

Theoretical Investigations of the Trimethylene Biradical¹

Sir:

There is currently much interest in establishing the mechanisms and potential surfaces involved in the geometric and structural isomerizations of small cyclic compounds such as cyclopropane.²⁻⁸ We report here the results of *ab initio* calculations on several configurations of trimethylene (open cyclopropane) using the generalized valence bond (GVB) method.⁹

We will use the following notation in describing the trimethylene configurations: θ is the central CCC angle; (90,90) indicates that the plane of each terminal CH₂ group is perpendicular to the CCC plane; (0,0) indicates that both terminal CH₂ groups are in the CCC plane; (0,90) is the obvious combination; a subscript *c* [e.g., (0,90_c)] indicates that the terminal group is canted from planar to the nearest staggered configuration^{7,8} (with respect to the bonds of the central carbon).

The geometric isomerizations of cyclopropane involve breaking of one C-C bond [in the (90_c,90_c) configuration] followed by rotation of one (path I) or both

(path II) terminal CH₂ groups. If the shape of each CH₂ group is kept fixed as one CH₂ group is rotated, there would occur three relative maxima in each of which both bonds of this group would eclipse the bonds of the central carbon; in between would be two points [both (0_c,90_c)] at which the bonds would be staggered,

(1) Partially supported by a grant (PF-013) from the President's Fund of the California Institute of Technology and by a grant (GP-15423) from the National Science Foundation.

(2) D. W. Setser and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, **86**, 564 (1964); B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(3) W. L. Carter and R. G. Bergman, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

(4) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(5) R. Hoffmann, *J. Amer. Chem. Soc.*, **90**, 1475 (1968).

(6) A. K. Q. Siu, W. M. St. John III, and E. F. Hayes, *ibid.*, **92**, 7249 (1970). This work used CC bond lengths of 1.30 Å, somewhat shorter than the 1.54 Å we used. They carried out a 2 × 2 CI calculation, starting with the Hartree-Fock triplet orbitals. This procedure corresponds to the first iteration in the GVB method and should be adequate for $\theta > 100^\circ$.

(7) L. Salem, *Bull. Soc. Chim. Fr.*, 3161 (1970).

(8) Y. Jean and L. Salem, *Chem. Commun.*, 382 (1971).

(9) P. J. Hay, W. J. Hunt, and W. A. Goddard III, *Chem. Phys. Lett.*, in press; see also W. A. Goddard III and R. C. Ladner, *J. Amer. Chem. Soc.*, **93**, 6750 (1971).

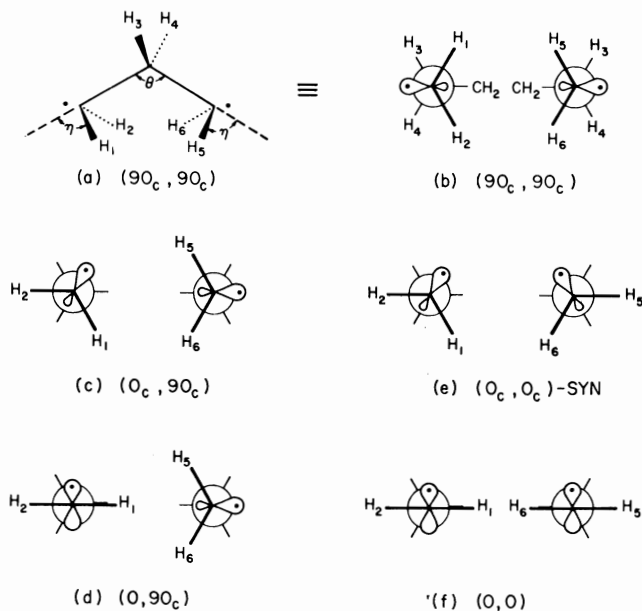


Figure 1. Schematic representation of some of the trimethylene configurations. In (b-f) the molecule is shown twice, each part emphasizing one of the terminal groups.

leading to relative minima. However, the minimum energy path for rotating the CH_2 by 360° need not keep the shape of the CH_2 group fixed. By allowing the CH_2 group to wobble as it rotates, one can avoid eclipsing more than one bond, leading to a slightly lower (~ 0.5 kcal) barrier height. The saddle point for this path (I) is expected to be $(0,90_c)$. For path II the two groups can be rotated either in a conrotatory or a disrotatory sense and the saddle point is expected to be $(0,0)$. Some of these configurations are shown schematically in Figure 1.

The calculated energy curves for the $(90_c,90_c)$, $(0,90_c)$, and $(0,0)$ configurations (Figure 2a) indicate that for $\theta \leq 130^\circ$ the unrotated $(90_c,90_c)$ configuration remains below both possible saddle points and that the saddle points for paths I and II have comparable energies (60.9 and 60.5 kcal) and angles (112 – 114°).

Keeping the terminal groups planar and conrotating from $(0,0)$ to $(90,90)$ leads to no hump in the potential curve, as shown in Figure 2b, and the similar rotation from $(0,90_c)$ to $(90,90_c)$ also should lead to no significant hump (at most a very slight one, ~ 0.5 kcal). We found that starting with trimethylene in the $(90_c,90_c)$ configuration and closing the ring involved no energy barrier; hence there should be no significant energy barrier to ring closure from either saddle point.

