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Chemistry of Triplet vs. Singlet Biradicals. An ab Initio MCSCF Study of Trimethylene

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Abstract: The major goal of this paper is to understand why triplet-derived trimethylene biradicals give cyclopropane products and virtually no propylenes, whereas singlet-derived trimethylenes give substantial amounts of both products. To examine this question, we have studied the singlet and triplet energies of trimethylene as a function of the independent rotation of each terminal methylene, both with and without pyramidalization of the methylenes. The 3-21G split-valence basis set is used with a restricted Hartree–Fock (RHF) triplet wave function and a two-configuration MCSCF singlet. The calculations suggest that two major factors contribute to the lack of propylene from triplet trimethylene: (1) the singlet–triplet (S–T) intersection appears to be lower in energy than the transition state for propylene formation on the singlet surface; (2) the entropy for propylene formation is relatively unfavorable. Simple formulas are derived which relate the singlet–triplet splitting of a biradical to the orbital energy difference of the singly occupied MOs and the overlap and exchange integrals between the two p-type AOs on the terminal carbons.

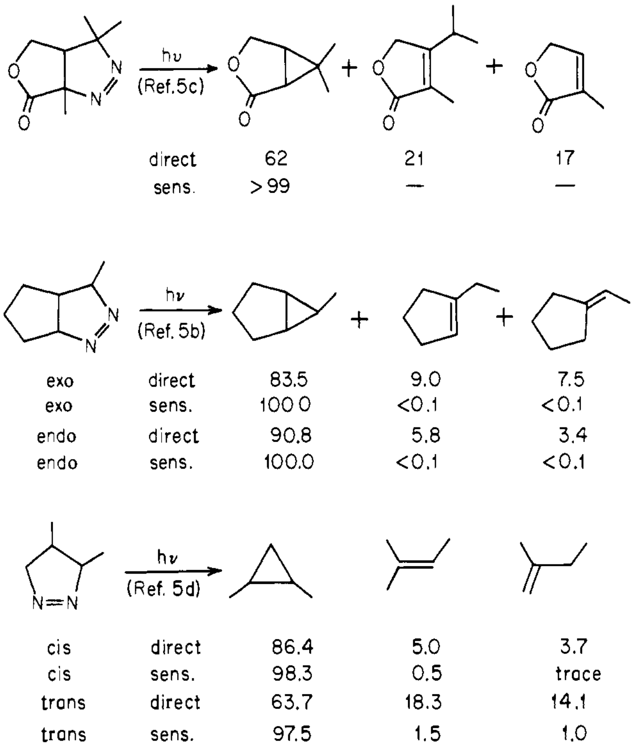
Introduction

As the simplest unconjugated 1,3 biradical, trimethylene is of considerable experimental[1] and theoretical[2] importance. The role of trimethylene in the one- and two-center stereomutations of cyclopropane has been particularly well studied.[1a,b] Theoretical calculations have therefore focused on the search for minima and saddle points on the singlet potential energy surface. Notable early achievements were the location of the transition state for geometrical isomerization of cyclopropane[2g] and the discovery that there appears to be no local minimum corresponding to singlet trimethylene.[2f,g]

The triplet potential energy surface was justifiably ignored in most of these calculations. However, it is remarkable that the ratio of cyclic to acyclic products from substituted trimethylenes is characteristically different depending on whether the biradicals are generated in the singlet or triplet state. This behavior is also found in tetramethylenes[3a,4] and larger biradicals.[3b,c] Examples of experimental results for trimethylenes are given in Scheme I.[5] The most important feature of these solution-phase, room-temperature results is that triplet-sensitized photolysis of the trimethylene precursor yields cyclopropanes and virtually *no olefins*, whereas direct photolysis (without a sensitizer) yields a mixture of cyclopropanes and olefins, mainly propylenes. (Thermolysis also yields both cyclopropanes and propylenes,[1d,5d] but typically in a different ratio.) Our purpose is to understand why the triplet- and singlet-derived product distributions are so different.

In formulating a mechanism we begin by assuming that triplet-sensitized photolysis in solution produces trimethylene in the lowest triplet state,[6] which then undergoes intersystem crossing (isc) to the ground singlet state with subsequent product formation on the singlet potential energy surface. For the direct photolysis we assume that only the singlet manifold is involved.[1d] More specific assumptions about direct photolysis are not necessary, since we are mainly interested in understanding why triplet trimethylene yields no olefins. Certainly the singlet and triplet reactions cannot proceed through a common singlet trimethylene, otherwise the product distributions would be the same. It may be that the difference is dynamical in nature. For example, in the triplet reaction isc may occur in such a way that triplet energy is disposed into vibrations on the singlet surface that favor cyclopropane formation. At the very least, a solution to the problem requires a knowledge of both the triplet and the singlet potential energy surfaces of trimethylene. In photochemical problems like this, one can envision cases[4e] in which even a complete knowledge of both potential energy surfaces gives no information about the product distribution without subsequent dynamical studies. Our results indicate that this is not the case here.

Scheme I



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The usual theoretical approach to resolving questions of mechanism is to calculate the relevant minima and saddle points on a potential energy surface. The problem here is much more difficult because two potential surfaces are involved and we must examine the regions of these surfaces where isc is most probable. Adopting the semiclassical Landau–Zener model,[7] we assume isc will occur only where the two 21-dimensional surfaces intersect, since the spin–orbit coupling is expected to be less than 1 cm^{-1}.[8] The intersection is in itself a surface of 20 dimensions. The problem can be made more tractable by assuming that there is a Boltzmann distribution of the vibrational levels of triplet trimethylene. This assumption is consistent with the spin correlation effect in biradicals,[1d,3a] the interpretation of which is that isc is slow compared to loss of stereochemistry at the radical centers. It allows us to restrict ourselves to regions of the S–T intersection that are low enough in energy to be accessible to a thermally equilibrated triplet trimethylene. We must examine these low-energy intersections to see whether spin–orbit coupling is large enough to give significant isc. If so, we may conclude that isc produces singlet trimethylenes in localized regions of configuration space—that is, in the regions of the low-energy S–T intersections. We may then ask which of the two products, cyclopropane or propylene, is more energetically and dynamically accessible from these regions of the singlet surface.

In this paper we report ab initio MCSCF calculations of trimethylene at geometries near the low-energy S–T interactions. We shall also find it useful to gain an insight into the electronic interactions that govern the S–T energy splitting. Part of this paper is therefore devoted to a detailed examination of the S–T splitting as a function of a few important geometrical variables.

Wave Functions. A biradical can be regarded as a system in which two unpaired electrons lie outside a closed shell of core electrons. In this paper we shall represent the lowest triplet state of this system of $2n + 2$ electrons by the restricted Hartree–Fock (RHF) wave function

$$\begin{aligned} {}^3\Psi &= [(2n+2)!]^{-1/2}|\phi_1(1)\bar{\phi}_1(2) \ldots \phi_n(2n-1) \times \\ &\qquad \bar{\phi}_n(2n)\phi_a(2n+1)\phi_b(2n+2)| \\ &= (\text{core}\cdot\phi_a\phi_b) \end{aligned} \tag{1}$$

where ϕ_a and ϕ_b are the singly occupied orbitals of the unpaired electrons. This wave function is invariant under an arbitrary orthogonal mixing of ϕ_a and ϕ_b, and one cannot characterize the RHF triplet MOs as being either localized or delocalized.

A simple singlet wave function for biradicals can be written as a superposition of three electronic configurations[8]

$${}^1\Psi = \sigma_A(\text{core}\cdot\phi_a{}^2) + \sigma_B(\text{core}\cdot\phi_b{}^2) + \sigma_{AB}(\text{core}\cdot\phi_a\phi_b) \tag{2}$$

This wave function is also invariant under an arbitrary orthogonal mixing of ϕ_a and ϕ_b provided that compensatory changes in the CI coefficients σ_A, σ_B, and σ_{AB} are also made. We remove this flexibility[9] by setting $\sigma_{AB} = 0$ and optimizing the resulting wave function with respect to both the orbitals and the CI coefficients. The result is the two-configuration MCSCF (2CSCF) wave function, in which the orbitals σ_a and σ_b tend to be delocalized and display bonding and antibonding features of Hartree–Fock molecular orbitals. Their occupation numbers are $2\sigma_A{}^2$ and $2\sigma_B{}^2$, respectively, since normalization requires $\sigma_A{}^2 + \sigma_B{}^2 = 1$. In the ground state, σ_A and σ_B have opposite signs and their sum measures the ionic vs. covalent character of the wave function. For example, $\sigma_A + \sigma_B = 0$ ($\sigma_A = -\sigma_B = 1/\sqrt{2}$) gives the purely covalent open-shell singlet whereas $|\sigma_A + \sigma_B| = 1$ gives the closed-shell singlet having equal ionic and covalent contributions.

