

by Walters and Spiro.¹² The LMCT absorptions for $(\text{CN})_5\text{Fe}(\text{imH})^{2-}$ have molar absorptivities on the order of ~ 1000 and ~ 300 for the short- and long-wavelength absorption bands, respectively. These are particularly low for charge-transfer transitions but are characteristic for the $(\text{CN})_5\text{Fe}(\text{imH})^{2-}$ complexes. In heme proteins the vibrational enhancement due to the heme $\pi^* \leftarrow \pi$ transitions is likely to mask the imidazole ring modes even if those modes was resonantly enhanced by an Fe-histidine charge-transfer band.

Resonance Raman data confirm the previous assignments of the 403- and 475-nm electronic absorptions as deriving from LMCT transitions involving the carbon and nitrogen-based π -imidazole orbitals to the iron. The excitation profile patterns can be used to examine which imidazole π orbitals are involved in particular LMCT transitions. The imidazole charge-transfer excited states of $(\text{CN})_5\text{Fe}(\text{imH})^{2-}$ involve the CN ligands as evidenced by both the excitation profile of the 2132-cm^{-1} $\text{C}\equiv\text{N}$ stretch and the spectral behavior of the Fe—C stretching and Fe—(C \equiv N) bending modes. The data also support the assignment of the electronic absorption band at 356 nm as a LMCT transition from the CN ligands to the iron.

Enhancement of the Fe—N(imH) stretching vibration is weak. Although the frequencies of the imidazole vibrations are sensitive to protonation of the pyrrole nitrogen (and presumably the hydrogen bonding at this nitrogen), new environmental information from the imidazole vibrations in the heme proteins is, unfortunately, not likely to derive from Raman studies which excite in the LMCT transitions which involve the two HOMO's of the imidazole ring of the proximal histidine. The Raman intensities are much too weak. However, it is possible that higher energy LMCT transitions will give much larger Raman enhancements.

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Registry No. $(\text{CN})_5\text{Fe}(\text{imH})^{2-}$, 61332-60-3; $(\text{NH}_3)_3\text{Ru}(\text{imH})^{3+}$, 80593-52-8; histidine, 71-00-1.

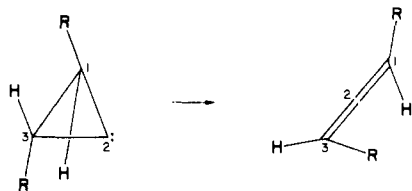
Isomerization of Cyclopropylidene to Allene

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Abstract: The isomerization of cyclopropylidene to allene has been investigated by ab initio methods. Analytical gradient techniques are used to locate stationary structures on the reaction potential hypersurface, and vibrational frequency analysis is used to characterize the structures as minima or saddle points as well as to provide an estimate of the zero-point corrections to the adiabatic surface. On the singlet potential energy surface, rearrangement of cyclopropylidene to allene involves a barrier of 48 kJ mol^{-1} . The transition structure is asymmetric with a CCC bond angle of 96° and asymmetrically disrotated methylene groups. The overall reaction is exoergic by 270 kJ mol^{-1} . The results are consistent with experimental observations for substituted, chiral cyclopropylidenes. The previously postulated bent-planar open-shell singlet structure is confirmed as the transition structure for internal rotation in allene. The calculated barrier for this process is 201 kJ mol^{-1} . The isomerization of triplet cyclopropylidene to triplet allene is hindered by a barrier of 99 kJ mol^{-1} . The transition structure is a nonrotated structure with unequal C—C bond lengths and a plane of symmetry. The reaction on the triplet potential surface is exoergic by 105 kJ mol^{-1} .

The ring opening of cyclopropylidenes (or the corresponding carbenoids) to yield allenes was first reported by Doering² in 1958 and has been extensively exploited as a convenient route to the preparation of cyclic^{3,4} and acyclic⁵⁻⁷ optically active allenes. The retention of optical activity negates the possibility that planar (and therefore achiral) structures are involved in the conversion. The reaction proceeds with a high degree of stereospecificity in the case of anti-substituted cyclopropylidenes, and the configuration of the product allene is that expected if the reaction proceeds via



