upon the formation of the reaction complex. Thus the largest negative temperature coefficients that can be justified on the basis of the relation $n = (2 + r)/2$ for these reactions are T^{-4}, $T^{-3.5}$, and $T^{-3.5}$, respectively. On the other hand, the total numbers of internal rotors in reactions 10, 11, 14, and 18 are 8, 9, 10 and 11 (some of these may already be hindered in the neutral reactants). Temperature coefficients as as large as T^{-6}–$T^{-7.5}$ could therefore be explained for these reactions, although it may be difficult, for example, to hinder seven rotors upon the formation of the transition complex from the reactants of reaction 14. The small temperature coefficient of $T^{-1.5}$ for reaction 13 can be justified on the basis that there are no free rotors in norbornane; in fact, TST requires that $r = -1$ in this case, i.e., a new rotor has to be formed in the complex in this reaction. Indeed, a new internal rotation can be seen around the bond $(CH_3)_3C^+ \cdots H-C(C_6H_{11})$ in the reaction complex. The simple TST relation of eq 4 is therefore consistent with the temperature dependences that we observe in the present set of reactions. We note that none of the 22 reactions examined shows a temperature coefficient large enough to rule out its rationalization on the basis of TST, i.e., eq 4. This is encouraging, since some reactions were studied specifically to test for this possibility. Thus a temperature coefficient of T^{-10} in any of the open-chain reactant cases, or as high as T^{-5} in the cyclic reactants, would have required the postulation of more hindered rotors in the reaction complexes than could possibly be accounted for in these reactions.

In summary, increasing exothermicity is observed to correlate with increasing rate constant throughout the set of 22 H^- transfer reactions that we observed. We also observe a trend of increasingly large negative temperature coefficients associated with decreasing rate constants and with increasing complexity of the reactants. The latter relations are justified by TST consideration. However, the relation between exothermicities and rate constants cannot be justified by the simple TST relation of eq 4. This relation may reflect the variation of internal energy barriers with the variation of exothermicities in a Polanyi-type relationship. In turn, the effect of the variation of internal energy barriers on the rate constants can be justified by the application of unimolecular dissociation theory to the reactions of the reaction complex, along the line suggested by Farneth and Brauman.[8] We note that the application of TST and unimolecular dissociation theory concepts to slow ion–molecule reactions is not incompatible, since both the entropy of the reaction complex and internal energy barriers associated with this complex will affect the rate constant and its temperature dependence.

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Theoretical Studies of Thermal Rearrangements. Methylenecyclopropane and Barriers to Internal Rotation in Biradicals

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Abstract: The surface for the degenerate thermal rearrangement of methylenecyclopropane has been investigated by a molecular orbital method (PRDDO). Optimized geometries are presented for methylenecyclopropane and for three forms of trimethylenemethane: D_{3h} triplet, C_{2v} perpendicular singlet, and C_{2v} planar singlet. The C_{2v} perpendicular singlet is stable by 1.8 kcal/mol over the planar C_{2v} singlet state. The maximum calculated activation energy, 47.7 kcal/mol is in reasonable agreement with the experimental activation energy of 40.1 kcal/mol for a similar rearrangement. The barrier to ring closure is approximately <3.3 kcal/mol. A low-energy path was found having a barrier of 2.8 kcal/mol for permutation of the unique methylene group. The barriers to internal rotation in the singlet states of two isomeric bisallyl molecules (2,2' and 2,4) are 2.1 and 2.6 kcal/mol, respectively. These low barriers to rotation are important in explaining the racemization observed in the thermal rearrangements of optically active, substituted methylenecyclopropanes and 1,2-dimethylenecyclobutanes.

Introduction

The interaction of radical centers on the same molecule is important in understanding the potential energy surfaces for thermal rearrangements of small organic molecules. A suitably

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simple system is methylenecyclopropane. Rearrangements of substituted methylenecyclopropanes have been the focus of numerous experimental studies and some theoretical work. Ullman[1] found that some chirality was retained in the thermal rearrangement of Feist's ester, **1**. Doering and Roth[2] showed that the rearrangement of **1** proceeded with inversion of con-

Table I. Energy Comparisons[a]

Method	Singlet rotation[b]	Symmetry of planar **4**
PRDDO[b]	1.8	C_{2v}
Yarkony and Schaeffer[d] (13)	2.8	C_{2v}
	50	D_{3h}
Hehre, Salem, and Willcott[d] (12)	32	C_{2v}
	52	D_{3h}
Dewar and Wasson[d] (11)	24	$C_{2h\,base}$
Davidson and Borden[d] (15)	2.6	C_{2v}
Davis and Goddard[d] (14)	6.2	C_{2v}

Method	Initial barrier	MCP–[e] TMM- (S)	MCP–[e] TMM- (T)	Activation energy	Pivot[f] interchange
PRDDO[c]	≤3.3	44.4	27.2	≤47.7	≤2.7
Hehre, Salem, and Willcott	8	35.9	17.6	~44	24

