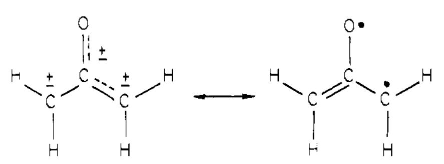
basis set might further decrease the energy difference.

As discussed above, the electronic structure of the $^1A_1$ state must be described with at least a two-configuration self-consistent-field (TCSCF) wave function.

$$\Psi(^1A_1) \simeq C_1|...1b_2^2 5b_1^2 2b_2^2| - C_2|...1b_2^2 5b_1^2 1a_2^2| + ...$$

The coefficients of these two configurations in the MCSCF wave function were found to be $C_1 = 0.786$ and $C_2 = 0.580$. The large magnitude of C_2 shows that the $^1A_1$ state of oxyallyl is a diradical, **3**, instead of **1**. This is, of course, consistent with the fact that the optimized geometry has a C–O double bond and long C–C bond lengths.

There are other possible structures for oxyallyl, such as **4** and **5**, which have C_s rather than C_{2v} symmetry. Although we tried, we were unable to find such optimized structures. They probably do not correspond to any equilibrium structure; the C–O double bond diradical structure (**1**) and the O$^-$–allyl$^+$ zwitterion structure (**2**) are probably more stable than corresponding **5** and **4**, respectively.



4 **5**

In order to examine whether $^1A_1$ is a true intermediate or a transition state, we determined the normal vibrational frequencies on the basis of the force constant matrix obtained by taking numerical differences of analytical MCSCF energy gradients. As in the case of TMM,[10] the vibrational analysis with the STO-3G basis set gives two imaginary frequencies corresponding to pyramidalization of two CH_2 groups. However, calculations with the 3-21G basis set show all the vibrational frequencies to have real values. This strongly suggests that the $^1A_1$ state of oxyallyl is the intermediate of the ring-opening reaction of cyclopropanone. This $^1A_1$ intermediate has a vibrational frequency of 170 cm^{-1} with the 3-21G basis (also 170 cm^{-1} with STO-3G) for a b_1 normal coordinate corresponding to disrotatory ring closure and 230 cm^{-1} (240 cm^{-1}) for an a_2 normal coordinate corresponding to conrotatory ring closure. Though we have not located transition states, these frequencies suggest that the barrier for the disrotatory ring closure from the $^1A_1$ intermediate to cyclopropanone would be lower than that for the conrotatory ring closure, a conclusion consistent with Woodward–Hoffmann rules.

Acknowledgment. The authors are grateful to Dr. T. Minato for stimulating discussions and helpful suggestions. Acknowledgment is also made to Dr. M. Dupuis for use of the GAMESS program. The numerical calculations were carried out at the IMS Computer Center.

Registry No. $\cdot CH_2COCH_2\cdot$, 17440-65-2; cyclopropanone, 5009-27-8.

Equilibrium Geometries for Triplet Trimethylene, $\dot{C}H_2CH_2\dot{C}H_2$

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Abstract: One of the lowest lying triplet electronic states for the C_3H_6 system is triplet trimethylene, a much-discussed diradical. Previous theoretical work has identified several triplet stationary points of $\dot{C}H_2CH_2\dot{C}H_2$ with one or more imaginary vibrational frequencies. Here are located and characterized two genuine minima on the triplet trimethylene potential energy hypersurface. Single-configuration self-consistent-field theory is used in conjunction with a standard Huzinaga–Dunning double-ζ basis set. These minima are of C_2 and C_s symmetry, respectively, and are separated by only 0.14 kcal. By reference to three other triplet stationary points, the potential surface for trimethylene internal rotation and pyramidalization is discussed.