This idea can be expressed succinctly by writing ${}^1\Psi$ in terms of its covalent and ionic contributions. Setting $\sigma_A = \cos(\pi/4 - \delta)$ and $\sigma_B = -\sin(\pi/4 - \delta)$, we can write ${}^1\Psi$ as

$${}^1\Psi = \cos\delta\ \text{core}\cdot\left(\frac{\phi_a{}^2 - \phi_b{}^2}{\sqrt{2}}\right) + \sin\delta\ \text{core}\cdot\left(\frac{\phi_a{}^2 + \phi_b{}^2}{\sqrt{2}}\right) \tag{3}$$

As δ varies from 0 to $\pi/2$, ${}^1\Psi$ varies from purely covalent to purely ionic, with the ground-state closed-shell wave function occurring midway at $\delta = \pi/4$. The symmetry of ${}^1\Psi$ is totally symmetric only if ϕ_a and ϕ_b are required to be symmetry orbitals. In some cases, such as the edge-to-face (0,90) trimethylene discussed later, the optimum 2CSCF orbitals are themselves combinations of orbitals of different symmetry.

A 2CSCF wave function is adequate for describing biradicals provided there is a large enough gap between the core orbitals and ϕ_a and ϕ_b. One expects this to be true for polymethylene biradicals. For trimethylene this was recently confirmed by Kato and Morokuma,[2m] who performed MCSCF calculations with three additional configurations and found their contributions to be negligible. Biradicals which have high-lying core orbitals such as n or π type, or which contain additional partly unpaired electrons (such as a biradical undergoing an additional bond-breaking process), will require singlet wave functions containing a larger number of configurations.

The same algorithm was used for the optimization of the MOs for the triplet and the singlet wave function, incorporated into the HONDO[11] system of programs, and will be reported elsewhere.[12] It is worthwhile to note that the converged triplet orbitals generally provide a very good initial guess for the singlet calculation. The evaluation of both the triplet and singlet wave functions at one molecular geometry requires only about twice the computer time as a closed-shell restricted Hartree–Fock calculation.

Unless stated otherwise, a 3-21G split-valence basis set was used throughout.[13a] This basis set has essentially the same characteristics as the more familiar 4-31G[13b] but is less expensive to use. In preliminary tests with a few trimethylene geometries,4-31G and 3-21G gave S–T splittings that differed at most by 0.1 kcal. In a later section of this paper we compare the split-valence basis sets with the STO-3G[13c] minimal basis set and find that the minimal basis is inadequate for certain regions of the potential surface.

Singlet–Triplet Energy Splitting. In order to interpret the computed results and to allow qualitative predictions, it is useful to have an approximate formula for the S–T splitting in terms of commonly used concepts. This formula (eq 8) is based on the assumption that the singlet and triplet orbitals are identical, which is sufficiently valid to allow qualitative interpretations.

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(9) If the wave function eq 2 is fully optimized without removing this flexibility, the result is generally known as a complete active space (CAS) MCSCF wave function (Siegbahn, P.; Heiberg, A.; Roos, B.; Levy, B. *Phys. Scr.* **1980**, *21*, 323–7) with two electrons in two active orbitals. Alternatively if both σ_A and σ_B are set equal to zero and ϕ_a and ϕ_b are allowed to overlap, the optimal result is a generalized valence bond[10] (GVB) wave function, in which ϕ_a and ϕ_b tend to be localized. The three forms 2CSCF, CAS MCSCF, and GVB are equivalent in this case.

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In the notation of Bobrowicz and Goddard,[10] the triplet and singlet energies can be written as

$$E_T = E^{\text{core}} + \epsilon_a + \epsilon_b - 2K' - K_{ab} \tag{4}$$

$$E_S = E^{\text{core}} + 2\sigma_A{}^2\epsilon_a + 2\sigma_B{}^2\epsilon_b + 2\sigma_A\sigma_B K_{ab} = E^{\text{core}} + \epsilon_a + \epsilon_b + (\epsilon_a - \epsilon_b)\sin 2\delta - K_{ab}\cos 2\delta \tag{5}$$

where

$$\epsilon_a = h^c_{aa} + \tfrac{1}{2}J_{aa}$$

$$\epsilon_b = h^c_{bb} + \tfrac{1}{2}J_{bb}$$

$$K' = \tfrac{1}{4}(J_{aa} + J_{bb} - 2J_{ab})$$

and δ is defined in eq 3.

The J's and K's are the usual Coulomb and exchange integrals taken over orbitals ϕ_a and ϕ_b. K' is the exchange integral taken over $(1/\sqrt{2})(\phi_a + \phi_b)$ and $(1/\sqrt{2})(\phi_a - \phi_b)$. The core energy is

$$E^{\text{core}} = \sum_i^{\text{closed}} (h_{ii} + h^c_{ii})$$

The core operator is defined as

$$\hat{h}^c = \hat{h} + \sum_j^{\text{closed}} (2\hat{J}_j - \hat{K}_j)$$

where $\hat{h}$, $\hat{J}$, and $\hat{K}$ are the usual bare nucleus core, Coulomb, and exchange operators.[10]

Using this notation and assuming the singlet and triplet orbitals are identical, we can write the S–T splitting (lowest singlet and triplet) as

$$E_{ST} = E_S - E_T = 2K' + (\epsilon_a - \epsilon_b)\sin 2\delta + (1 - \cos 2\delta)K_{ab} \tag{6}$$

The first and last terms in eq 6 are always positive and therefore favor a triplet ground state. As illustrated below, the second term is negative and favors a singlet ground state.

Since E_T does not depend on δ, we may obtain the condition for minimizing E_S with respect to δ by minimizing E_{ST}. Setting the derivative of eq 6 equal to zero we obtain, after a little manipulation

$$\sin 2\delta = -(\epsilon_a - \epsilon_b)[(\epsilon_a - \epsilon_b)^2 + K_{ab}{}^2]^{-1/2} \tag{7}$$

This gives rise to

$$E_{ST} = 2K' + K_{ab} - [(\epsilon_a - \epsilon_b)^2 + K_{ab}{}^2]^{1/2} \tag{8}$$

In many cases ϕ_a and ϕ_b are the bonding and antibonding combinations of the terminal AOs χ_1 and χ_2: $\phi_{a(b)} = (2 \pm 2S_{12})^{-1/2}(\chi_1 \pm \chi_2)$, where S_{12} is the overlap integral between χ_1 and χ_2. Under these conditions K' is very nearly equal to K_{12}, the exchange integral over χ_1 and χ_2 (i.e., $K' \rightarrow K_{12}$ as $S_{12} \rightarrow 0$).

The sign of E_{ST} depends critically on the difference between $2K'$ and $|\epsilon_a - \epsilon_b|$. We henceforth refer to ϵ_a and ϵ_b as the orbital energies of ϕ_a and ϕ_b, respectively, with the characteristic that the lower-energy orbital has the larger occupation number.[14] In other words, given that $\epsilon_a < \epsilon_b$, the occupation number $2\sigma_A{}^2 = 1 + \sin 2\delta$ is greater than $2\sigma_B{}^2 = 1 - \sin 2\delta$. The interplay of $|\epsilon_a - \epsilon_b|$, $2K'$, and δ described in eq 6–8 provides a simple model for understanding S–T intersections. When $|\epsilon_a - \epsilon_b|$ is large $E_{ST} < 0$ (singlet ground state), and when $|\epsilon_a - \epsilon_b|$ is small $E_{ST} > 0$. In the limit that $\epsilon_a = \epsilon_b$ we have triplet ground state with $\sin 2\delta = 0$, and the occupation numbers of ϕ_a and ϕ_b are each 1. Clearly, in seeking S–T intersections we should look for geometrical changes in which $|\epsilon_a - \epsilon_b|$ varies from large to small.

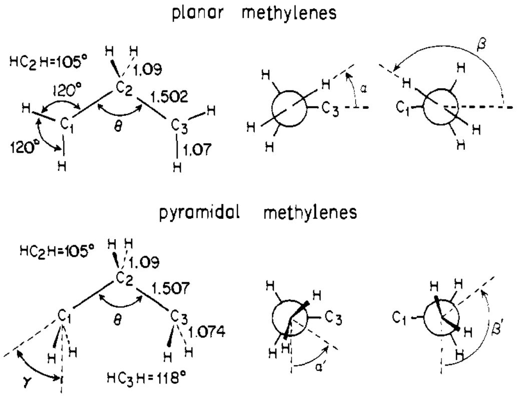

Figure 1. Geometrical coordinates used in the calculations (see text). Bond lengths are in angstroms. At upper left is the C_{2v} (0,0) geometry. At lower left is the C_{2v} (90′,270′) geometry.