Method	Triplet[g] rotation barrier	Triplet–singlet[h] splitting-perpendicular diradical (C_{2v})
PRDDO	15.8	1.3
Yarkony and Schaeffer	17	1.5
Dewar and Wasson	9	3
Davidson and Borden	15.7	1.2
Davis and Goddard	18.2	2

[a] All energies in kcal/mol. [b] Perpendicular geometry is more stable than planar geometry. [c] This work. [d] Reference numbers are given in parentheses. [e] MCP = methylenecyclopropane, TMM = trimethylenemethane. S = singlet, T = triplet. [f] Disrotatory motion. [g] D_{3h} planar diradical is more stable than the perpendicular diradical (C_{2v}). [h] Triplet is more stable than singlet.

figuration and proposed a pivot mechanism to account for their experimental results. Doering and Birladeanu[3] studied the thermal rearrangement of **2**, which contains smaller substit-

uents than found in **1**. They were able to exclude concerted mechanisms following either the Woodward–Hoffmann or Berson–Salem analyses as the only pathway available for the rearrangement.
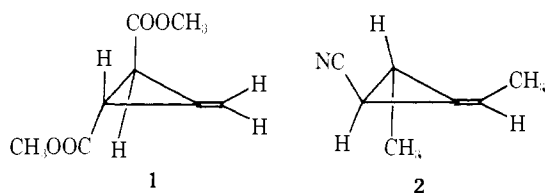
It is to be emphasized that some racemization has always been observed in these thermal rearrangements. For example, Doering and Birladeanu[4] showed extensive racemization for optically active **2**. If the rearrangement proceeds in a single step, racemization is not consistent with the pivot mechanism[2] through an orthogonal allylic transition state, **3**. Moreover,
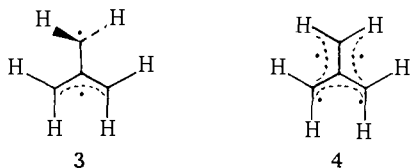

some optical activity is retained, and therefore one cannot invoke a planar symmetric D_{3h} state based on singlet trimethylenemethane (**4**) as the sole intermediate. However, a detailed computer simulation of the kinetics has been achieved using competing one- and two-step processes which allows for the

pivot mechanism.[5] In addition, Roth and Wegener[6] have found partial racemization in the methylenecyclopropane rearrangement using optically active *syn*- and *anti*-3-methyl-6-ethylidenebicyclo[3.1.0]hexane. They estimate that the orthogonal diradical is ~2.5 kcal/mol more stable than the planar radical. Other experimental results on trimethylenemethane are summarized in the review by Dowd.[7]

Trimethylenemethane has long been of interest to theoretical chemists because of its unique properties. Coulson,[8] who used trimethylenemethane in developing the concept of free valence, showed that the central carbon atom has the maximum attainable free valence index, 4.732. This molecule also played an important role in the development of the theory of zero field splittings in triplet states of organic molecules.[9] Using electron spin resonance as a detector, Dowd[10] was able to prepare and identify **4** in the triplet ground state by photolysis of **5**. Recent
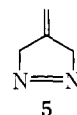

theoretical work[11-15] on trimethylenemethane has centered on the electronic properties of the triplet ground state and lowest lying singlet excited state, and on the relationship (Table I) of the singlet state to the thermal rearrangement of methylenecyclopropane **6**. In light of the experimental results, a
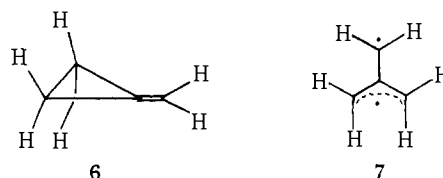

major question is the size of the energy difference between **3** and **7**, which corresponds to a rotation barrier about the C–C bond. The higher energy planar singlet diradical is best represented by **7** which results from a Jahn–Teller distortion from D_{3h} to C_{2v} symmetry. Dewar and Wasson[11] and Hehre, Salem, and Willcott[12] find a high rotation barrier while Yarkony and Schaefer,[13] Davis and Goddard,[14] and Davidson and Borden[15] find a low barrier. Borden[16] has given a qualitative discussion of this difference. Davidson and Borden[15b] have studied pseudorotation pathways for interchanging the radical center in the singlet. Geometries were partially optimized for the calculations[11,12] yielding a high rotation barrier (Table I). However, for the calculations which yield a low barrier only one group[15b] attempted partial optimization for only one geometry (C_{2v} planar).

In order to test conclusively the theoretical results and to help explain the experimental results we have performed extensive calculations on the methylenecyclopropane surface using the method of partial retention of diatomic differential overlap (PRDDO).[17] This self-consistent field (SCF) approximate method yields results comparable to minimum basis set ab initio results which use either Slater type orbitals[18] or an STO-3G basis.[19] Before describing our calculations in more detail, we outline our approach based on the experimental results of Doering and Birladeanu[4] where we assume that a single step mechanism accounts for the kinetics. Geometries were optimized for **3, 6,** and **7** and the energies were compared. In order to establish that **7** is indeed at the top of the rotational barrier, the path from **3** to **7** was examined. If the barrier to go from **3** to **7** is low, then racemization can be an important feature in the reaction. The experimental results[4] suggested that another pathway for racemization besides rotation of the symmetry-unique methylene group may be important. Thus, we studied the geometric exchange of the symmetry-unique methylene group with an allyl methylene group (**3** to **3′**). In

3   3′
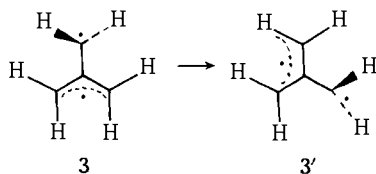
order to obtain a more complete view of the surface, the pathway from **6** to **3** was also examined in some detail. We also did calculations on some portions of the ground state triplet surface.