In recent years there has been considerable interest, both experimental[1–7] and theoretical,[8–17] in the trimethylene biradical, $\dot{C}H_2CH_2\dot{C}H_2$. Most of this interest has been rightly directed at the stereoisomerization of cyclopropane, a process with which is associated an activated energy of 59.8 kcal/mol.[18] Although earlier there was considerabl support[19] for the idea that trimethylene might be a true intermediate (i.e., a minimum on the C_3H_6 energy surface), more recently the weight of theoretical evidence is for trimethylene as a transition state.[11,12,14,17,18] Following the classic work of Woodward and Hoffmann,[20] the question of conrotatory vs. disrotatory singlet pathways has attracted much attention, with the consensus now being that the conrotatory pathway to ring closure of the "π cyclopropane" should

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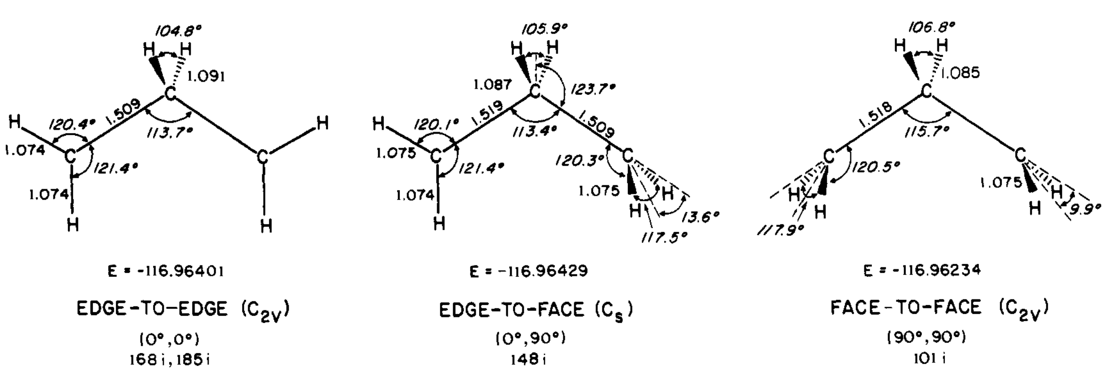
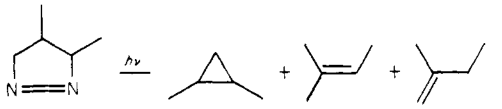


Figure 1. Precise ab initio geometrical predictions of the three "standard" conformations of triplet trimethylene. Bond distances are in Å. The imaginary vibrational frequencies associated with each stationary point are indicated, showing that the E–F and F–F structures are transition states.

occur without activation energy.

In their recent theoretical study, Doubleday, McIver, and Page (DMP)[14] have emphasized the role of *triplet* trimethylene[21] when nitrogen (N_2) is extruded from a number of five-membered rings,[22-25] for example



(1)

DMP note[14] 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. Specifically, the triplet-sensitized photolysis of the trimethylene precursor [e.g., the reactant in eq 1] yields cyclopropanes and less than 1% olefins.[14] By qualitatively mapping out the potential surfaces for triplet and singlet trimethylene in the region of intersection, DMP were able to provide an explanation for these unusual product yields.

In light of the above, it is now of interest to precisely determine the theoretical equilibrium geometry or geometries (if more than one conformer exists) of triplet trimethylene. For the three most obvious triplet methylene structures (edge-to-edge, edge-to-face, and face-to-face) precise geometrical predictions have recently been reported.[17] However, none of these three structures correspond to a minimum on the C_3H_6 potential energy hypersurface. As noted by DMP,[14] the triplet potential surface is very flat with respect to internal rotations in the vicinity of trimethylene. Here we report a relatively complete characterization of the triplet equilibrium structure(s) of trimethylene, including predictions of their vibrational frequencies.

