should have bisected geometry.

For the planar geometry we calculate that the vertical transition energy from ground state ³A₂' to ³E' (³B₂ and ³A₁) corresponds to λ_{max} 266 nm with an oscillator strength of *f* = 1.7 × 10⁻³. For the bisected geometry we find that the first vertical transition energy from the lowest singlet state (¹A₂ ← ¹B₁) corresponds to λ_{max} 359 nm with *f* = 7.9 × 10⁻⁴. For the planar geometry the first absorption of the singlet state is calculated as λ_{max} 289 nm with *f* = 0.10. This planar singlet state, however, may be too short lived for sufficient population to observe the transition in absorption experiments. Berson and Platz¹⁴ are attempting to observe these transitions in the low-temperature ultraviolet spectrum.

A possibly significant difference between **1** and **4** is that the lowest ¹E state of **1** splits into two nondegenerate states (¹A₁ and ¹B₂) of **4**. Of these, the ¹A₁ state seems more likely formed. If ¹A₁ is lower than ¹B₂ for the planar geometry (only the ¹B₂ state prefers twisting to the bisected form), the ¹A₁ state may live long enough to do some chemistry or to convert (intersystem cross) directly to the lower triplet state. In this circumstance there could be three reactive forms of trimethylenemethane (planar ³B₂ and ¹A₁ and bisected ¹B₂). With proper substituents on **4** it may be possible to stabilize planar ¹A₁ lower than bisected ¹B₂ so that all the chemistry would involve the two planar states. Such possibilities could be probed by observing the absorptions at 266 (planar ³B₂), 359 (bisected ¹B₁), and 289 nm (planar ¹A₁) as a function of reaction conditions and time for various substituents.

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References and Notes

- (1) D. R. Yarkony and H. F. Schaefer III, *J. Am. Chem. Soc.*, **96**, 3754 (1974).
- (2) W. J. Hehre, L. Salem, and M. R. Wilcott, *J. Am. Chem. Soc.*, **96**, 4328 (1974).
- (3) M. J. S. Dewar and J. S. Wasson, *J. Am. Chem. Soc.*, **93**, 3081 (1971).
- (4) W. T. Borden, *J. Am. Chem. Soc.*, **97**, 2906 (1975).
- (5) W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).
- (6) For the planar and bisected states we used *R*_{CH} = 1.086Å, *R*_{CC} = 1.400Å, and ∠HCH = 120°.
- (7) T. H. Dunning, Jr., *J. Chem. Phys.*, **53**, 2823 (1970).
- (8) Calculated total energies (configuration interaction) are as follows: *E* (planar triplet) = -154.87378 hartree, *E* (bisected triplet) = -154.84478 hartree.
- (9) W. J. Hunt, W. A. Goddard III, and T. H. Dunning, Jr., *Chem. Phys. Lett.*, **6**, 147 (1970); W. J. Hunt, P. J. Hay, and W. A. Goddard III, *J. Chem. Phys.*, **57**, 738 (1972).
- (10) G. Levin and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 1649 (1975).
- (11) For a review of trimethylenemethane chemistry through 1972, see P. Dowd, *Acc. Chem. Res.*, **5**, 242 (1972).
- (12) P. Dowd, *J. Am. Chem. Soc.*, **88**, 2587 (1966).
- (13) J. A. Berson, L. R. Corwin, and J. H. Davis, *J. Am. Chem. Soc.*, **96**, 6177 (1974).
- (14) J. A. Berson and M. Platz, private communication.

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