Barriers to rotation in other related diradicals are also important in explaining the stereochemical consequences of thermal rearrangements. We have therefore done preliminary studies on the barriers to rotation about the single bond in **8** and **9**. The relation to the work of others is as follows. The

8   9
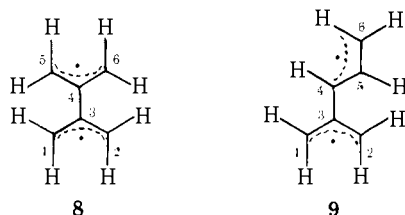
2,2′-bisallyl diradical (or tetramethyleneethane) **8** has often been invoked as the intermediate in the thermal dimerization of allene[20] **10**, and in the thermal rearrangement[21] of **11**. It has also been suggested as the possible intermediate in the thermal rearrangements of **12–15** as shown in Scheme I.

Scheme I

$$2(H_2C=C=CH_2)$$

10
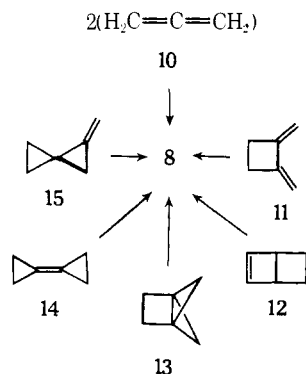
Recent experiments by Gajewski[22] on a substituted 1,2-dimethylenecyclobutane (**11**) have demonstrated that the barrier to rotation in **8** is quite likely to be low. Calculations by Gajewski[22] and by Hoffmann and co-workers[23a] have suggested low rotation barriers in the singlet state. Using the MINDO/2 method, Schoeller[23b] has investigated rotation barriers in **8** and **9** after confirming the results of Dewar and Wasson[11] on **3**. For **8**, he finds that the planar form is more stable and that the rotation barrier is ~5 kcal/mol. For **9** he finds that the perpendicular form is more stable, and that the rotation barrier is about 10 kcal/mol. However, the question of the relative energy of the isomers **8** and **9** has not yet been studied. Borden and Davidson[23c] have studied the singlet-triplet splitting in **8** at the minimum basis set level with a configuration interaction calculation spanning the π space. They find the singlet to be more stable than the triplet at this level but did not discuss any rotation barriers.

Calculations

The PRDDO method as originally described by Halgren and Lipscomb[17] was used for closed-shell states. Open-shell calculations were carried out by a modified restricted Hartree-Fock (RHF) procedure.[24] All electrons were included in a

minimum Slater basis set for which we used standard Slater exponents on carbon (1s = 5.70, 2s = 2p = 1.625) and a 1s exponent of 1.2 on hydrogen.

Some care must be exercised in performing SCF calculations on open-shell systems. Borden[16] has noted that a problem exists in Nesbet's[25] method which incorporates symmetry and equivalence restrictions in a single F matrix. This problem can lead to spurious results unless an extensive configuration interaction (CI) is included. The 3 × 3 CI employed by Hehre, Salem, and Willcott[12] is not sufficient. A similar problem exists in the treatment of the open-shell SCF equations which employ the half-electron model developed by Dewar and co-workers.[26] Our open-shell restricted Hartree-Fock (RHF) procedure is equivalent to that of Yarkony and Schaefer[13] and Davis and Goddard.[14] Variational treatment of Roothaan's[27] open-shell energy expression is carried out by a basis set partitioning, explicit rotation technique like that described by Hunt, Dunning, and Goddard.[28] This SCF procedure for open shells is somewhat more time consuming than that for closed shells because three density matrices must be solved to self-consistency, rather than one for either an open-shell singlet or a triplet state. A complete single-excitation configuration interaction of the occupied orbitals to the two single occupied open-shell orbitals was carried out to obtain corrections to the lowest singlet state. There is no single excitation configuration interaction correction for C_{2v} geometries due to symmetry restrictions. However, a small configuration interaction correction is present for geometries of lower symmetry. For the calculations on **8** and **9** we found it necessary to use GVB[29] (MCSCF) methods[24] to examine the wave functions as discussed below.