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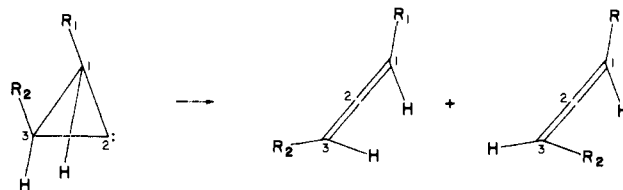
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a conrotatory motion under steric control.^{5,6} Although a sum of 90° is required for the rotations of the two terminal groups in order that the final configuration be achieved, the two groups need not, and in an asymmetric molecule will not, rotate by the same amount. The "conrotatory" mechanism merges with a "nonrotatory" mechanism in the extreme case where only one of the two groups rotates. In syn-disubstituted cyclopropylidenes, neither direction of conrotatory motion is favored by steric factors. However, resolved syn-substituted cyclopropylidenes also yield optically active allenes. In this case, the degree of stereoselectivity



appears to be much lower.⁷ Borden⁸ has suggested that a monorotatory mechanism under electronic control may be operating. Other initial motions of the nuclei may also be envisaged, for example, corresponding to disrotatory or nonrotatory ring opening. These also are compatible with the results of stereochemical

(8) Related in ref 7.

Table I. Calculated Total Energies (hartrees) and Zero-Point Vibrational Energies (ZPVE, kJ mol⁻¹) of Structures Optimized with the 3-21G Basis Set

	structure		3-21G	6-31G	6-31G**	MP2/6-31G	MP3/6-31G	ZPVE ^a
1	¹ A ₁	C _{2v}	-115.10360	-115.71023	-115.77311	-115.95177	-115.97797	151.6
2	¹ A ₁	D _{2d}	-115.21991	-115.82134	-115.86849	-116.08025	-116.10107	157.2
3	³ B ₁	C _{2v}	-115.11324	-115.71895	-115.77632	-115.94663	-115.97030	156.9
4	¹ B ₁ ^b	C _{2v}	-115.07302	-115.67866	-115.74170	-115.91390	-115.93925	153.3
5	¹ A ₂	C _{2v}	-115.19180	-115.79719	-115.84062	-115.99957	-116.02462	141.8 ^c
6	³ A ₂	C _{2v}	-115.17112	-115.77618	-115.82321	-115.99221	-116.01739	147.4
7	¹ A ₁	C _s	-115.07666	-115.68257	-115.74676	-115.94427	-115.96306	148.0 ^c
8	¹ A ₁	C _{2v}	-115.07776	-115.68382	-115.74336	-115.94406	-115.96120	146.9 ^c
9	¹ A _g	D _{2h}	-115.10287	-115.70801	-115.75678	-115.95886	-115.97586	149.3 ^d
12	³ A _u	D _{2h}	-115.15848	-115.76348	-115.81029	-115.98129	-116.00660	142.6 ^c
13	³ A ₁	C _s	-115.14252	-115.74755	-115.79455	-115.95469	-115.98072	141.3 ^c
14	³ A ₁ ^e	C _s	-115.08893	-115.69247	-115.74600	-115.90707	-115.93253	143.3 ^c

^a Calculated at the 3-21G level. ^b Single determinantal wave function (ref 23). ^c One imaginary frequency. ^d Internally unstable (ref 24). The Hessian matrix was determined numerically.

investigations provided that planar structures are not involved along the reaction pathway.

The singlet cyclopropylidene–allene surface has been the subject of several theoretical investigations.^{9–11} Using the semiempirical MINDO/2 method, Dewar and co-workers⁹ concluded that cyclopropylidene opens in a nonrotatory fashion with an activation energy of 58.2 kJ mol⁻¹. The rotation of the groups into the allene configuration does not occur until after the nonrotated transition structure has been passed but before the carbon skeleton becomes linear. Dillon and Underwood,¹⁰ using the INDO method and the SIMPLEX algorithm, found that the ring opens initially by a disrotatory motion but that motion of one of the methylene groups is reversed until an unsymmetrical transition structure with the C₁C₂C₃ angle near 96° is achieved. From the transition structure, the reaction proceeds via a conrotatory motion. The barrier hindering the ring opening was calculated to be 302 kJ mol⁻¹. In the only reported ab initio investigation of the reaction, Pasto and co-workers¹¹ proposed a third and quite similar mechanism. They found that the reaction proceeds initially in a disrotatory fashion almost to the transition structure near which there occurs a rapid transition from the disrotatory structure to a distorted monorotated structure. The sudden change occurs between the C₁C₂C₃ bond angles of 90° and 100°. The reaction finishes by nonrotatory conversion of the 100° structure to allene. The transition structure was found to lie between 90° and 94.5°. Calculations at the 4-31G level on structures optimized at the STO-3G level yielded a barrier of about 76 kJ mol⁻¹ and an exoergicity of about 310 kJ mol⁻¹ for the reaction.