Estimated Triplet Energetics

Triplet trimethylene is of particular interest since it is one of the lowest lying minima on the triplet potential energy hypersurface for C_3H_6. Given the experimental activation energy[18] of 59.8 kcal for cyclopropane isomerization and the trimethylene singlet–triplet separation of 0.8 kcal,[17] we readily predict that triplet trimethylene lies ~59 kcal above cyclopropane. Actually, the 59 kcal is an upper limit, since it is based on the edge-to-face triplet structure which in fact was demonstrated to be a transition state.[17] As noted above, the triplet minimum will be reported in this research, and necessarily lies somewhat lower than the edge-to-face transition state. The lowest suggested spectroscopic assignment[26-28] of a triplet state of cyclopropane is at 52 300 cm^{-1} or 150 kcal. Thus triplet trimethylene lies energetically below triple cyclopropane. The other low-lying closed-shell isomer of C_3H_6 is propene, $CH_3CH{=}CH_2$, which lies 33.1 kcal[29] below cyclopropane. Since the lowest triplet state of propane is known[30-32] to display an absorption maximum 4.2 eV (96.9 kcal) above the ground-state singlet, it may be concluded that triplet propene lies about 63.8 kcal above the singlet ground state of cyclopropane.

Putting all three triplet species on the same energy scale, one sees that trimethylene, propene, and cyclopropane lie respectively about 59, 64, and 150 kcal above the closed-shell cyclopropane minimum. These relative energies would appear to be upper limits to the true adiabatic[33] excitation energies T_e, since the triplet geometries are not fully relaxed to equilibrium. But it does seem likely that triplet trimethylene is the absolute minimum among conventional triplet C_3H_6 structures. A fourth contender is ethylcarbene $CH_3CH_2\ddot{C}H$, a species which probably[34,35] has a triplet electronic ground state, but for which there is apparently no experimental heat of formation. One can estimate the energy of ethylcarbene relative to that of propene from theoretical studies of the analogous but simpler methylcarbene/ethylene pair. In the latter case, the best theoretical predictions[34-36] suggest that triplet methylcarbene lies ~70 kcal above the closed-shell singlet ground state of ethylene. Thus one may estimate that triplet ethylcarbene lies 70 – 33 ≃ 37 kcal above the cyclopropane ground state. Roughly the same thermochemical conclusion should apply to dimethylcarbene $CH_3\ddot{C}CH_3$, a fifth C_3H_6 isomer, and it thus seems likely that one of these two carbene species is the absolute minimum for triplet C_3H_6.

Theoretical Approach and Review of Earlier Predictions

From a methodological perspective, our principal goal in this research was continuity with the earlier study of Yamaguchi, Osamura, and Schaefer (YOS).[17] They employed one- and two-configuration self-consistent-field (SCF) methods in conjunction with a standard double-ζ basis set[37,38] of contracted Gaussian functions. This Huzinaga–Dunning basis set is designated C(9s 5p/4s 2p), H(4s/2s), and the hydrogen s functions are scaled by a factor of 1.2. Equilibrium geometries and force constants were evaluated by using analytic first and second energy derivative methods.[39]

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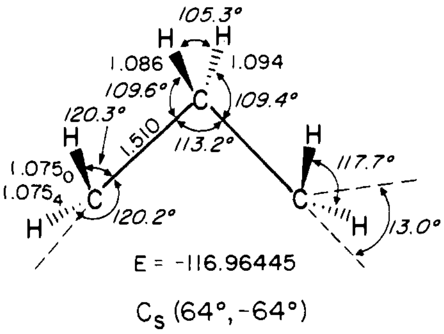

Figure 2. Predicted structure for the C_s symmetry secondary minimum of triplet trimethylene, with bond distances in Å. Note that this structure lies only 0.14 kcal above the C_2 absolute minimum seen in Figure 3.

The earlier reported stationary points of YOS for triplet trimethylene are illustrated in Figure 1. Torsional angles are defined relative to the C_{2v} edge-to-edge (E–E) structure, also labeled (0°,0°) to indicate that both torsional angles are by definition zero. Also of some interest are the methylene pyramidalization angles, 13.6° for the edge-to-face (E–F) structure and 9.9° for the face-to-face (F–F) geometry. Following DMP[14] the pyramidalization angle is defined to be the angle between the HCH bisector and a line extending from the C–C bond.