We can make a closer connection between E_{ST} and the geometry of the biradical by expressing $\epsilon_a - \epsilon_b$ in terms of the overlap integral S_{12}. Using the definitions of ϕ_a, ϕ_b, ϵ_a, ϵ_b and neglecting the contribution from $J_{aa} - J_{bb}$, we obtain

$$\epsilon_a - \epsilon_b \approx (1 - S_{12}{}^2)^{-1}[2h^c_{12} - S_{12}(h^c_{11} + h^c_{22})] \tag{9}$$

Equation 9 can be simplified by noting that $S_{12}{}^2 \ll 1$ for biradicals and by analogy with the Mulliken approximation[15]

$$h^c_{12} \approx \left(\frac{C+1}{2}\right)S_{12}(h^c_{11} + h^c_{22}) \qquad C > 0$$

Equation 9 then becomes

$$\epsilon_a - \epsilon_b \approx CS_{12}(h^c_{11} + h^c_{22}) \tag{10}$$

in which S_{12} contains the geometry dependence. Substitution of eq 10 into eq 8 shows that large overlap of the terminal AOs favors a singlet ground state and small overlap favors a triplet ground state. This was previously pointed out by Salem and Rowland[8] and has been mentioned by many others. Equations 8 and 10 provide an approximate quantitative description of this phenomenon.

Equation 8 and 10 are useful in interpreting the S–T splitting in simple biradical-like systems. For example, we have found that for a pair of planar methyl radicals $E_{ST} < 0$ (singlet ground state) for all C–C separations in both the face-to-face and edge-to-edge geometries, indicating (by analogy with H_2) the dominance of the overlap term over the exchange term. At any given C–C separation $|E_{ST}|$ is larger for the face-to-face than for the edge-to-edge geometry, since σ-type overlap is larger than π-type. For the edge-to-face geometry the overlap integral is zero and the triplet is lower. This is also true for edge-to-face trimethylene.

In some cases, such as edge-to-edge trimethylene discussed later, eq 10 cannot be used and one must rely on the more general eq 8. This is because ϕ_a and ϕ_b cannot be written as simple bonding and antibonding combinations of two AOs.

Geometrical Coordinates. The internal geometrical coordinates are shown in Figure 1. We used two slightly different sets of fixed bond lengths and angles depending on whether the terminal methylenes were planar or pyramidal. It is clear from earlier calculations[2f,g] that the most important variables are the CCC angle θ, the methylene torsional angles, and the degree of pyramidalization of the terminal methylenes. When the methylenes are kept planar (top of Figure 1), the torsional angles α and β are defined by a counterclockwise rotation from the CCC reference plane. For a given θ the molecular conformation is labeled (α,β).

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(14) This characteristic justifies the identification of ϵ_a and ϵ_b as orbital energies. However, ϵ_a and ϵ_b are not eigenvalues of a one-electron Fock operator. Instead, they closely resemble the SCF orbital energies in closed-shell theory, in which the total electronic energy is twice the sum of the SCF orbital energies. This can be verified by setting $\sigma_A = 1$ and $\sigma_B = 0$ in eq 5.

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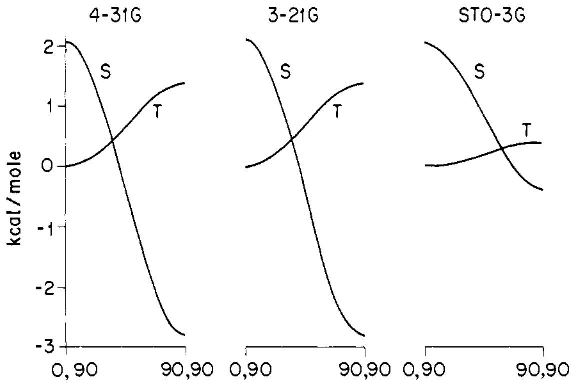

Figure 2. Comparison of the 4-31G, 3-21G, and STO-3G basis sets for calculating the singlet and triplet energies of (0,90) and (90,90) trimethylene ($\theta = 112°$). See also Table I. The intermediate points on each curve were generated by fitting the end points to a cosine function. The triplet (0,90) is defined as the zero of energy.

Table I. Singlet Energy (hartrees) and S-T Splitting E_{ST} (kcal/mol) of (0,0), (0,90), and (90,90) Geometries with 4-31G, 3-21G, and STO-3G Basis Sets

geometry	4-31G	3-21G	STO-3G
(0,0)	−116.8226, 0.61	−116.3413, 0.64	−115.5867, 0.46
(0,90)	−116.8209, 2.04	−116.3397, 2.13	−115.5850, 2.04
(90,90)	−116.8286, −4.17	−116.3475, −4.21	−115.5889, −0.82

With this definition, (0,0), (90,90), and (0,90) coincide with the edge-to-edge, face-to-face, and edge-to-face geometries, respectively. The molecule has C_{2v} symmetry for (0,0) and (90,90) and C_s symmetry for (0,90). Note that with planar methylenes α and β are equivalent to $\alpha + 180°$ and $\beta + 180°$, respectively. When the methylenes are pyramidal, this is not the case and a new convention is necessary. We choose the pyramidal "(0,0)" to be the result of viewing the (0,0) edge-on in the CCC plane, with the terminal methylenes toward the observer, and canting all terminal hydrogens downward out of the CCC plane. α' and β' are then defined as counterclockwise rotations of the left- and right-hand groups from this reference geometry. The primes denote pyramidalized terminal methylenes. With this convention, the C_{2v} geometry with both methylenes pyramidalized directly inward, shown in the bottom left of Figure 1, is labeled (90′,270′). The geometry with both methylenes pyramidalized directly outward is (270′,90′). The pyramidalization angle γ is the angle between the HCH bisector and a line extending from the C–C bond. For most calculations $\gamma = 20°$.

The values of the fixed coordinates in Figure 1 were chosen to be essentially those reported by Kato and Morokuma[2m] for (0,0) and (0,90), fully optimized within their respective symmetries. Their calculations were performed with a 4-31G basis set and an MCSCF wave function slightly larger than but virtually identical with ours. Kato and Morokuma[2m] report an inward pyramidalization of 20.2° for the perpendicular methylene of (0,90).[16]

Results and Discussion

Basis Set. The Necessity for a Split Valence Shell. Since the computational effort required for variational optimization of the MOs increases as the fourth power of the number of basis functions, the goal is to find the smallest number of basis functions that can describe the phenomena of interest.

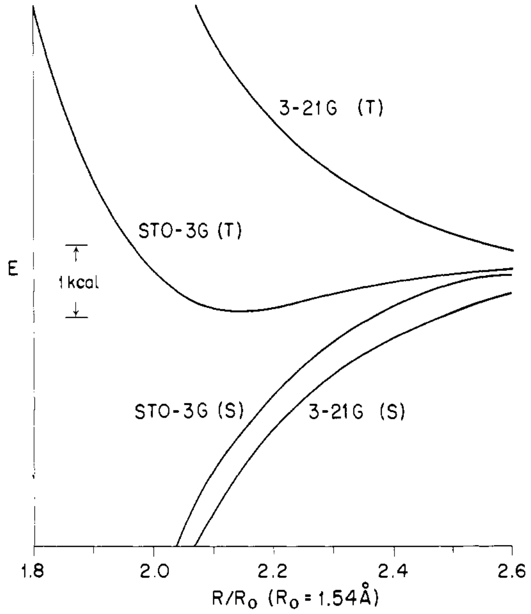

Figure 3. Comparison of 3-21G and STO-3G basis sets in the dissociation of ethane to two planar, face-to-face methyl radicals. The dissociation was done with continuous depyramidalization of the methyl groups until planarity was reached at R = 3.0 Å (R/R_0 = 1.95), and the methyls remained planar for larger R. S and T refer to singlet and triplet.

In this spirit, we examined the geometry dependence of the singlet and triplet energies for three basis sets: the STO-3G minimal basis set and the 3-21G and 4-31G split-valence basis sets (see Figure 2 and Table I). For a given singlet or triplet spin state, as the terminal methylenes are rotated, the three calculated energies tend to parallel each other except in the vicinity of the (90,90) geometry. In this region the minimal basis set, which does not have a long-range diffuse component in its valence shell, grossly underestimates the stabilization due to incipient bond formation. The two split-valence basis sets parallel each other throughout. The same sort of behavior is seen in the homolytic cleavage of a bond to form a radical pair. When a minimal basis set is used in the calculation, the dissociation limit is reached too early. This is illustrated in Figure 3, which compares STO-3G with 3-21G in the dissociation of ethane to form two methyl radicals. For biradical calculations it is just this region of the curve (approaching the dissociation limit) which requires accurate description.

The use of a minimal basis set for the study of biradicals can clearly lead to errors. For example, GVB + STO-3G calculations on trimethylene[2f] with $\theta = 120°$ place the (90,90) geometry higher in energy than (0,0). Our calculations with the same wave function and a 3-21G basis set reverse the ordering. An even more serious discrepancy occurs when a minimal basis set is applied to tetramethylene. We have recently shown[17] that there is no local minimum corresponding to the gauche conformer of singlet tetramethylene when a 3-21G basis set is used. The potential well of at least 2 kcal/mol predicted by earlier ab initio CI calculations[18] was shown to be an artifact of the minimal basis set.