The conversion of triplet cyclopropylidene to triplet allene has also been investigated by Dillon and Underwood¹⁰ as well as by Pasto and co-workers.¹¹ Both groups have concluded that the ring opening occurs initially by a nonrotatory rupture of the C₁C₃ bond until the transition structure is approached at a C₁C₂C₃ angle of about 105°¹⁰ or 90°.¹¹ In both studies, disrotatory motion commences near 90° and is essentially complete (in relation to the final planar product) at 105°. In both studies, a plane of symmetry was preserved throughout the course of the reaction although it is not clear whether unsymmetrical structures were examined in the ab initio study.¹¹ The reaction was found¹¹ to be exoergic by 155 kJ mol⁻¹ and to have an activation energy of 80 kJ mol⁻¹.

We report below the results of a reexamination of the key features of the reaction potential surface connecting cyclopropylidene (1) and allene (2) at levels of theory significantly higher than those used previously, with the aim of resolving the discrepancies which exist in the previous investigations. Analytical gradient techniques are used to locate stationary points on the potential hypersurface which have been rigorously characterized through vibrational analysis.

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Method and Results

Ab initio molecular orbital calculations have been carried out with modified^{13,14} versions of the GAUSSIAN 80¹⁵ and GAUSSIAN 82¹⁶ systems of programs. Geometries of equilibrium structures and transition structures have been determined at the Hartree–Fock (HF) level with analytical gradient procedures and the split-valence 3-21G¹⁷ basis set. Improved estimates for relative energies were obtained by recalculation of the 3-21G structures at the 6-31G^{18,19} and 6-31G**^{18,19} levels, estimation of the correlation energy changes by Møller–Plesset perturbation theory truncated to third order (MP3),²⁰ and use of the additivity relationship²¹

$$\Delta E(\text{MP3}/6\text{-}31\text{G}^{**}) = \Delta E(\text{MP3}/6\text{-}31\text{G}) + \Delta E(\text{HF}/6\text{-}31\text{G}^{**}) - \Delta E(\text{HF}/6\text{-}31\text{G}) \quad (1)$$

Equation 1 assumes the additivity of the effects of electron correlation and basis set enhancement and has been found to provide a useful approximation when full correlated calculations with large basis sets are not feasible.

Vibrational frequencies were determined, firstly to characterize stationary points as minima or saddle points and secondly to evaluate zero point corrections to relative energies. For the latter purpose, the frequencies were scaled by 0.9 to account for their overestimation at this level of theory.²² The structures of all species obtained in this manner are shown in Figure 1. The total energies are given in Table I, and the relative energies are given in Table II.

Parts of the potential surface were reinvestigated at the 6-31G*^{18,19} level. The 6-31G* stationary structures thus obtained are given in Figure 2. In this part of the study, correlation energy changes were estimated in a manner similar to the above by the additivity relationship²¹

$$\Delta E(\text{MP3}/6\text{-}31\text{G}^{**}) = \Delta E(\text{MP3}/6\text{-}31\text{G}^*) + \Delta E(\text{HF}/6\text{-}31\text{G}^{**}) - \Delta E(\text{HF}/6\text{-}31\text{G}^*) \quad (2)$$

The total and relative energies are presented in Tables III and IV, respectively.

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(23) The single determinantal wave function is approximately a 1:1 mixture of singlet and triplet states. The geometry of such a wave function should more closely resemble the corresponding singlet than would that of the pure triplet. The energy of the singlet state may be obtained approximately by adding the value of the exchange integral (see Table II).

Table II. Calculated Relative Energies (kJ mol⁻¹) of Structures Optimized with the 3-21G Basis Set

structure	3-21G	6-31G	6-31G**	MP2/6-31G	MP3/6-31G	MP3/6-31G*** ^a	MP3/6-31G*** ^b	exptl
1	¹ A ₁	305	292	251	337	323	282	277
2	¹ A ₁	0	0	0	0	0	0	0
3	³ B ₁	280	269	242	351	343	316	316
4	¹ B ₁ ^c	444	433	391	495	483	441	438
5	¹ A ₂ ^c	78	67	77	216	205	215	210 ^d
6	³ A ₂	128	119	119	231	220	220	211
7	¹ A ₁ ^e	376	364	320	357	362	318	310
8	¹ A ₁	373	361	329	358	367	335	326
9	¹ A _g	307	298	293	319	329	324	317
12	³ A _u	161	152	153	260	248	249	236
13	³ A ₁ ^e	203	194	194	330	316	316	302
14	³ A ₁ ^e	344	338	322	455	443	427	415

^a Estimated with eq 1. ^b Includes ZPVE. ^c Includes the exchange integral (ref 23). **4**: $K_{2b_1,6a_1} = 58$ kJ mol⁻¹. **5**: $K_{6a_1,1a_2} = 4$ kJ mol⁻¹. ^d Estimated from racemization studies of 1,3-dialkylallenes (ref 25 and 26).