Results

Methylenecyclopropane. A complete geometry optimization of methylenecyclopropane **6** was carried out starting from coordinates from the crystal structure data for Feist's acid.[30] These optimizations are accurate to ±1 kcal/mol in the PRDDO approximation. The geometries of the orthogonal **3** and planar **7** diradicals were optimized in the open-shell singlet configuration within a constraint of C_{2v} symmetry, except for the four C–H bonds in the allylic fragment which were required to have the same bond length. The optimum geometries are given in Figure 1. Energy comparisons are shown in Table I, and the total energy and important energy differences as determined by PRDDO are presented in Table II. The geometry of the carbon skeleton of methylenecyclopropane as determined by PRDDO [$r(C=C) = 1.32$ Å, $r(C_1-C_3) = 1.49$ Å, $\angle C_1-C_3-C_2 = 62°$] is very close to the experimental result [$r(C=C) = 1.32$ Å, $r(C_1-C_3) = 1.69$ Å, $\angle C_1-C_3-C_2 = 62°$] while the C–H bond lengths, 1.09 Å, are close to known C–H bond lengths, between 1.08 and 1.10 Å. The STO-3G geometry of Hehre, Salem, and Willcott[12] has dimensions $r(C=C) = 1.30$ Å, $r(C_1-C_3) = 1.47$ Å, and $\angle C_1-C_3-C_2 = 62°$. The geometries of the orthogonal diradical **3** as determined by STO-3G[12] [$r(C_3-C_4) = 1.52$ Å, $r(C_1-C_3) = 1.37$ Å, and $\angle C_1-C_3-C_2 = 122°$] is very similar to that found by PRDDO [$r(C_3-C_4) = 1.51$ Å, $r(C_1-C_3) = 1.41$ Å, and $\angle C_1-C_3-C_2 = 120°$]. The PRDDO results also show that very little change in bond distance and CCC angle takes place on rotating from the perpendicular **3** to the planar C_{2v} diradical **7**; the C–C single bond is slightly longer and the C–C bonds in the allylic moiety are slightly contracted in the planar C_{2v} diradical. The results of the partial optimization of **7** carried out by Davidson and Borden[15b] [$r(C_3-C_4) = 1.54$ Å, $r(C_1-C_3) = 1.40$ Å for $\angle C_1-C_3-C_2$ set at 120°] are in reasonable agreement with our more fully optimized results. Our geometry optimization shows that the singlet diradical in both planar and perpendicular forms is best represented as an allyl fragment in which the
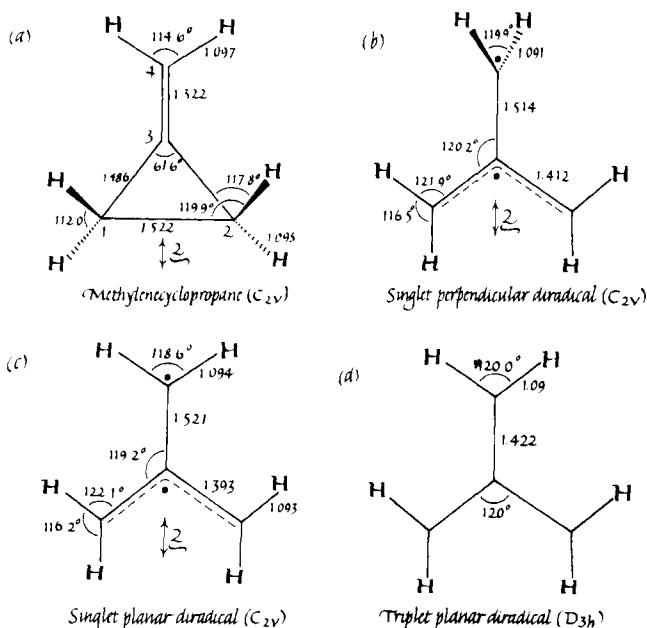
Figure 1. PRDDO optimized geometries. The numbering is given in a. Bond distances are given in Å and bond angles in degrees. The positions of the twofold axes are shown. Hydrogen atoms above the plane are denoted by heavy lines while hydrogen atoms below the plane are denoted by dashed lines. (a) Methylenecyclopropane **6**; (b) singlet perpendicular C_{2v} diradical **3**; (c) singlet planar C_{2v} diradical **7**; and (d) triplet planar D_{3h} diradical.

symmetry unique methylene group is joined by a C–C single bond to the central carbon of the allylic radical.

The energy difference between **3** and **6** is found to be 44.4 kcal/mol, in good agreement with the activation energy, 40.4 kcal/mol, found by Chesick[31] for the rearrangement
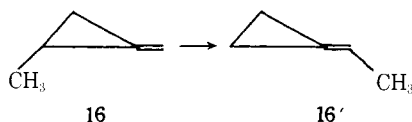
We have also calculated the energy difference between **3** and **6** starting from a generalized valence bond[25] wave function and using a 4 × 4 configuration interaction (CI) incorporating all single and double excitations. This corresponds to a CI in the π space for **3** while for **6** the CI includes the π and π^* orbitals and the σ and σ^* orbitals between C_1 and C_2. We find that the perpendicular diradical **3** becomes slightly more stable with respect to methylenecyclopropane **6**; the energy difference decreases to 41.4 kcal/mol. These calculated values are energy differences, not activation energies. Also, zero-point vibration effects have been neglected.