One might ask whether a further increase in the quality of the basis set, e.g., the inclusion of d-type (polarization) functions, would reveal yet another significant change in the potential functions. Reported calculations on a related system suggest that this is not the case. Schaefer and co-workers[19] calculated the energy separation between the ground-state triplet (D_{3h}) and the lowest singlet state (C_{2v}) of trimethylenemethane. At the SCF

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(16) Using Kato and Morokuma's reported geometries, we calculated the singlet (0,90) to be 0.94 kcal/mol *higher* than the singlet (0,0) whereas they reported it to be 1.0 kcal/mol *lower*. In view of the following facts, we suspect that their numbers were inadvertently reversed. (1) Our results reverse theirs almost exactly. (2) We are in agreement with previous calculations using STO-3G[2f,g] (probably qualitatively reliable at these two geometries) which also place (0,90) above (0,0). (3) We are in agreement with experiment[1a,b] in predicting optical isomerization (via (0,0)) to be faster than geometrical isomerization (via (0,90)). (4) They also claim to be in agreement with experiment, which could only be true if their numbers were reversed.

(17) Doubleday, C.; McIver, J. W., Jr.; Page M. *J. Am. Chem. Soc.* **1982**, *104*, 3768.

(18) Segal, G. *J. Am. Chem. Soc.* **1974**, *96*, 7892–8.

(19) Hood, D. M.; Schaefer, H. F., III; Pitzer, R. M. *J. Am. Chem. Soc.* **1978**, *100*, 8009–10.

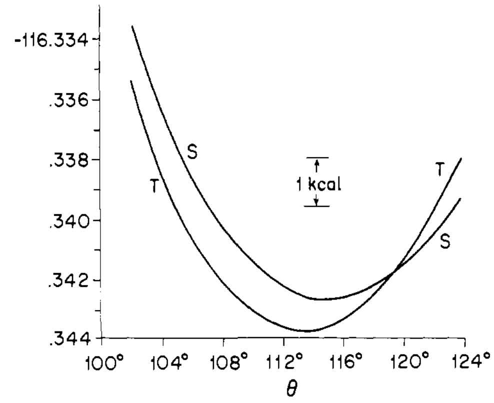


Figure 4. Singlet and triplet energies (in hartrees) of (0,0) trimethylene as a function of θ. (1 kcal/mol = 0.0016 hartree.)

level of theory, addition of polarization functions to a standard double-ζ basis set lowered both the singlet and triplet energies by more than 30 kcal/mol. However, the separation between them changed by less than 2%, from 15.1 to 14.9 kcal/mol. We have in addition calculated E_{ST} for (0,0) and (90,90) trimethylene with a 6-31G* basis set.[13d] The results, 0.70 and −5.05 kcal/mol, respectively, differ by only 9% and 20% from the corresponding values calculated with the smaller 3-21G basis set (cf. Table I).

(0,0) Trimethylene. We first studies E_{ST} as a function of a few important geometrical variables in an effort to understand some of the factors which influence E_{ST}. We started by looking at the (0,0) geometry. The motivation for this was the interesting results of Buchwalter and Closs, who showed that cyclopentane-1,3-diyl (**1**) has a triplet ground state with a barrier to reclosure to bicyclopentane of 2.3 kcal/mol.[20] Schaefer[21] has calculated that **1** has a (0,0) type geometry in the triplet state with E_{ST} = 0.9 kcal/mol. This result thus agrees with experiment in predicting a triplet ground state.

1

This is an interesting result because it stands in contrast to the known singlet ground states for 1,7 through 1,12 biradicals.[22] Biradicals of intermediate size (1,5 and 1,6) have regions on their potential surfaces with $E_{ST} > 0$ and other regions with $E_{ST} < 0$.[23] In order to understand why **1** has a triplet ground state, we first checked to see whether the ethano bridge in **1** has any effect on E_{ST}. In a preliminary calculation using STO-3G we compared **1** (at Schaefer's geometry) with a (0,0) trimethylene **2**, obtained from **1** by replacing the ethano bridge by two hydrogens while keeping the rest of the molecule the same. We obtained E_{ST} = 0.63 kcal for **1** and 0.65 kcal for **2**. Obviously the S–T splitting in **1** is determined by the 1,3-biradical moiety. The difference from Schaefer's result of 0.9 kcal is due to the basis set, since our S and T wave functions are identical with his.

Next we looked at a series of (0,0) trimethylenes differing only in the CCC angle θ, with other geometrical parameters as shown in Figure 1 (planar methylenes). For this and subsequent calculations we used the 3-21G basis. The results are plotted in Figures 4 and 5. Figure 4 shows that as θ gets larger E_{ST} diminishes until a crossing occurs around θ = 119°. The singly occupied orbitals are either symmetric (S) or antisymmetric (A) with respect to the plane passing through the central methylene.

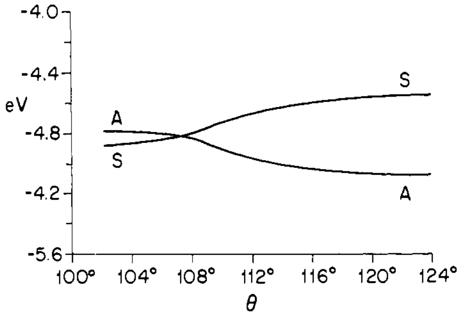


Figure 5. Orbital energies (eV) or ϕ_A and ϕ_S as a function of θ for (0,0) trimethylene.

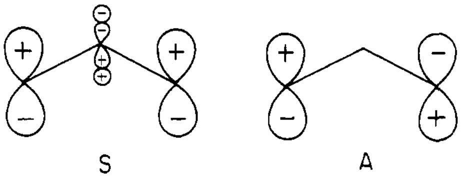
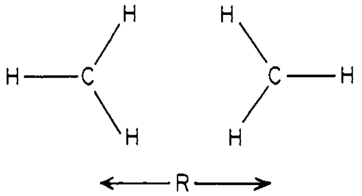


Figure 5 shows the dependence of the orbital energies on θ.

We suspected that an interaction of the terminal p orbitals with the central methylene was responsible for the triplet ground state of (0,0) trimethylene. To test this we examined the approach of two coplanar methyl radicals with the C–C distance R as the only variable. As expected



$E_{ST} < 0$ (singlet ground state) for all R, and the S MO was always below the A MO. For R = 2.5, 3.0, 4.0 Å, E_{ST} = −3.9, −0.62, −0.01 kcal, respectively, and the A/S splittings were 0.60, 0.24, 0.03 eV. The singlet ground state is reasonable for a system in which S_{12} and K_{12} decrease together, but in which overlap apparently dominates (see eq 10).

The S–T intersection at θ = 119° in Figure 4 can be understood in terms of the MOs in Figure 5 with the aid of eq 8. In the vicinity of the MO crossing in Figure 5, eq 8 predicts a triplet ground state. As θ increases beyond this region and the A and S MOs split apart, eq 8 predicts that at some value of θ the orbital energy difference will become dominant and the singlet will drop below the triplet. This situation is aided by a simultaneous decrease in the exchange integral between the two terminal AOs, since the end-to-end distance increases as θ increases. The tendency of the singlet to put two electrons into the lower MO is shown by σ_A, which varies from 0.73 to 0.715 to 0.77 for θ = 102°, 108°, 124°, respectively. The dip in σ_A at θ = 108° is associated with the near orbital degeneracy.

The reason that the orbital energies split apart as θ increases past 108° has its basis in an argument due to Hoffmann.[2a] He pointed out that the S MO will have a contribution from a high-lying core MO that the A MO lacks. These MOs, shown above, can be represented as

$$\phi_S = (1/\sqrt{2})(\chi_1 + \chi_3)\cos\alpha - \chi_2 \sin\alpha$$

$$\phi_A = (1/\sqrt{2})(\chi_1 - \chi_3)$$

where χ_1 and χ_3 are the p AOs of the terminal methylenes, χ_2

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[20] (a) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857–8. (b) Buchwalter, S. L.; Closs, G. L. *Ibid.* **1979**, *101*, 4688–94.

[21] Conrad, M.; Pitzer, R.; Schaefer, H., III. *J. Am. Chem. Soc.* **1979**, *101*, 2245–6.

[22] (a) Closs, G. L.; Doubleday, C. *J. Am. Chem. Soc.* **1973**, *95*, 2735. (b) Closs, G. L. *Adv. Magn. Reson.* **1974**, *7*, 157.

[23] (a) Doubleday, C., Jr. *Chem. Phys. Lett.* **1981**, *77*, 131. (b) Doubleday, C., Jr. *Ibid.* **1981**, *79*, 375.