Figure 1 indicates that none of the three structures identified earlier[17] is a minimum. The E–E structure in fact has *two* imaginary vibrational frequencies, indicating that the energy is a maximum with respect to two vibrational degrees of freedom. Specifically, the two imaginary frequencies correspond to the conrotatory (a_2 = 185 i) and disrotatory (b_2 = 168 i) rotations about the two C–C bonds. The F–F structure in Figure 1 is a true transition state, having one imaginary vibrational frequency (b_2 = 101 i), corresponding to the symmetric combination of CH_2 twisting motions about the two carbon–carbon single bonds. It should also be noted that the F–F structure is the highest lying energetically of the three triplet stationary points in Figure 1.

The lowest energy structure found[17] for triplet trimethylene is the edge-to-face stationary point, which is a transition state. The single imaginary vibrational frequency (a'' = 148 i) or reaction coordinate corresponds to rotation about the C–C bond of the left-hand (Figure 1) terminal CH_2 group. Relative to the E–F transition state, the E–E and F–F stationary points are predicted to lie at 0.18 and 1.22 kcal, respectively.

In light of the above, it is clear that the goal of the present research is first to identify the minimum (or minima) of triplet trimethylene. That such a minimum exists is apparent from Figure 1. However, it is equally important to establish the different relationships between the trimethylene minima and the three stationary points already characterized.

A Secondary Minimum for Triplet Trimethylene

By way of a disrotatory (two CH_2 groups rotating in opposite directions) motion relative to the E–E stationary point, one locates a potential minimum, seen in Figure 2. This potential minimum has C_s point-group symmetry, with the reflection plane being that of the central CH_2 group. Note also that the two terminal methylene groups are (equivalently) pyramidalized, with a pyramidalization angle of 13.0°, quite close to the 13.6° value seen in Figure 1 for the E–F transition state.

The two torsional angles (α,β) describing rotation about the C–C bonds are 64° and −64° for the C_s minimum. The fact that the two torsional angles are opposite is consistent with the disrotatory path from the E–E structure to the C_s minimum and our earlier definition that the F–F structure is labeled (90°,90°) in Figure 1.

The central CCC angle for the C_s minimum is 113.2°, rather close to the 113.4° predicted (Figure 1) for the E–F transition state. For comparison the E–E and F–F central angles are 113.7° and 115.7°, respectively. The C–C bond distance for the C_s minimum is 1.510 Å, compared to values of 1.509 (E–E), 1.519 (E–F), and 1.518 Å (F–F) for the more "standard" structures reported previously.[17] Thus we conclude that the four triplet trimethylene conformations considered are very similar skeletally.

Table I. Vibrational Frequencies Predicted for the C_s Symmetry Secondary Minimum of Triplet Trimethylene[a]

symmetry	normal mode description	freq, cm^{-1}
a'	CH_{2B} a stretch	3435
	CH_{2B} s stretch	3316
	CH_{2A} a stretch	3224
	CH_{2A} s stretch	3115
	CH_{2A} scis	1630
	CH_{2B} scis	1603
	CH_{2B} rock	1267
	CC s stretch	993
	CH_{2A} rock	899
	CH_{2B} wag	471
	CCC deformation	414
	torsion (CH_{2B} twist)	170
a''	CH_{2B} a stretch	3431
	CH_{2B} s stretch	3312
	CH_{2B} scis	1582
	CH_{2A} wag	1506
	CH_{2A} twist	1295
	CC a stretch	1184
	CH_{2B} rock	979
	CH_{2B} wag	436
	torsion (CH_{2B} twist)	110

[a] Note that this structure lies only 0.14 kcal above the energetically lower C_2 minimum. Note that carbon atom A is the central carbon atom of trimethylene.