Table III. Calculated Total Energies (hartrees) and ZPVE's (kJ mol⁻¹) of Structures Optimized with the 6-31G* Basis Set

structure	6-31G*	6-31G**	MP2/6-31G*	MP3/6-31G*	ZPVE ^a	
1	¹ A ₁ , C _{2v}	-115.76732	-115.77445	-116.12337	-116.15386	152.4
2	¹ A ₁ , D _{2d}	-115.86110	-115.86855	-116.23307	-116.25762	156.1
8	¹ A ₁ , C _{2v}	-115.73741	-115.74398	-116.10720	-116.12933	147.7 ^b
9	¹ A _g , D _{2h}	-115.74795	-115.75688	-116.11571	-116.13860	147.8 ^{c,d}
10	¹ A, C ₁	-115.73999	-115.74676	-116.11232	-116.13533	150.8 ^c

^a Calculated at the 6-31G* level. ^b Two imaginary frequencies. ^c One imaginary frequency. ^d Internally unstable (ref 24). The Hessian matrix was determined numerically.

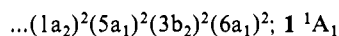
Table IV. Calculated Relative Energies (kJ mol⁻¹) of Structures Optimized with the 6-31G* Basis Set

structure	6-31G*	6-31G**	MP2/6-31G*	MP3/6-31G*	MP3/6-31G*** ^a	MP3/6-31G*** ^b	
1	¹ A ₁	246	247	288	272	273	270
2	¹ A ₁	0	0	0	0	0	0
8	¹ A ₁	325	327	331	337	339	331
9	¹ A _g	297	293	308	313	309	302
10	¹ A	318	320	317	321	323	318

^a Estimated from eq 2. ^b Includes ZPVE.

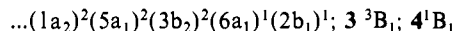
Discussion

Cyclopropylidene (1). The lowest electronic state of **1** has the configuration



Except for the bond lengths, the geometry determined at the 6-31G* level is similar to that obtained at the 3-21G and STO-3G levels.²⁷ The best estimate for the energy of **1** places it 270 kJ mol⁻¹ above allene **2**.

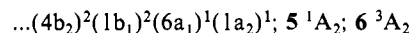
The lowest excited states of **1** is a triplet state **3**. The lowest excited singlet state, **4**, has the same configuration as **3**



and is calculated to lie 161 kJ mol⁻¹ above **1**.²³ Because of this large energy separation between **1** and the lowest excited singlet state **4**, it is unlikely that the conversion of cyclopropylidene to allene proceeds via the excited singlet state.

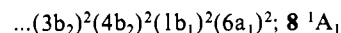
Allene (2). Allene has been the subject of numerous investigations by nonempirical methods.^{26,28-32} Torsion about the C₁C₂C₃

unit has been shown by Pople and co-workers²⁶ to proceed via a planar C_{2v} open-shell singlet structure **5** with 3π electrons, which was estimated to lie 210 kJ mol⁻¹ above **2**. The transition structure **5** has the electronic configuration

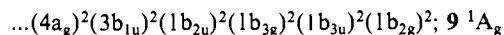


In the previous work,²⁶ the energy of **5** was obtained by adding twice the exchange integral, $K_{6a_1,1a_2}$, to the energy of **6** which has the same configuration. It was assumed that the geometry and correlation energy of the two states would be very similar. The present method, which involves direct unrestricted HF calculations on the single-determinantal configuration,²³ predicts that **5** is 201 kJ mol⁻¹ higher than **2**. Frequency analysis establishes that **5** is indeed a transition structure (i.e., has one imaginary frequency), albeit on the pseudosinglet surface.