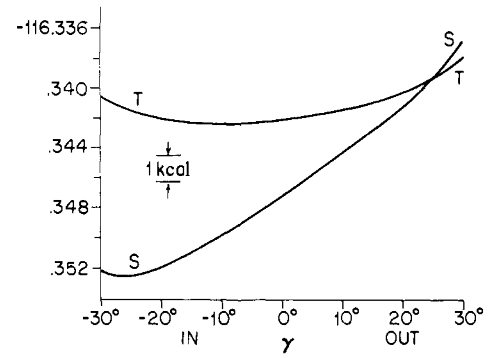
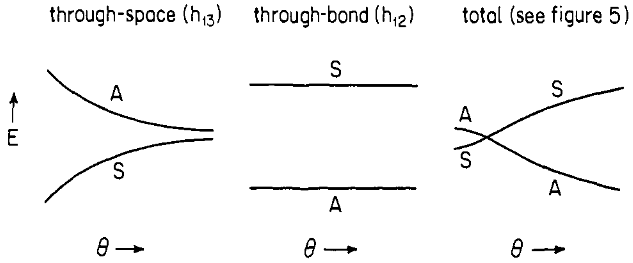


Figure 6. Singlet and triplet energies (hartrees) of pyramidalized (90,90) trimethylene as a function of γ ($\theta = 112°$). $\gamma < 0$ corresponds to (90′,270′) and $\gamma > 0$ corresponds to (270′,90′). All structures are C_{2v}.

Scheme II



is a π-type CH_2 MO of the central methylene, and χ_1, χ_2, χ_3 are regarded as orthonormal. The negative sign in ϕ_S reflects the fact that χ_2 mixes into the S MO in an antibonding way, thereby pushing it above the A MO.

In terms of the matrix elements $h^c_{ij} = \langle\chi_i|h^c|\chi_j\rangle$, the orbital energy gap can be approximately written as

$$\epsilon_S - \epsilon_A \approx \langle\phi_S|h^c|\phi_S\rangle - \langle\phi_A|h^c|\phi_A\rangle = (2 - \sin^2\alpha)h^c_{13} - (\sqrt{2}\sin 2\alpha)h^c_{12} \quad (11)$$

In eq 11 we have ignored the Coulomb terms and imposed the C_{2v} symmetry requirements $h^c_{11} = h^c_{33}$ and $h^c_{12} = h^c_{23}$, and have made the simplying approximation $h^c_{11} = h^c_{22}$. Both h^c_{12} and h^c_{13} are negative, so that for $\epsilon_S < \epsilon_A$ the h^c_{13} term must dominate, which depends on direct overlap of χ_1 and χ_3. This is the case for small θ, since the two ends are close together. As θ increases h^c_{13} will decrease, and at some larger angle the second term in eq 11 will become dominant to give $\epsilon_S > \epsilon_A$. Note that, although h^c_{13} depends on θ, the h^c_{12} term involving "through-bond" coupling with the central methylene is essentially independent of θ. As shown in Scheme II, eq 11 predicts that the orbital energy gap is just the sum of the through-space and through-bond contributions. It is important to note that a clean separation of these two contributions is possible only because the C_{2v} symmetry cancels the interaction terms involving both contributions. For nonsymmetrical biradical conformations a rigorous separation will not be possible.

(90,90) Trimethylene. Effect of Pyramidalization. In previous ab initio studies on trimethylene it was noted that the singlet energy of (90,90) was very sensitive to pyramidalization of the terminal methylenes,[2d,g,f] with a strong preference for pyramidalization inward. We investigated this by varying the pyramidalization angle γ outward ($\gamma > 0$) and inward ($\gamma < 0$), keeping C_{2v} symmetry. (For the present discussion it is convenient to give γ an algebraic sign. All subsequent discussions of pyramidalized methylenes will employ our original definitions of γ, α', and β' in Figure 1.) Our results in Figure 6 show two interesting features. First, although both S and T states favor pyramidalization inward, the preference in the singlet is very pronounced. Second, pyramidalization produces an S–T intersection at about $\gamma = +25°$. Figure 7 shows the orbital energies of the singly occupied MOs as a function of γ. As before they are labeled by their symmetry with respect to reflection in the plane through the central methylene.

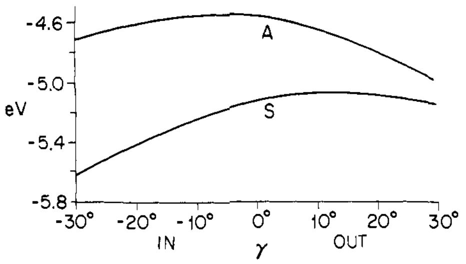
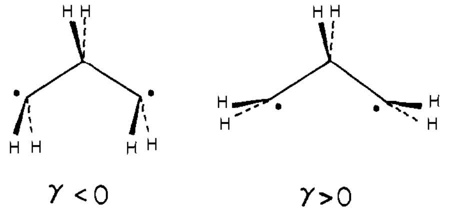


Figure 7. Orbital energies (in electron volts) of ϕ_A and ϕ_S as a function of γ for pyramidalized (90,90) trimethylene ($\theta = 112°$).



The origin of the pyramidalization appears to be more complex than has been supposed. It was originally proposed that the preference for $\gamma < 0$ over $\gamma = 0$ in the singlet state is due to an increase in ionic character and accompanying hyperconjugation with the central hydrogens.[2d] The ionic character as measured by $\sigma_A + \sigma_B$ increases from 0.27 ($\gamma = 0°$) to only 0.31 ($\gamma = -20°$). In fact, the coefficients of the central hydrogens in the S MO are actually *smaller* for $\gamma < 0$ than for $\gamma > 0$, a result inconsistent with the hyperconjugation argument. It has also been suggested[1c] that inward pyramidalization produces increased bonding between the radical centers. However, we have looked at the degree of direct overlap between the terminal carbons in the S MO and have found that it is greater for $\gamma > 0$ than for $\gamma < 0$, and therefore cannot account for the preference for $\gamma < 0$.

Both the pyramidalization and the S–T intersection are associated with the change in the A/S gap in Figure 7. Each active MO can interact with a high-lying core MO and at least two low-lying virtual MOs. In such a case the usual qualitative first-order perturbation treatment gives minimal insight, and it is best to defer to the computed results in Figure 7. The strong preference of the singlet state for $\gamma < 0$ is associated with the lowering of the S MO when $\gamma < 0$ and the strong tendency of the singlet to put both electrons into the lower MO for all these geometries. The σ_A values for $\gamma = +20°, 0°, -20°$ are 0.80, 0.83, 0.84, respectively, and are expected to be large for a biradical with significant σ overlap between the ends. The relative insensitivity of the triplet energy to γ is due largely to the necessity of putting one electron in each MO, since the average of the two orbital energies changes little. Given Figure 7, one expects from eq 8 that E_{ST} should be large and negative for $\gamma < 0$ and should approach 0 or perhaps reverse sign for $\gamma > 0$. It happens that the exchange integral is large enough for E_{ST} to become positive for $\gamma > +25°$.

One sees from these analyses that it is possible to make qualitative predictions about the behavior of the S–T splitting by using simple, familiar chemical concepts. For both (0,0) and (90,90) the behavior of E_{ST} follows directly from the changes in the orbital energy difference via eq 8. The real problem is to understand how the MOs change as the geometry changes, and the techniques for doing this have been well-known since Walsh's analysis of molecular geometries.[24]

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(24) Walsh, A. D. *J. Chem. Soc.* **1953**, 2260–317.

(25) (a) Crawford, R. J.; Mishra, A. *J. Am. Chem. Soc.* **1966**, *88*, 3963. (b) This interpretation has recently been challenged. See: Clarke, T. C.; Wendling, L. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1977**, *99*, 2740.

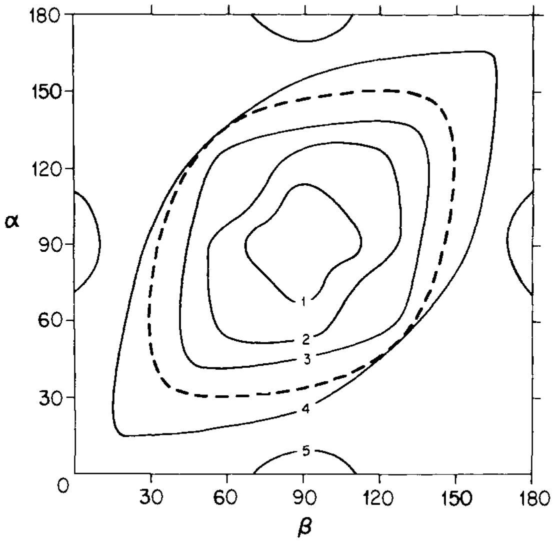

Figure 8. Singlet potential energy surface for trimethylene with planar terminal methylenes and θ = 112°, as a function of α and β. Contours are in kcal/mol above the lowest point on the surface at (90,90). The dotted line is the S–T intersection. The (30,150) = (150,30) geometry is 4.85 kcal/mol above (90,90), and appears to be a local maximum on this surface.