The energy difference between **3** and **7** is very low, 1.8 kcal/mol, in the sense that the perpendicular diradical **3** is the more stable form. This low energy barrier is consistent with the negligible change in geometry in going from **3** to **7**. In order to test for a rotational barrier between **3** and **7**, the path for rotation from **3** to **7** was examined for every 15°, starting from both the planar *and* orthogonal optimal geometries. No additional barrier was found. This barrier of 1.8 kcal/mol to rotation is remarkably similar to the barrier of 2.5 kcal/mol obtained experimentally by Roth and Wegener.[6]

The pathway for pivot interchange (**3** to **3′**) was calculated using the synchronous transit approach developed by Halgren and Lipscomb.[32] We connected **3** and **3′** by a disrotatory linear synchronous transit (LST) path, because less steric interaction is present for this path. The barrier to pivot interchange was found to be 3.3 kcal/mol. Here, the structure of maximum energy occurred at 0.50 on the LST path, corresponding to

Table II. PRDDO Energies

A. Singlet Surface

Species	Energy[a]
(1) Methylenecyclopropane (**6**)	−43.9
(2) **3** perpendicular C_{2v}	0.5
(3) **7** planar C_{2v}	2.3
(4) **7** planar $\sim D_{3h}$	11.3[b]
(5) Pivot interchange TS	3.8 (3.3)[c]
(6) 1st point 0.20[d]	−35.8
(7) 1st point 0.45[d]	−10.8
(8) 1st point 0.60[d]	1.1
(9) 1st point 0.75[d]	3.8
(10) 1st point 0.90[d]	0.5

B. Singlet Energy Differences

Difference[e]	Δ energy[f]
2 − 1	44.4[g]
3 − 2	1.8
5 − 2	2.8[h]
9 − 2	3.3

C. Triplet Surface

Species	Energy[a]
D_{3h}	−16.7
C_{2v} perpendicular	−0.6
C_{2v} planar[i]	−12.0

[a] Energies in kcal/mol. Total energy is given by $E_{(total)} = -97\,000$ + energy. [b] Planar C_{2v} singlet with near D_{3h} geometry of optimum triplet. [c] Optimization of 1 mode gives the value in parentheses. [d] The 1st path is defined between 0.0 and 1.0 with 1st point 0.0 being **6** and 1st point 1.0 being **3**. [e] Energy difference between A − B where the numbers correspond to the order given in part a. [f] Energy differences in kcal/mol. [g] A calculation of this difference using GVB + 4 × 4 CI gives 41.4 kcal/mol. [h] Calculated using partially optimized energy. [i] Energy of planar C_{2v} triplet using perpendicular C_{2v} triplet geometry.

rotation of both groups by 45°. After constraining the geometry to remain at the point 0.50 on the LST path, we found that the C–C bonds connecting the interchanging pivot carbons to the central carbon lengthened slightly upon optimization, thereby lowering the barrier to 2.8 kcal/mol (Figure 2a).

An LST path from methylenecyclopropane **6** to the perpendicular diradical **3** yielded, at point 0.75 on this path, an energy of 3.3 kcal/mol above the energy of **3** (Table II). The unoptimized geometries for this point, and for point 0.60 on the LST path (slightly higher in energy than **3**), are shown in Figures 2b and 2c. The major increase (42.7 kcal/mol) in energy in going from **6** to **3** occurs between 0.20 and 0.60 on the LST path (Table II). Geometry optimization at 0.75 on this LST pathway would be desirable, but at present is prohibitively expensive. It is possible that optimization would eliminate any barrier between **6** and **3**. The activation energy, excluding zero-point vibration effects, must be less than 47.7 kcal/mol even if a small barrier is included.

Energy comparisons for our partial study of the triplet surface are presented in Table I, and total energies are given in Table II. We find that the singlet–triplet splitting for the perpendicular diradical at the optimum singlet geometry is 1 kcal/mol. Geometry optimization of the C–C bonds in the perpendicular triplet diradical showed that both the C–C single bond (1.50 Å) and C–C allyl bonds (1.40 Å) are slightly shorter in the triplet state, but this optimization only increased the stability of this state by 0.3 kcal/mol. For the planar D_{3h} geometry, the C–C bond was optimized using r(C–H) = 1.09 Å and all angles at 120°. This optimized C–C distance of 1.422 Å (see Figure 1d) can be compared to a value of 1.437 Å found for $C(CH_2)_3$–$Fe(CO)_3$[33] and a value of 1.429 Å obtained by

Davidson and Borden. The optimized distance is similar to that employed by Yarkony and Schaefer[13] (1.43 Å) but somewhat longer than the distance of 1.40 Å employed by Davis and Goddard[14] in their calculations. The D_{3h} triplet is 15.8 kcal/mol more stable than the perpendicular diradical triplet, and is 27.2 kcal/mol less stable than methylenecyclopropane. The singlet–triplet splitting at the optimum planar singlet (C_{2v}) geometry is 14.3 kcal/mol in the sense that the triplet is more stable. Also this C_{2v} planar triplet is only 4 kcal/mol less stable than the D_{3h} triplet.