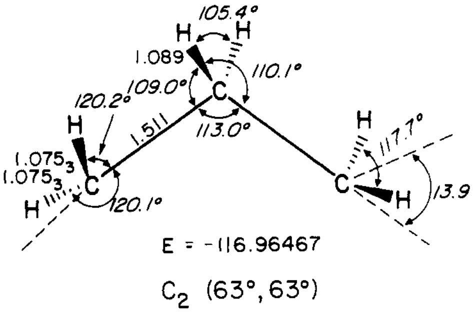

Figure 3. Theoretical geometry for the lowest minimum of triplet trimethylene. As discussed in the text, this also appears to be the global minimum for triplet C_3H_6. Bond distances are given in Å.

Predicted vibrational frequencies for the C_s minimum are given in Table I. The fact that all frequencies are real establishes beyond doubt that at the DZ SCF level of theory, the C_s structure of Figure 2 is a true minimum. As expected, the two lowest vibrational frequencies 170 cm^{-1} (a') and 110 cm^{-1} (a'') correspond to twisting motions about the two C–C single bonds. Next lowest is the CCC deformation at 414 cm^{-1}. Among the other vibrational frequencies, the two C–C stretches (s 993 cm^{-1}, a 1184 cm^{-1}) are perhaps most interesting. These may be compared with the C–C stretching frequencies for the E–E (949, 1189 cm^{-1}), E–F (951, 1179 cm^{-1}), and F–F (1021, 1157 cm^{-1}) stationary points. In every case, as expected, the antisymmetric C–C stretch lies higher, with the difference being most (240 cm^{-1}) for the E–E structure and least (136 cm^{-1}) for the F–F structure.

The Lowest Minimum for Triplet Trimethylene

If one again takes the E–E structure as a starting point, the second triplet trimethylene minimum is found via a conrotatory motion (two CH_2 groups rotate in the same direction) accompanied by pyramidalization. This minimum lies 0.14 kcal/mol below the C_s structure just discussed and therefore appears to be the absolute minimum for triplet C_3H_6. The absolute minimum, illustrated in Figure 3, has C_2 point-group symmetry, with the C_2 axis bisecting the central CH_2 group. The two terminal methylene groups

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Table II. Theoretical Vibrational Frequencies (Harmonic Approximation) for the Lowest Minimum of Triplet Trimethylene[a]

symmetry	normal mode description	freq, cm^{-1}
a	CH_{2B} a stretch	3433
	CH_{2B} s stretch	3314
	CH_{2A} s stretch	3161
	CH_{2A} scis	1634
	CH_{2B} scis	1599
	CH_{2A} twist	1341
	CH_{2B} rock	1179
	CC s stretch	957
	CH_{2B} wag	515
	CCC deform	403
	torsion (CH_{2B} twist)	163
b	CH_{2B} a stretch	3430
	CH_{2B} s stretch	3310
	CH_{2A} a stretch	3190
	CH_{2B} scis	1582
	CH_{2A} wag	1501
	CC a stretch	1181
	CH_{2B} rock	1101
	CH_{2A} rock	866
	CH_{2B} wag	486
	torsion (CH_{2B} twist)	146

[a] Note that carbon atom A is the central carbon atom of trimethylene.

are (equivalently) pyramidalized, with a pyramidalization angle of 13.9°, quite close to the value of 13.0° predicted for the C_s structure. The two torsional angles (α,β) are 63° and −63°, quite similar except for phase from the torsional angles of the C_s structure. This comparison makes it apparent that the C_s and C_2 minima differ qualitatively by an inversion about the central carbon atom of one of the terminal CH_2 groups.

The CCC central angle (113.0°) and C–C single-bond distance (1.511 Å) of the global triplet minimum of C_3H_6 are very similar (0.2°, 0.001 Å) to those of the C_s minimum. This observation is consistent with the finding (see below) that the C_s and C_2 structures are nearly degenerate conformational isomers separated by a small barrier. The most obvious difference between the C_s and C_2 structures arises from the fact that for the former the two C–H bonds of the central methylene are not equivalent. In fact, the difference in bond distances (0.008 Å = 1.094 − 1.086) is substantial. For the C_2 structure, these two C–H distances are equivalent and take on an intermediate value, 1.089 Å.