Besides the structures discussed above, two additional planar structures, **8** ¹A₁ and **9** ¹A_g, having 2 and 4π electrons, respectively, were located in the singlet manifold. **8** has C_{2v} symmetry and the electronic configuration



9 has D_{2h} symmetry and the configuration



Although both structures are stationary points, frequency analysis reveals that neither corresponds to a local minimum. Both **8** and **9** are unstable with respect to torsion in a conrotatory sense and collapse without activation to **2**. At the RHF/3-21G level, **9** is only 2 kJ mol⁻¹ higher in energy than **1**. The best estimate places it 32 kJ mol⁻¹ above **1**. At the RHF/3-21G level, **8** is 68 kJ mol⁻¹ above **1** while the best estimate places it 49 kJ mol⁻¹ above **1**. At

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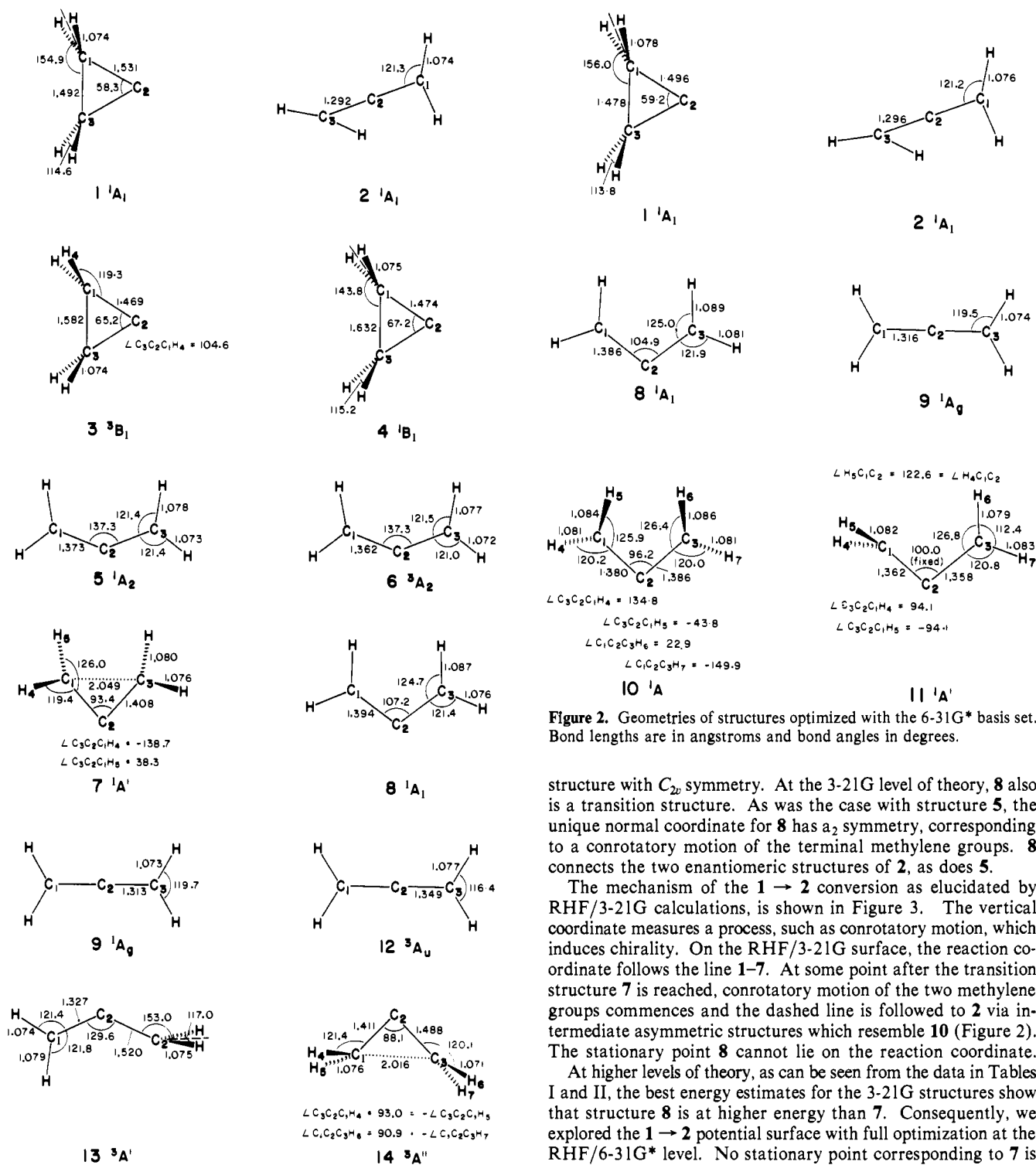


Figure 1. Geometries of structure optimized with the 3-21G basis set. Bond lengths are in angstroms and bond angles in degrees.

higher levels of theory, **8** is also unstable toward disrotatory torsion about the terminal methylene groups. Structure **8** is discussed in more detail in the following section.