We have summarized various energy quantities of interest in Table 1 in order to compare our results with the previous calculations. All workers[11-15] find that the perpendicular diradical **3** is the most stable singlet geometry above methylenecyclopropane **6**. However, Dewar and Wasson[11] and Hehre, Salem, and Willcott[12] find high barriers for rotation from **3** to the planar C_{2v} diradical **7** while PRDDO, Yarkony and Schaefer,[13] and Davis and Goddard[14] find low barriers to rotation. The error in the work of Dewar and Wasson[11] and Hehre, Salem, and Willcott[12] is their incorrect handling of the open-shell singlet wave function for the planar C_{2v} geometry.[16]

In addition, we find that geometry optimization is important in significantly lowering the rotation barrier. In Davis and Goddard's[14] work the barrier is too high owing to a poor choice of geometries. Yarkony and Schaefer[13] used a longer C–C bond and consequently found a lower rotation barrier. The barrier obtained by Davidson and Borden[15b] (2.6 kcal/mol) is somewhat higher than our calculated barrier, probably owing to the difference between optimized and partically optimized geometries. We also find that if the D_{3h} singlet wave function for the planar geometry is employed, the barrier to rotation is too large (50 kcal/mol) no matter which open-shell procedure is employed.[13]

All methods give a comparable low value to the singlet–triplet splitting at the perpendicular diradical geometry in the sense that the triplet lies lower by 1–2 kcal/mol. The PRDDO and ab initio results[12-15] all give high splittings of 16–18 kcal/mol as the D_{3h} planar radical goes to the perpendicular C_{2v} diradical in the triplet state. The MINDO calculations of Dewar and Wasson[11] give too low a splitting (9 kcal/mol).

We now compare other features of the surface with the work presented by Hehre, Salem, and Willcott,[12] who find the perpendicular diradical to be more stable with respect to methylenecyclopropane than we do. However, Hehre, Salem, and Willcott[12] find a large approach barrier of 8 kcal/mol owing to their choice of the reaction path while a more nearly optimal reaction path generated by the LST approach shows a much lower approach barrier, possibly zero, but no more than 3.3 kcal/mol. This again demonstrates the virtue of choosing a reaction path by an approach such as the synchronous transit method rather than an approach based on a reaction coordinate method.[32] The other major difference in the two studies is the barrier found for the disrotatory pivot interchange process where PRDDO yields a barrier <2.8 kcal/mol while the barrier found by Hehre, Salem, and Willcott[12] is 24 kcal/mol. Their barrier for this exchange is also too high owing to the incorrect handling of the open-shell wave function at the symmetric intermediate geometry.[16]

Bisallyl Molecules 8 and 9. The geometry of the allyl fragments of **8** was assumed to be like the allyl fragment in **3** while the two allyl radicals were connected by a C–C single bond of length 1.52 Å. We used the same framework geometry for both the planar and perpendicular forms. The allyl fragment $C_1-C_3-C_2$ in **9** was taken from **3**, while the geometry of the allyl fragment $C_4-C_5-C_6$ in **9** was chosen as an idealized allyl radical with $r(C-C) = 1.39$ Å, $r(C-H) = 1.09$ Å, and all angles at 120°. A distance of 1.52 Å was assigned to the C–C single bond, and, as before, the same framework geometry was
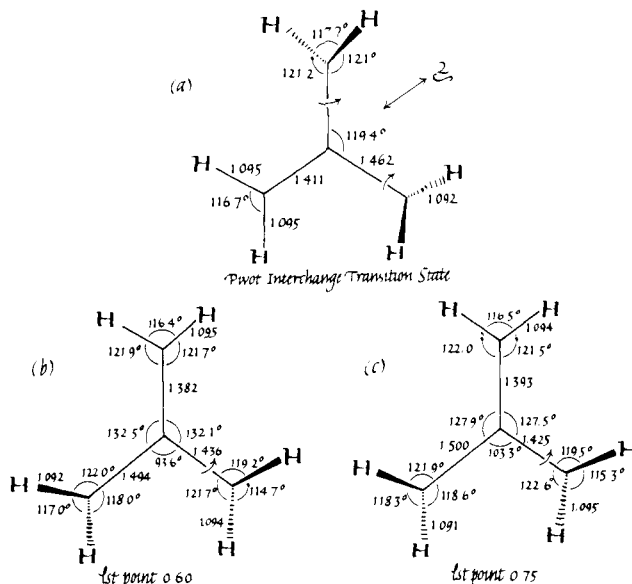

Figure 2. PRDDO unoptimized lst geometries. See Figure 1. The sense of rotation about C–C bonds is shown by arrows. (a) 0.50 on pivot interchange (3 → 3′) path (45° rotation about the C–C bonds). (b) 0.60 on lst path from **6** to **3**. (c) 0.75 on lst path from **6** to **3**. In (b) and (c) the significant rotation is about the C2–C3 bond, while the hydrogens at C1 remain in a plane perpendicular to that of the carbons throughout the reaction.

employed for both the planar and perpendicular forms. These geometries are appropriate for the open-shell singlet states of these molecules. Probably, the geometry of **8** is more accurate than that assumed for **9**.