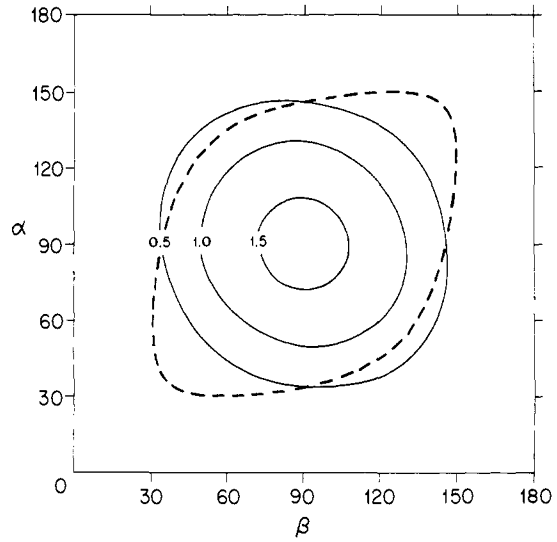

Figure 9. Triplet potential energy surface for trimethylene (planar terminal methylenes, θ = 112°) as a function of α and β. Contours are in kcal/mol above the lowest point on the surface at (0,90). The dotted line is the S–T intersection.

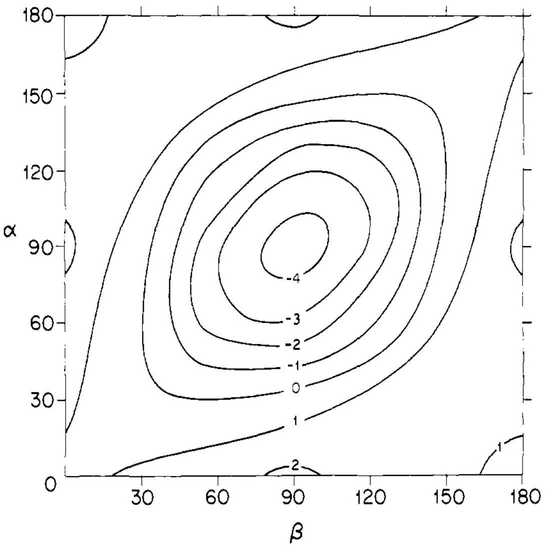

Figure 10. E_{ST} for trimethylene (planar terminal methylenes, θ = 112°) as a function of α and β. $E_{ST} < 0$ indicates a singlet ground state, $E_{ST} > 0$ a triplet ground state.

Table II. Energies of Important Points in Figures 8–12

geometry	E_T[a]	E_S[a]	σ_A[b]	E_{ST}[c]
(0,0)	-116.3436	-116.3423	0.73	0.08
(0,90)	-116.3442	-116.3407	0.707	2.17
(90,90)	-116.3414	-116.3491	0.84	-4.79
(30,150)	-116.3438	-116.3414	0.72	1.54
(90′,270′)	-116.3422	-116.3519	0.84	-6.11
(270′,90′)	-116.3404	-116.3411	0.80	-0.40
(90′,90′)	-116.3416	-116.3460	0.82	-2.73
(90′,30′)	-116.3447	-116.3427	0.76	1.26
(210′,30′)	-116.3449	-116.3438	0.74	0.72
(330′,30′)	-116.3446	-116.3423	0.72	1.45
(30′,330′)	-116.3420	-116.3398	0.73	1.34

[a] Potential energy in hartrees. (1 kcal/mol = 0.0016 hartree). [b] CI coefficient. [c] In kcal/mol.

(0,90) Trimethylene. This species is calculated to have a triplet ground state. As we pointed out earlier, the zero overlap between the terminal carbons implies that the exchange term dominates E_{ST}. In fact the singly occupied MOs are essentially degenerate and $\sigma_A = -\sigma_B = 1/\sqrt{2}$, so eq 8 gives $E_{ST} = 2K' = 2K_{13}$, the exchange integral over the terminal AOs. The S–T splitting is relatively insensitive to the geometry. For a range of θ, C–C bond lengths, etc., and even with 20° pyramidalization of either or both terminal methylenes, $E_{ST} = +2.0 \pm 0.3$ kcal/mol.

Singlet and Triplet Surfaces (Planar Methylenes). Qualitative Prediction of Product Ratios from the Triplet Biradical. We began our search for S–T intersections by restricting the terminal methylenes to be planar. Using the coordinates at the top of Figure 1, θ = 112°, we generated a two-dimensional grid by varying α and β independently in 30° increments to give 13 unique geometries. At each geometry the singlet and triplet energies were calculated. Figures 8–10 show the singlet, triplet, and E_{ST} surfaces. Three other sets of surfaces (not shown) were similarly generated by using a set of geometrical parameters slightly different from Figure 1 and differing only in their θ values of 108°, 112°, and 116°. They are all qualitatively the same as Figures 8–10. The

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(26) (a) Rabinovitch, B. S.; Schlag, E. W.; Wiberg, K. B. *J. Chem. Phys.* **1958**, *28*, 504–5. (b) Schlag, E. W.; Rabinovitch, B. S. *J. Am. Chem. Soc.* **1960**, *82*, 5996–6000. The high-pressure Arrhenius parameters are log k(cis–trans) = 16.41 − (65.1 ± 0.5)/θ and log k(propylene) = 15.12 − (65.4 ± 1.1)/θ. (c) Waage, E. V.; Rabinovitch, B. S. *J. Phys. Chem.* **1972**, *76*, 1695. These authors report that E_a(structural) − E_a(geometric) = 3.7 kcal/mol.

(27) A search for this transition state is currently underway using a CAS SCF wave function with four electrons in four orbitals (20 single configurations). The CAS SCF program was written by: Camp, R. N.; King, H. F. *J. Chem. Phys.*, in press.

(28) Beckwith, A.; Phillipou, G. *Aust. J. Chem.* **1976**, *29*, 123.

(29) When the structural features of a 1,4 biradical prevent β scission to two ethylenes via a transition state in which the p orbitals and the breaking C–C bond are periplanar, only cyclization takes place. See: Urry, W. H.; Trecker, D. J. *J. Am. Chem. Soc.* **1962**, *84*, 118. Yang, N. C.; Thap, C. *Tetrahedron Lett.* **1966**, 3671.

(30) (a) Dewar, M. J. S.; Olivella, S. *J. Am. Chem. Soc.* **1978**, *100*, 5290–5. (b) Nagase, S.; Kern, C. W. *Ibid.* **1980**, *102*, 4313–5. (c) Nagase, S.; Fueno, T.; Morokuma, K. *Ibid.* **1979**, *101*, 5849.

(31) Agosta, W. C.; Wolff, S. *Ibid.* **1977**, *99*, 3355–61.

(32) (a) Zimmerman, H. E. *Acc. Chem. Res.* **1972**, *5*, 393. (b) Bodor, N.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1972**, *94*, 9103. (c) Altmann, J.; Csizmadia, I.; Yates, K. *Ibid.* **1974**, *96*, 4196. (d) Altmann, J.; Tee, O.; Yates, K. *Ibid.* **1976**, *98*, 7132.

(33) (a) Kyba, E. P. *J. Am. Chem. Soc.* **1977**, *99*, 8330–2. (b) Nickon, A.; Huang, F.; Weglein, R.; Matsuo, K.; Yagi, H. *Ibid.* **1974**, *96*, 5264.

(34) Using a semiempirical SINDO potential function, K. Jug (*Theor. Chim. Acta* **1976**, *42*, 303–10) located a saddle point for the cyclopropane to propylene reaction. Unfortunately, the entire geometry search was performed with a closed-shell wave function, which precluded the accurate description of biradical-like structures. His transition-state geometry was compact—essentially a severely distorted cyclopropane.

major effect of decreasing θ is to make E_{ST} more negative in the vicinity of (90,90) and to widen the intersection contour $E_{ST} = 0$ to enclose a larger area.

The general features of the surfaces are as one expects from the qualitative arguments given earlier. The singlet prefers geometries with large overlap between the terminal AOs and the triplet prefers geometries with small overlap. For example, the lowest point on the singlet surface (the zero of energy) is (90,90), while the lowest point on the triplet surface is (0,90). On the singlet surface (0,90) is above (0,0) because (0,90) benefits neither from direct overlap nor from indirect overlap through the bonds. On the triplet surface the preference is reversed. The energies of (0,0), (0,90), and (90,90) are listed in Table II.

One might ask whether dynamic spin polarization,[35,36] not accounted for at the RHF/2CSCF level, would dramatically change the results reported herein. This effect, for example, has been the explanation for the violation of Hund's rule in cyclobutadiene[35] and twisted ethylene.[37] We concur with Salem[38] that the effect on trimethylene, if any, would be preferentially to stabilize the triplet relative to the singlet. It will become apparent that this would not qualitatively change the results of this section.

The singlet surface (Figure 8) contains an interesting feature that other authors have noticed in previous calculations.[2a,f,g] In going from (0,0) = (0,180) to (90,90) (and then to cyclopropane without activation) the conrotatory path via (30,30) and (60,60) proceeds without activation, whereas the disrotatory path via (30,150) and (60,120) passes over a 0.6 kcal/mol barrier, the top of which corresponds approximately to (30,150) (see Table II). Of course, a 0.6 kcal/mol difference is small and may be an artifact of our method. Nevertheless, it has long been noted that a preference for conrotatory double rotation in (0,0) trimethylene neatly explains the stereochemical crossover effect in pyrazoline pyrolyses.[25] Hoffmann[2a] has suggested that the preference for conrotation can be understood in terms of the energy of the A and S singly occupied MOs of (0,0). The A MO lies below S, and, if it were doubly occupied, then conrotation would be strongly favored because a bonding relationship could be maintained by double occupancy of the *lower* MO. Disrotation would require double occupancy of the *higher* MO. Configuration interaction almost erases this preference, but, since $|\sigma_A| > |\sigma_B|$, the lower A MO has a slightly higher occupation number than the S MO, and a weak preference evidently survives. An interesting possible consequence is that the singlet biradical **1** might lie in a local minimum on its potential surface, since it can form bicyclopentane only by a disrotatory closure.

