explanation.[22] A barrier of 20.3 kcal/mol has been reported for an *N-tert*-butyl ketimine of similar structure to **1–3**.[23] If steric factors were primarily responsible for the barriers in **1–3** the low barriers observed for **3** would not have been anticipated since a *tert*-butyl group is certainly larger than a sulfonyl group.

The barriers to planar inversion obtained for sulfenamides **1–3**, and selenenamides **4–5** clearly demonstrate that ligand electronegativity is unimportant in determining the barriers in these compounds. Although steric factors may account for a portion of the barriers in **1–3**, our results are best interpreted assuming that (p-d) π conjugation between sulfur and nitrogen is important in stabilizing the transition state to stereomutation.

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References and Notes

(1) Part IX: F. A. Davis, J. M. Kaminski, E. W. Kluger, and H. W. Freilich, *J. Am. Chem. Soc.*, **97**, 7085 (1975).
(2) For a review on the chemistry of the sulfur–nitrogen bond see F. A. Davis, *Int. J. Sulfur Chem.*, **8**, 71 (1973).
(3) For recent reviews see A. Rauk, L. C. Allen, and K. Mislow, *Angew. Chem., Int. Ed. Engl.*, **9**, 400 (1970); J. M. Lehn, *Fortschr. Chem. Forsch.*, **15**, 311 (1970); H. Kessler, *Angew. Chem., Int. Ed. Engl.*, **9**, 219 (1970); J. B. Lamert, *Top. Stereochem.*, **6**, 19 (1971).
(4) M. Raban and F. B. Jones, Jr. *J. Am. Chem. Soc.*, **93**, 2692 (1971); M. Rabin, D. A. Noyd, and L. Bermann, *J. Org. Chem.*, **40**, 752 (1975).
(5) D. Kost, W. A. Stacer, and M. Raban, *J. Am. Chem. Soc.*, **94**, 3233 (1972); M. Raban and D. Kost, *ibid.*, **94**, 3234 (1972).
(6) D. Kost and A. Zeichner, *Tetrahedron Lett.*, 3239 (1975).
(7) F. E. Davis, W. A. R. Slegeir, and J. M. Kaminski, *J. Chem. Soc., Chem. Commun.*, 634 (1972); see also C. Brown, B. T. Grayson, and R. F. Hudson, *Tetrahedron Lett.*, 4925 (1970).
(8) F. A. Davis and E. W. Kluger, unpublished results.
(9) F. Bernardl, I. G. Csizmadia, A. Mangini, H. B. Schlegel, M. Whangbo and S. Wolfe, *J. Am. Chem. Soc.*, **97**, 2290 (1975); A. Streitwieser, Jr., and S. P. Ewing, *ibid.*, **97**, 190 (1975); A. Streitwieser, Jr., and J. E. Williams, Jr., *ibid.*, **97**, 191 (1975).
(10) R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **92**, 4758 (1970).
(11) R. D. Baechler and K. Mislow, *J. Chem. Soc., Chem. Commun.*, 185 (1972).
(12) R. D. Baechler and K. Mislow, *J. Am. Chem. Soc.*, **93**, 773 (1971).
(13) R. J. Cook and K. Mislow, *J. Am. Chem. Soc.*, **93**, 6703 (1971).
(14) For a discussion of the possible mechanisms for stereomutation at the C–N double bond see ref 3. The lateral shift (inversion mechanism) is assumed to account for the present results.
(15) E. J. Grubbs, J. D. McCullough, Jr., B. H. Weber and J. R. Maley, *J. Org. Chem.*, **31**, 1098 (1966).
(16) F. A. Davis, A. J. Friedman, and E. W. Kluger, *J. Am. Chem. Soc.*, **96**, 5000 (1974).
(17) For a discussion on the use of this equation see ref 3 and D. Kost, E. H. Carlson, and M. Raban, *Chem. Commun.*, 656 (1971).
(18) D. Y. Curtin and J. W. Hausser, *J. Am. Chem. Soc.*, **83**, 3474 (1961).
(19) T. Jorden, H. W. Smith, L. L. Hohr, Jr., and W. N. Lipscomb, *J. Am. Chem Soc.*, **85**, 846 (1963).
(20) C. A. Coulson, *Nature (London)*, **221**, 1106 (1969).
(21) A. L. Allred, *J. Inorg. Nucl. Chem.*, **17**, 215 (1961).
(22) Using Raban's[5] modification of the Hammett equation a plot of $\Delta G^{\ddagger}$ for **1a**, **2a**, **3a**, vs. σ_m values for MeS, MeSO, and MeSO$_2$ gave a $\rho' = 2325 \pm 59$ and $\rho_{300} = 7.75 \pm 0.20$, correlation coefficient = 0.999.
(23) W. B. Jennings and D. R. Boyd, *J. Am. Chem. Soc.*, **94**, 7187 (1972).