Energies for both forms of **8** and **9** were calculated using GVB (MCSCF) techniques, rather than by ordinary RHF open-shell methods which give less accurate energies. When the two nonbonding orbitals of the allyl radicals which are singly occupied are coupled, we find the following molecular orbitals for the planar geometry
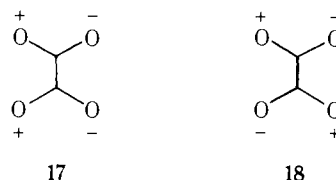
In the RHF wave function we place one electron in each orbital and then take the appropriate (negative) linear combination. Because each molecular orbital has density on the same atoms, these two electrons interact strongly giving rise to a large destabilizing exchange (K) integral. A more appropriate description is obtained by localizing the two electrons in two different allyl nonbonding orbitals, because this procedure significantly reduces their interaction. This reduction of the interaction energy is well treated by a GVB or MCSCF treatment which is equivalent to using both $\psi(17 + 18)$ and $\psi(17 - 18)$ in the molecular wave function.

The energies of **8** and **9** are given in Table III. The singlet ground state of **8** corresponds to the perpendicular form, described simply by the wave function


The planar form is less stable by 2.1 kcal/mol, a result which is similar to that found for trimethylenemethane. On the other

Table III. Bisallyl Energies[a]

Species	Planar	Perpendicular	Rotation barrier
8	−0.9	−3.0	2.1
9	−5.6	−3.0	2.6
2 allene[b]	36.5		

[a] Energies in kcal/mol. Total energy is given by E(total) = −145 170 + energy. [b] Energy of 2 allene molecules.

hand, the wave function for **9** is somewhat more complicated. For the perpendicular form a qualitative description is shown in **20**, while for the planar form the description shown in **21** is that described by bond overlap populations.[34] The description given in **21** shows a diradical where the excess spin corresponding to the open-shell electrons is localized on two carbon atoms. In contrast to the results found for **3** and **8**, the more stable form of **9** is probably the planar geometry, not the perpendicular form. However, the rotation barrier is low, only 2.6 kcal/mol. Because the geometries for these states (**20** and **21**)

20   **21**
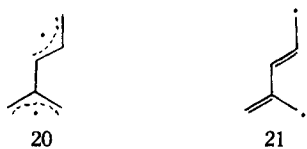
are unoptimized, we are not certain that the planar form is more stable. At least, the results show that the rotation barrier is small. In his MINDO/2 studies, Schoeller[23b] found significantly higher barriers, and found preferred states for **8** and **9** opposite to those found by us. As discussed above, we think that these differences are most probably due to the inability of the half-electron method employed MINDO/2 to handle properly these open-shell configurations.

Comparison of the most stable forms of **8** and **9** shows that planar **9** is slightly more stable than perpendicular **8** by 2.6 kcal/mol. We therefore suggest that rearrangements having geometric access to either **8** or **9** may be complicated, proceeding through competing intermediates. Gajewski has previously noted that ΔH_f for **8** is below that of two allene molecules (**10**). Our new estimate of ΔH_f of **8** indicates that **8** is 14 kcal/mol more stable than two allenes, assuming no stabilizing interactions between the two allyl moieties.[35] As a qualitative check of our energy surface, we also have calculated the energy of allene, and find that two allenes are 40 kcal less stable than **8**. This calculation probably overestimates this difference because **8** is more accurately treated at the GVB level than is the closed-shell species, allene, at the SCF level. However, the qualitative trend demonstrates the marked stability of the biallyl radicals **8** and **9**. Therefore, it is unlikely that **8** (or **9**) is merely a transition state for the reactions shown in Scheme I, but rather is a true intermediate.

Discussion

The calculations demonstrate that the lowest lying singlet state of trimethylenemethane is very floppy as seen in the low rotation barrier in going from **8** to **7** and the low barrier to pivot interchange, **3** to **3′**. Further evidence is provided by the geometries at 0.60 and 0.75 of the LST path from methylenecyclopropane **6** to the perpendicular diradical **3**. These geometries are quite distorted, but their energies are still comparable to the energy of the perpendicular diradical **3**. Davidson and Borden[15b] have examined a pseudorotation process which permutes the pivot atom in the planar form of the singlet. The pivot interchange mechanism involving twisted methylene groups also permutes the pivot atom. Both processes occur with very low barriers further demonstrating the flat surface present in this molecule.

The optimum singlet C_{2v} geometries for both planar and

perperdicular diradicals are best represented as an allyl fragment plus a lone pair p orbital on the symmetry-unique methylene group. Thus, the experimental result of large amounts of racemization with sterically small substituents can be explained in a single-step mechanism by the low rotation barrier of the symmetry-unique methylene group. Methylenecyclopropane opens to the perpendicular diradical, the unique methylene group can rotate, and then reclosure of the C–C bond occurs akin to the continuous diradical proposed for the cyclopropane rearrangement.[36] There is no need to invoke a crossing to the triplet surface. The more complicated series of electronic rearrangements involved in this crossing is as follows. The perpendicular diradical crosses to the triplet surface, then rotates to the planar form, and can now drop into a significant well even at the C_{2v} geometry. This diradical must then climb back up the well to the perpendicular form at the singlet–triplet seam, cross to the singlet, and reclose. This process is probably especially difficult in solution, where energy transfer is fast. Here, trapping of the triplet would be expected. Buchwalter[37] did not observe any trapping of the triplet by oxygen for the thermal rearrangement of **22**. Although our

22
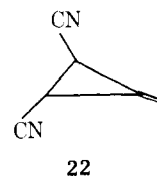
results predict that racemization should be an important process, we cannot predict quantitative values for the amount of optical activity retained, because we have ignored dynamical effects that can only be accounted for by trajectory studies. Moreover, the experimental energies are not defined narrowly enough for us to estimate the importance of the rotational barrier on the experimental results.