If the terminal groups of trimethylene are taken as planar, we obtain the potential curves in Figure 2c. The $(0,0)$ energy curve shows a minimum for $\theta = 114^\circ$, which is essentially at the angle (115°) where the $(90,90)$ curve crosses the $(0,0)$ curve. On the other hand, the $(0,90)$ curve remains about 1 kcal above the $(0,0)$ curve in the $\theta = 110$ – 120° region. These results are in qualitative agreement with the extended Hückel calculations of Hoffmann⁶ who found the $(90,90)$ and $(0,0)$ curves to cross at $\theta \sim 117^\circ$ with the $(0,90)$ curve somewhat higher. [He found the $(0,0)$ minimum to occur at $\theta = 125^\circ$ with an energy 44 kcal above that of cyclopropane; considering an extensive set of geometries, he found a cycle-closing barrier of about 1 kcal.] Our

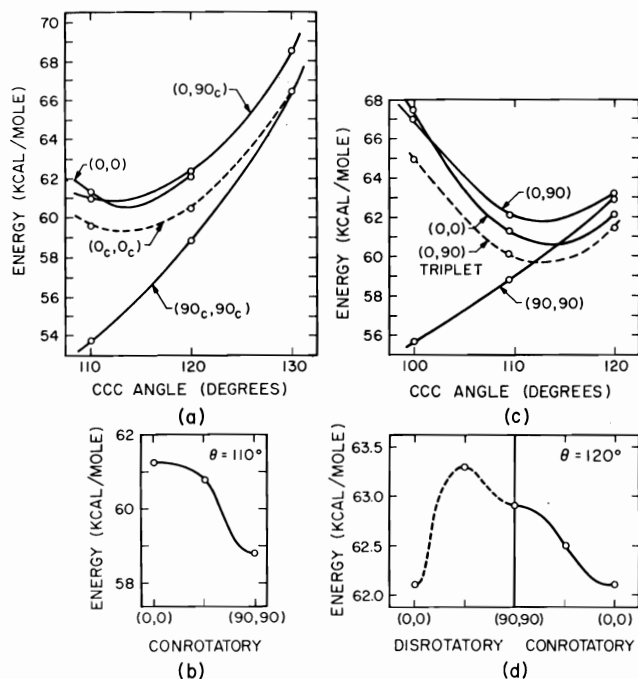


Figure 2. (a) Energy curves for the $(0,0)$ and $(0,90_c)$ saddle points of trimethylene compared with $(0_c,0_c)$ and $(90_c,90_c)$ curves; (b) and (d) potential curve for rotation of planar terminal CH_2 groups at $\theta = 110$ and 120° , respectively; (c) energy curves for the case of planar terminal groups.

results are also in fair agreement with *ab initio* calculations on the $(0,0)$ and $(90,90)$ states by Siu, St. John, and Hays⁶ [they find the crossing to occur at $\theta = 109.5^\circ$ and the minimum in the $(0,0)$ curve at 114.3° with an energy of 32 kcal above that of cyclopropane (leading to a cycle-closing barrier of about 1 kcal if the surface between $(0,0)$ and $(90,90)$ is assumed to be smooth)].

We also examined the energy changes for disrotatory and conrotatory motions of the planar terminal groups (see Figure 2d). As suggested earlier by Hoffman,⁵ the conrotatory motion is favored, but only slightly.

Although for planar terminal groups the $(0,0)$ form is more stable than the $(90,90)$ for $\theta > 115^\circ$, staggering of the terminal bonds relative to the central bonds lowers the energy (1.6 and 4.0 kcal, respectively, at 120°), with $(90_c,90_c)$ remaining more stable than $(0_c,0_c)$ for $\theta < 130^\circ$ (Figure 2a). There are both syn and anti forms of $(0_c,0_c)$, but at $\theta = 120^\circ$ these differ only by 0.1 kcal. The extra stability due to canting was first pointed out by Salem⁷ who found energy lowerings of 1 kcal for $(0_c,0_c)$ relative to $(0,0)$ and 6.2 kcal for $(90_c,90_c)$ relative to $(90,90)$ (at $\theta = 113^\circ$).

We have ignored the triplet states in most of this discussion since the singlet states are most relevant for these reactions. For triplet states the $(0,90_c)$ configuration was an energy about 1 kcal lower than $(0,0)$ and $(90_c,90_c)$. The $(0,90)$ triplet is compared with some singlet curves in Figure 2c.

Summarizing we find that the barrier height for cis-trans isomerization of cyclopropane is essentially the same (calculated value, 60.5 kcal) whether one or both of the terminal CH_2 groups are rotated after opening of the CC bond. The calculated barrier height compares well with the estimate of 61.1 kcal by Lin and Laidler¹⁰ based on RRKM calculations using the ex-

(10) M. C. Lin and K. J. Laidler, *Trans. Faraday Soc.*, **64**, 927 (1968).

perimental results¹¹ ($E_a = 64.2$ kcal). However, we find no justification for the common assumption⁴ of a large ring-closing barrier (usually assumed to be about 9 kcal⁴) for trimethylene biradical.¹² This result of no significant ring-closing barrier does not contradict experimental results³ and is in agreement with extended Hückel calculations on trimethylene⁵ and tetramethylene.¹³

(11) B. S. Rabinovitch, E. W. Schlag, and K. B. Wiberg, *J. Chem. Phys.*, **28**, 504 (1958).

(12) In the usual calculation⁴ of the ring-closing barrier of trimethylene, one starts with propane and breaks a terminal CH bond on each end. This procedure leads to a mixed spin state (neither singlet nor triplet). The singlet state is strongly bound for configurations near (90, 90) and leads to energies *below* the saddle point, which may explain the low values usually obtained.⁴

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