The C_2 structure is proven to be a minimum in Table II, which gives its DZ SCF vibrational frequencies. In general, these frequencies are quite similar to those discussed above for the C_s secondary minimum. The two torsional vibrational frequencies remain low (163 and 146 cm^{-1}) and are somewhat closer (17 cm^{-1}) than predicted for the C_s minimum (60 cm^{-1}). The next lowest frequency, as for the C_s minimum, is the CCC deformation, at 403 cm^{-1} for the C_2 minimum. The C–C single-bond stretching frequencies for the C_2 structure are predicted to be 957 (s) and 1181 cm^{-1} (a), compared to 993 and 1184 cm^{-1} for C_s.

Discussion

The predicted relationships between the different triplet trimethylene stationary points are summarized in Figure 4. Let us begin with the C_s minimum, which may be derived via a disrotatory motion (accompanied by pyramidalization of the two terminal methylene groups) relative to the E–E stationary point (left-hand side, Figure 1). A further disrotatory motion of the C_s secondary minimum leads to the F–F transition state. Figure 4 shows that the F–F transition state connects two equivalent C_s structures (labeled C_s and C_s' in Figure 4), which are mirror images. Continuing disrotatory motion (simultaneous rotation of the two CH_2 groups in opposite directions) beyond the C_s' structure leads to geometries for which the CH_2 groups are pyramidalized outward. Such geometries of triplet trimethylene lie higher energetically than the conformations shown in Figure 4. In contrast, it is worth noting that for *singlet* trimethylene, the F–F stationary point has the CH_2 groups slightly pyramidalized outward.[17]

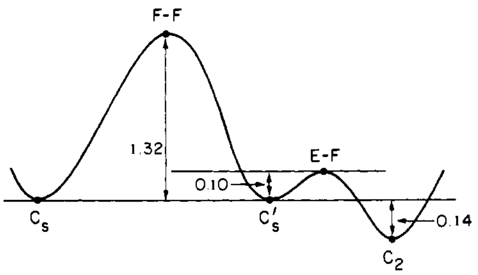

Figure 4. Qualitative view of the triplet trimethylene potential energy hypersurface. This sketch shows the relationships between the two transition states (F–F and E–F) and the two minima (C_2 and C_s, which is the mirror image of C_s').

Figure 4 shows that the E–F structure (Figure 1) is a transition state connecting the C_s'(mirror image of C_s) and C_2 equilibrium geometries. This is confirmed by inspecting the reaction coordinate (148 i cm^{-1}) associated with the E–F transition state. From the E–F structure, following this reaction coordinate in one direction leads to the C_s' structure and in the other direction to the C_2 structure. The feature of the E–F structure not present in either the C_s or C_2 equilibria is the planar $\cdot CH_2CC$ arrangement. To move from the E–F structure to either the C_s or C_2 structure requires pyramidalization of the left-hand methylene in Figure 1 (center structure).

From the broadest perspective, the outstanding feature of the triplet trimethylene potential energy hypersurface is its flatness in the vicinity of the five stationary points characterized here. From the highest energy structure (E–F) to the lowest energy structure (C_2), the entire range is only 1.46 kcal. Thus, for the conditions encountered in experimental studies,[1-7] where the trimethylene would be formed with perhaps 10 kcal/mol of internal energy, the triplet has essentially free internal rotation about the two C–C bonds. In addition, pyramidalization about the two terminal carbon atoms will readily occur, making the overall internal vibration–rotation motions rather complicated indeed.

This theoretical research was carried out at a level of theory significantly higher than previously attempted for triplet trimethylene. Further, internal rotation potential energy surfaces for hydrocarbon systems are typically insensitive to the addition of polarization functions to the basis set and to the incorporation of electron correlation effects.[40] Nevertheless, our claim here is for the qualitative correctness of the predicted energy surfaces—and not to small details that might be affected by higher levels of theory.

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Registry No. $\cdot CH_2CH_2\cdot CH_2$, 32458-33-6.

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