The rotational barriers in **8** and **9** are also very small ($\lesssim 2.6$ kcal/mol), and provide further evidence for low barriers to rotation about the single bond connected to the central carbon of an allyl fragment. These low barriers are independent of the preferred ground state geometry (planar or perpendicular) and the amount of spin density which has been formally varied from 1.0 (**3**) to 0.5 (**9**) to 0.0 (**8**). The low barrier to rotation in **8** is consistent with the racemization observed by Gajewski[22] in the pyrolysis of optically active *trans*-3,4-dimethyl-1,2-dimethylenecyclobutane. The low barrier to racemization in **9** has been invoked to explain results found in the thermal rearrangements of allylidenecyclopropane.[38]

The LST path for the rearrangement of methylenecyclopropane shows a very small barrier, which may well be zero. This barrier is equivalent to a barrier to ring closure ≥ 3.3 kcal/mol in going from **3** to **6**. Gajewski's thermodynamic arguments,[21] which are partially substantiated by our calculation of the stability of **8** with respect to two allenes, suggest to us that the barrier to ring closure for systems involving **8** as an intermediate is much higher than that found in going from **3** to **6**. Theoretical studies of the reactions shown in Scheme I are being undertaken in order to examine the question of the height of the barrier to ring closure and the possibility of **8** and **9** as competing intermediates.

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Localized Molecular Orbitals for N_2O_2, N_2O_3, and N_2O_4

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Abstract: Localized molecular orbitals, LMO's, are derived from the MO's calculated by a CNDO method for N_2O_4, N_2O_2, and N_2O_3. The theoretical Lewis structures are given. The molecules have σ-type nitrogen–nitrogen bonds of high p-orbital character, but no π bonds; oxygen lone pair delocalization to both nitrogen atoms is antibonding, reducing the strength of the nitrogen–nitrogen bond. The present results from a semiempirical CNDO method are in good agreement with those from previous ab initio studies using canonical MO's.

Introduction

The nitrogen oxides, N_2O_2, N_2O_3, and N_2O_4 have many peculiar features: very long, weak N–N bonds, 2.18, 1.864, and 1.782 Å, with heats of dissociation 2.7,[1] 9.5,[2] and 12.7[3] kcal mol^{-1}; a typical N–N single bond length is 1.47 Å (hydrazine), with heat of dissociation[4] 71 kcal mol^{-1}. The molecules are planar although the O–O repulsions are a maximum for this configuration. The barrier to internal rotation about N–N is higher than would be expected for such long bonds, being 2.9 kcal mol^{-1} for N_2O_4.[3] The dinitrogen oxides are diamagnetic, whereas the building units, NO_2 and NO, are paramagnetic. The ONO bond angles in N_2O_3 and N_2O_4 are unusually large, being 129.8 and 135.4°. The nitroso NNO angles in N_2O_2, 101.3°, and N_2O_3, 105.1°, are smaller than in other NO compounds: in the nitrosyl halides, the NO halide angle ranges between 110 and 116°.

Bonding between linked groups with identical formal charges is unfavorable but occurs in N_2O_2 and in the most stable form of N_2O_4, which has three different rotational and

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structural isomers.[5,6] At liquid nitrogen temperatures, a twisted O_2NNO_2 form can be trapped in an inert matrix, while at approximately 4 °K the $ONONO_2$ isomer also exists. Similarly, N_2O_3 has two forms, the unstable ONONO isomer and the more stable $ONNO_2$ isomer.[7]

There have been many attempts to explain the geometry and electronic structures of these oxides, mainly for N_2O_4: Chalvet and Daudel[8] favored a N–N σ bond with partial π character, giving a total N–N bond order of 1.164 in N_2O_4. Smith and Hedberg[9] described the N–N bond as π only. Coulson and Duchesne[10] suggested a π-bond model with the σ and σ^* levels both occupied, to give a net π bond order of 0.3. McEwan[11] superposed the separate NO_2 and charge-transfer structures. Green and Linnett,[12] by an extended Hückel calculation, concluded that the N–N bond was mainly σ, with additional π-bond stabilization. Bent[13] favored a "splayed single bond" for the central bond in N_2O_4. Brown and Harcourt[14] used the variable electronegativity SCF–MO method to suggest a σ + π model, in which the lone pair oxygen electrons delocalize into the σ^* N–N orbital. Redmond and Wayland,[15] by extended Hückel theory, proposed that the barrier to internal rotation