For convenience the intersection $E_{ST} = 0$ has been superimposed as a dotted line in Figures 8 and 9. The triplet surface is nearly flat, the highest and lowest points differing only by about 1.6 kcal/mol. On this surface the entire S–T intersection is accessible to a thermally equilibrated triplet biradical. From Figure 8 is clear that, once a biradical enters the singlet surface at the geometry of an S–T intersection, it can proceed directly downhill to the (90,90) geometry. Since this geometry is on a steep energy slope leading to cyclopropane, any S–T crossing can lead to cyclopropane without activation.

The key question is the relative efficiency with which isc leads to propylene. Starting from a thermally equilibrated triplet biradical, the formation of both cyclopropane and propylene requires activation. From considerations given later, it appears that the low-energy S–T intersections, such as the $E_{ST} = 0$ line in Figures 8 and 9, are the regions where most biradicals undergo isc. For cyclopropane formation this is the only barrier that must be surmounted. For propylene formation we argue below that the barrier to H transfer on the singlet surface lies about 5.2–5.7 kcal/mol higher than the $E_{ST} = 0$ line. Cyclopropane is thus predicted to be the energetically favored product. At room temperature, the above numbers give a Boltzmann factor of roughly 10 000. In addition, cyclopropane appears to be highly favored by entropy. From Figures 8 and 9 one can see that the $E_{ST} = 0$ line encompasses a wide range of terminal methylene orientations, yet the energy changes by only a few tenths of a kcal/mol. The barrier for cyclopropane formation can almost be thought of as having the $E_{ST} = 0$ line as a free internal rotation, yielding a favorable entropy of activation. On the other hand, the H transfer to form propylene is expected to have much tighter geometrical requirements. Since the transition state lies only a few kcal/mol above the low-energy S–T intersections, any C–H bond breaking must be energetically balanced by partial bonding in the rest of the molecule. The resulting geometrical restrictions imply that only a small region of configuration space about the transition state will be energetically accessible. Experimental support for this conjecture is the fact that, for thermal reactions on the singlet surface, the Arrhenius A factor for cis–trans isomerization of cyclopropane-d_2 is about 10–20 times larger than the A factor for propylene-d_2 formation.[26] In qualitative pictorial terms, only a small fraction of sufficiently energetic trajectories undergoing isc from the thermally equilibrated triplet will be "aimed" at the narrow trough leading propylene, the remainder being trapped in the cyclopropane energy well.

For photochemical reactions generally, and triplet-derived trimethylene in particular, it is apparent that *thermal equilibration on the triplet surface introduces a bias in favor of products that can be formed without activation on the singlet surface after isc occurs.* A product that requires activation after isc is burdened with an unfavorable Boltzmann factor. The bias against such a product increases exponentially with the energy difference between the S–T intersection and the transition state for product formation. It is remarkable that in 1968 Crawford,[5d] in one of his pioneering studies on pyrazoline decompositions, proposed a mechanism for the decay of triplet trimethylene that has much in common with our mechanism. Quoting an unpublished PPP calculation by H. E. Simmons that triplet trimethylene lies a full 0.5 eV below the singlet, he proposed that the small yields of olefins from triplet trimethylenes were due to thermal equilibration of the triplet biradicals prior to isc.

The missing link in our chain of reasoning is the transition state for propylene formation, which we have not yet located.[27] We cannot, therefore, make any rigorous predictions based solely on our surfaces. Although the H transfer to form propylene has several chemical analogies (β scission of radicals,[28,29] radical additions to double bonds,[30] intramolecular disproportionation of 1,5 biradicals,[31] and 1,2 hydrogen shifts of alkyl carbenes),[32,33] it would be premature to speculate on the application of these related reactions to the present reaction because the structure of the transition state is unknown.[34] We do note that the thermal isomerization of 1,2-dideuteriocyclopropane to propylene-d_2 has an experimental activation energy 3.7 kcal/mol higher than that for cis–trans isomerization.[26c] This latter transition state has a calculated[2g] geometry close to (0,90) trimethylene, which is about 2 kcal/mol above the S–T intersection on our surface. (Salem's transition state[2g] had the perpendicular methylene pyramidalized inward. When this is done on our surface, the energy decreases by less than 0.5 kcal/mol relative to (0,90).) Our calculations therefore suggest that the S–T intersection is 1.5–2.0 kcal/mol *below* what is experimentally known to be the *lower* of the two transition states, and thus 5.2–5.7 kcal/mol below the transition state for propylene formation. In view of this, we propose that *the low yield of propylenes from triplet trimethylenes is a result of* (1) *thermal equilibration on the triplet surface prior to isc, and* (2) *the less favorable entropy for propylene formation.* A rigorous theoretical prediction must await, at the very least, the location of the H-transfer transition state.

So far we have ignored higher-energy S–T intersections because of their low Boltzmann factors. However, if the low Boltzmann factors were offset by large spin–orbit couplings, we would be forced to consider these intersections because they might lead to propylene without activation. In fact, there is no reason to expect the spin–orbit coupling to be any greater at a higher-energy

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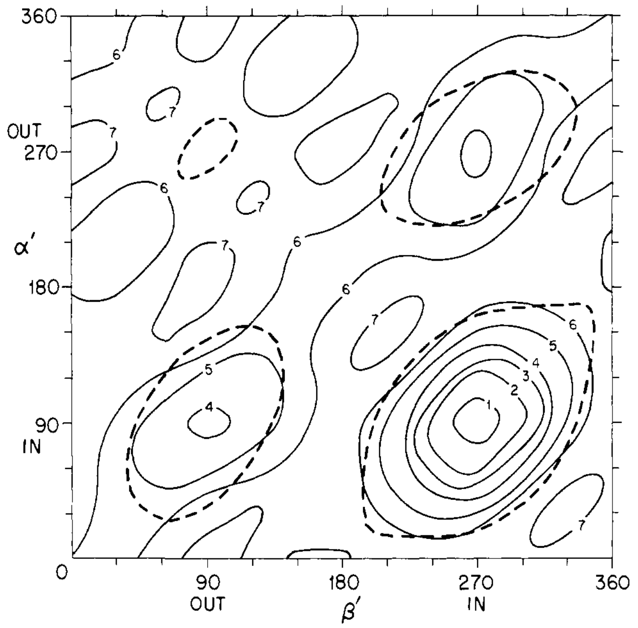

Figure 11. Singlet potential energy surface for trimethylene (pyramidalized terminal methylenes, $\gamma = 20°$, $\theta = 114°$) as a function of α' and β'. Contours are in kcal/mol above the lowest point on the surface at (90′,270′). The dotted lines are the S–T intersection contours. "In" and "out" refer to the direction of pyramidalization of the terminal methylenes.

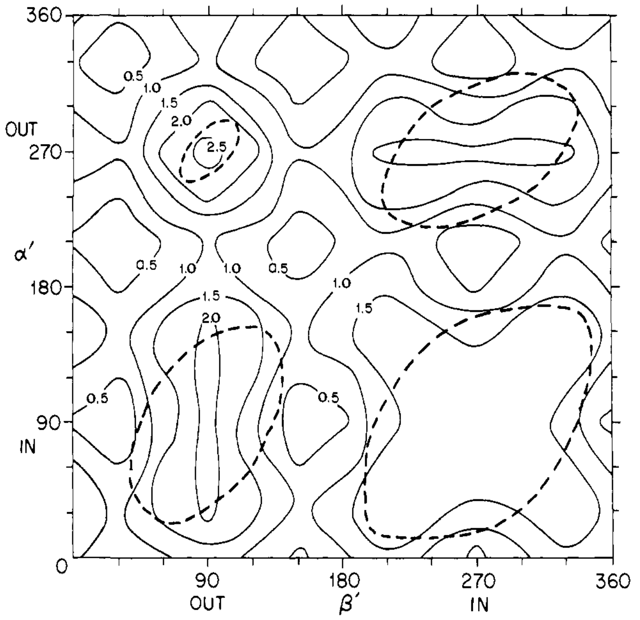

Figure 12. Triplet potential energy surface for trimethylene (pyramidalized terminal methylenes, $\gamma = 20°$, $\theta = 114°$) as a function of α' and β'. Contours are in kcal/mol above the lowest point on the surface at (210′,30′). The dotted lines are the S–T intersections.

intersection. Salem and Rowland[8] have pointed out that spin–orbit coupling in biradicals depends on the ionic character of the singlet and the mutual orientation of the terminal AOs (spin–orbit coupling is greatest when they are orthogonal). At both high and low energy the S–T intersection encompasses a variety of such mutual orientations (see Figure 10), all with about the same ionic character, and on average the spin–orbit coupling will be nearly independent of the energy. Take, for example, the intersection encountered on going from (0,90) with $E_{ST} > 0$ to (90,90) with $E_{ST} < 0$. (0,90) has no ionic contribution, (90,90) has a large ionic contribution, and the intersection has an intermediate value. The two p orbitals are orthogonal in (0,90) and intersect at a 58° angle in (90,90) when $\theta = 112°$. The S–T intersection therefore has a large orthogonal component to the orientation of the p orbitals as well as an ionic contribution to the singlet wave function. The same argument holds for any θ in the range of interest and in fact the CI coefficient $\sigma_A = 0.76–0.78$ at the S–T intersection for $\theta = 108–116°$. We conclude that spin–orbit coupling is about the same at higher-energy intersections (e.g., nonoptimal values of θ) as it is at the lowest intersections, and that high-energy intersections are unimportant if they have small Boltzmann factors.