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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-
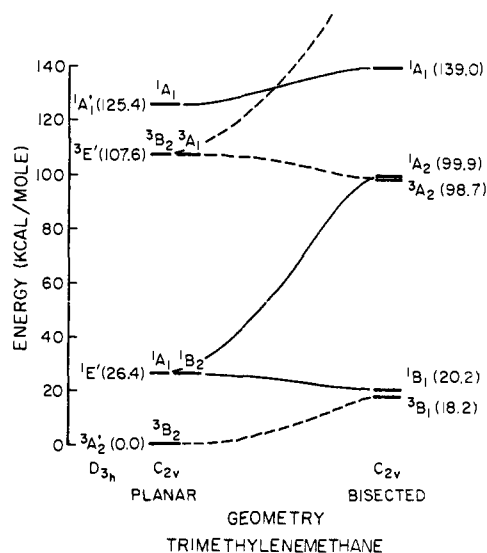

Figure 1

let state; however, calculations of the lowest planar singlet state lead to energies of 21,[1] 68,[1] and 88 kcal/mol[2] from ab initio Hartree–Fock (HF) wave functions and 35 kcal/mol[3] 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 bond[5] (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-

1   **2**
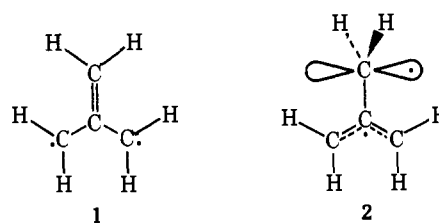
tries[6] of trimethylenemethane using HF, GVB, and CI wave functions. For all calculations, Dunning's[7] "double zeta" contracted Gaussian basis set was used. In the GVB calculations, the orbitals corresponding to the CC and CH σ bonds and the carbon 1s core orbitals were not correlated. In the planar 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 energies[8] 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 $\sim$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-

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 ($^3B_2$) or in a singlet way ($^1B_1$) 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 work[11] 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-Δ^1-pyrazoline (**3**), probably has a

3
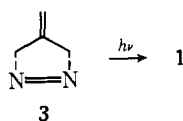
triplet ground state.[12] In 1974, Berson and co-workers[13] showed that the trimethylenemethane analogue **4** has at

4
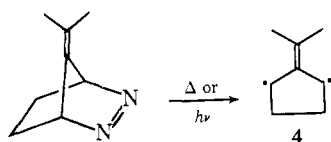
least two reactive electronic states, only one of which is a triplet. In fact, Berson suggests that the reactive singlet should have bisected geometry.

For the planar geometry we calculate that the vertical transition energy from ground state $^3A_2'$ to $^3E'$ ($^3B_2$ and $^3A_1$) corresponds to λ_{max} 266 nm with an oscillator strength of $f = 1.7 \times 10^{-3}$. For the bisected geometry we find that the first vertical transition energy from the lowest singlet state ($^1A_2 \leftarrow ^1B_1$) corresponds to λ_{max} 359 nm with $f = 7.9 \times 10^{-4}$. 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 Platz[14] 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 ($^1A_1$ and $^1B_2$) of **4**. Of these, the $^1A_1$ state seems more likely formed. If $^1A_1$ is lower than $^1B_2$ for the planar geometry (only the $^1B_2$ state prefers twisting to the bisected form), the $^1A_1$ 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 $^3B_2$ and $^1A_1$ and bisected $^1B_2$). With proper substituents on **4** it may be possible to stabilize planar $^1A_1$ lower than bisected $^1B_2$ so that all the chemistry would involve the two planar states. Such possibilities could be probed by observing the absorptions at 266 (planar $^3B_2$), 359 (bisected $^1B_1$), and 289 nm (planar $^1A_1$) as a function of reaction conditions and time for various substituents.

References and Notes

(1) D. R. Yarkony and H. F. Schaefer III, *J. Am. Chem. Soc.*, **98**, 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 $R_{CH} = 1.086$Å, $R_{CC} = 1.400$Å, and $\angle$ 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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Spectroscopic Studies of Bicyclo[2.2.2]octa-2,5,7-triene. Magnetic Circular Dichroism Spectrum in the Region 200–350 nm[1]

Sir:

Bicyclo[2.2.2]octa-2,5,7-triene (barrelene, I) has been of considerable theoretical interest, even prior to its synthesis in 1960.[2] Most theoretical studies have focused on the problem of predicting features of the excited electronic states of I,[2a,3-9] though the availability of high resolution photoelectron spectrometers has stimulated interest in the dominant mechanism (through-bond vs. through-space) of coupling among the three π subunits.[10,11] Spectral data have been

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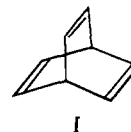
sparse, on the other hand, with only two maxima in ethanol having been reported:[2] N $\rightarrow$ V$_2$, 208 nm (5.96 eV, $\epsilon \simeq$ 1100); N $\rightarrow$ V$_1$, 239 nm (5.19 eV, $\epsilon \simeq$ 300). Now barrelene occupies a critical position in relation to semiempirical spectral calculations. It may serve as (1) a probe for the limits of π-σ separability based on the success or failure of π-electron (Pariser–Parr–Pople, or PPP) calculations, and (2) an important benchmark for gauging the reliability of semiempirical all-valence-electron (AVE) calculations. It is