The triplet trimethylene problem appears to be an example (possibly a rare one) of a photochemical reaction in which a knowledge of the S and T surfaces is sufficient by itself to predict the product distribution, without having to calculate the spin–orbit couplings or the nuclear dynamics.

Singlet and Triplet Surfaces (Pyramidal Methylenes). It is known that pyramidalization of the terminal methylenes lowers the energy of the biradical, and our S–T intersection may therefore represent to some extent a high-energy intersection. In order to see whether pyramidalization changes the picture, we examined another set of S and T surfaces in which both methylenes were pyramidalized with $\gamma = 20°$, using the geometrical parameters at the bottom of Figure 1. A grid was generated by rotating α' and β' independently in 30° increments to give 43 unique geometries.

The singlet and triplet surfaces are shown in Figures 11 and 12, with the S–T intersection ($E_{ST} = 0$) superimposed in dotted lines on each surface. Many of the qualitative features of Figures 8 and 9 are preserved here. The plateaus of one surface generally correspond to valleys on the other. The lowest points on the singlet surface correspond to pyramidalization of (90,90) trimethylene to (90′,270′) and (90′,90′). The lowest regions of the triplet surface correspond roughly to pyramidalization of (0,90) trimethylene. Triplet (90′,30′), (210′,30′), and (330′,30′) seem to be distinct local minima, although we have not verified this with a complete optimization. The total energies of these conformers are included in Table II.

Before considering the S–T crossings, we can draw several conclusions from the two surfaces. On the triplet surface the barriers to rotation of a single methylene (e.g., (330′,30′) → (210′,30′)) are around 0.5 to 0.8 kcal/mol, about the same as the analogous barrier for rotation in the 1-propyl radical.[33] The barriers for synchronous rotation of both methylenes (e.g., (330′,30′) → (210′,150′)) are significantly larger. Therefore triplet trimethylene should undergo geometrical (cis–trans) isomerization much faster than optical isomerization. However, if it were possible to fix one of the methylenes in a 90′ or 270′ orientation, e.g., by incorporation in a ring, the barrier for single rotation would be significantly higher. For example, the single rotation (90′,30′) → (90′,150′) would have a barrier around 2.0 kcal/mol. Thus, although triplet trimethylene can lose stereochemistry very rapidly, our results suggest that the rate of single methylene rotation is critically dependent on the orientation of the other methylene.

The singlet surface presents a different picture. Here synchronous double rotation is preferred over single rotation, in qualitative agreement both with Figure 8 and with Berson's thermolysis experiments on 1,2-dideuteriocyclopropane.[1a,b] The lowest-energy synchronous process is a conrotation going from (90′,270′) to (0′,180′), followed by depyramidalization to (0,0), repyramidalization to (180′,0′) = (180′,360′), and then on to (90′,270′) with mirror-image stereochemistry. The barrier for this appears to be about 1 kcal/mol lower than a single rotation path from (90′,270′) to (0′,270′), followed or accompanied by depyramidalization of the rotating methylene to the planar form, then continuing the rotation in the same direction with accompanying repyramidalization to form (90′,270′) with the opposite cis–trans stereochemistry. If the rotating methylene is not allowed to become planar, the preference for double rotation is even greater (ca. 1.5 kcal/mol on this surface). We should point out that (90′,270′), (90′,90′), (270′,90′), and (270′,270′) are all pyramidalized distortions of (90,90) and hence are unstable with respect to a decrease in θ to form cyclopropane. Another interesting feature is that pyramidalization does not affect the qualitative preference for conrotatory ((90′,270′) → (0,180′)) over disrotatory ((90′,270′) → (180′,180′)) synchronous double rotation.

Although part of the reason for examining pyramidal methylenes was to look for lower-energy S–T intersections, most of the intersections are actually higher than the intersection in Figure 10. In fact, many segments of the S–T intersection lie above the 1.5 kcal contour on the triplet surface (Figure 12) and have unfavorable Boltzmann factors. Other than this, the qualitative features of these surfaces are identical with those of Figures 8 and 9. Figure 11 shows that after isc occurs cyclopropane can be formed without activation, starting from any point on the S–T intersection. Figure 11 also shows that the intersection is 1 kcal below (0′,270′), a good approximation to the calculated[2a] geometry of the transition state for geometrical isomerization of cyclopropane. Since the transition state for propylene formation is known to be higher still, we presume that H transfer requires activation after the isc step. The basic conclusions of the previous section are therefore unchanged by pyramidalizing the terminal methylenes.

Summary and Conclusion

In this paper we have explored the relation between the S–T splitting and the geometry of trimethylene. In particular, we have identified some of the interactions responsible for S–T intersections. In many cases the S–T splitting can be understood as a competition between the orbital energy difference, favoring a singlet ground state, and the exchange integral between the terminal AOs, favoring a triplet ground state.

Examination of the singlet and triplet surfaces generated by twisting the terminal methylenes, both with and without pyramidalization, yielded several interesting conclusions. On the triplet surface single methylene rotation is faster than synchronous double rotation. The opposite is true on the singlet surface. Of the two possible double rotation pathways, singlet trimethylene prefers conrotation. Finally, the lack of propylene in the products from triplet-derived trimethylenes is ascribed to two features of the potential surfaces: (1) the S–T intersections accessible to the triplet are below the transition state for propylene formation on the singlet surface, and (2) the formation of propylene on the singlet surface is entropically unfavorable. Decay of triplet trimethylene thus appears to be an example of a photochemical reaction whose product distribution can be understood substantially on the basis of the potential surfaces alone. Explicit consideration of the dynamics or even of the S–T crossing probabilities does not seem to be needed.

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Picosecond Dynamics of Ion Pairs: The Effect of Hydrogen Bonding on Ion-Pair Intermediates

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Abstract: The dynamics of the interconversion between the solvent-separated ion pair and the contact ion-pair intermediates in the photoreduction of benzophenone by *N*,*N*-diethylaniline and diazabicyclo[2.2.2]octane have been elucidated by use of picosecond absorption spectroscopy. The dynamics were studied in ethanol/acetonitrile mixtures to ascertain the role of the solvent in the interconversion process.

The concept of the ion pair was introduced by Bjerrum[1] to account for the behavior of ionophores in solvents of low dielectric. Since then, intermediates in organic reactions have been frequently described as ion pairs.[2] Though a continuum in distribution of ion pairs may exist, their structures are usually formulated in terms of the solvent-separated ion pair and the contact ion pair.[3,4] Spectral changes resulting from the interconversion between the solvent-separated ion pair and the contact ion pair have been extensively studied.[5] However, our present understanding of ion pairs is restricted to equilibrium distributions among the various ion-pair forms; there have been no experimental or theoretical treatments of the dynamics of interconversion between ion-pair structures in solution. In this paper, we employ picosecond absorption spectroscopy to elucidate the effect of the solvent on ion-pair dynamics.

Ion-pair intermediates have been invoked for the photoreduction of aromatic ketones by amines.[6,7] We have recently reported that the photoreduction of benzophenone by *N*,*N*-dimethylaniline, *N*,*N*-diethylaniline, and diazabicyclo[2.2.2]octane[8] proceeds by electron transfer, resulting in the formation of the solvent-separated ion pair comprised of the radical cation of the amine and the radical anion of benzophenone. Subsequent to solvent-separated ion-pair formation, a contact ion pair is formed betwen these species. The half-lives of contact ion-pair formation from the solvent-separated ion pair for the photoreduction by *N*,*N*-diethylaniline and diazabicyclo[2.2.2]octane are 200 ± 50 ps and 100 ± 25 ps, respectively. Our studies in the photoreduction process were performed in acetonitrile, a solvent that is both a weak electron-pair donor and a weak electron-pair acceptor.[9] In acetonitrile, the equilibrium distribution between the ion-pair forms lies in favor of the contact ion pair. In this paper, we will dem-

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