Cyclopropylidene \rightarrow **Allene** (**1** \rightarrow **2**). A search for intermediate stationary structures on the path **1** \rightarrow **2** with the 3-21G basis set revealed two structures **7** and **8** which were 71 and 68 kJ mol⁻¹ (RHF/3-21G), respectively, higher than **1**. Structure **7** is related to **1** by a partial rupture of the C₁-C₃ bond and partial rotation about each methylene group in a disrotatory fashion, preserving a plane of symmetry. Frequency analysis revealed that **7** is a true transition structure at this level of theory. The unique normal coordinate along which the energy decreases has a' symmetry and points from **7** toward **8**. As mentioned above, the latter is a planar

Figure 2. Geometries of structures optimized with the 6-31G* basis set. Bond lengths are in angstroms and bond angles in degrees.

structure with C_{2v} symmetry. At the 3-21G level of theory, **8** also is a transition structure. As was the case with structure **5**, the unique normal coordinate for **8** has a₂ symmetry, corresponding to a conrotatory motion of the terminal methylene groups. **8** connects the two enantiomeric structures of **2**, as does **5**.

The mechanism of the **1** \rightarrow **2** conversion as elucidated by RHF/3-21G calculations, is shown in Figure 3. The vertical coordinate measures a process, such as conrotatory motion, which induces chirality. On the RHF/3-21G surface, the reaction coordinate follows the line **1**-**7**. At some point after the transition structure **7** is reached, conrotatory motion of the two methylene groups commences and the dashed line is followed to **2** via intermediate asymmetric structures which resemble **10** (Figure 2). The stationary point **8** cannot lie on the reaction coordinate.

At higher levels of theory, as can be seen from the data in Tables I and II, the best energy estimates for the 3-21G structures show that structure **8** is at higher energy than **7**. Consequently, we explored the **1** \rightarrow **2** potential surface with full optimization at the RHF/6-31G* level. No stationary point corresponding to **7** is found. Frequency analysis of **8** revealed two imaginary frequencies corresponding to normal coordinates of a₁ and a₂ symmetry. The former represents a conrotatory motion which connects **2** to its enantiomer, **2'**; the latter describes a disrotatory motion which connects **1** to its enantiomer (not shown in Figure 3). When the ring opening of **1** is followed at fixed values of the C₁C₂C₃ angle but without other constraints, the structures obtained have C_s symmetry from disrotatory opening of **1** and the energy increases along the solid line shown in Figure 4 up to about 96°. Structure **8**, which is planar (C_{2v} symmetry), is not achieved. Rather, an attempt to continue along the dotted line to **8** results in a transition by conrotatory motion without activation to the lower dashed line, as was previously found by Pasto and co-workers.¹¹ If one approaches from the other direction, i.e., from **2**, the energy increases along the dashed line. At each point between 180° and 90° the minimum energy configuration (at fixed C₁C₂C₃ angle) also has

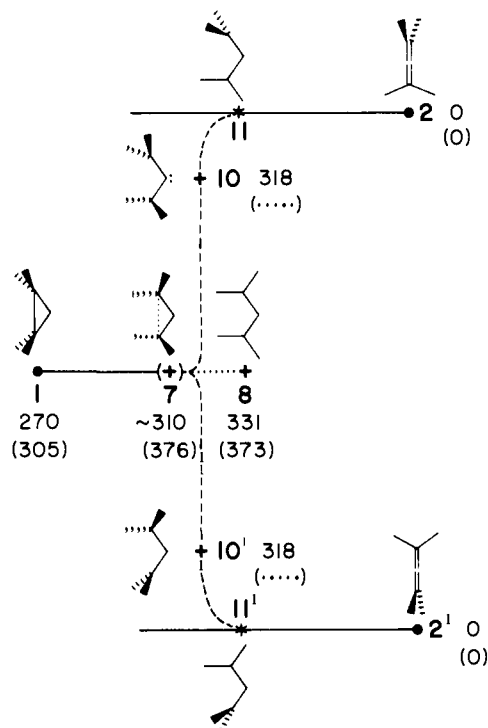


Figure 3. Schematic representation of the singlet cyclopropylidene (**1**) \rightarrow allene (**2**) conversion. The horizontal axis is a measure of the CCC bond angle. The vertical displacement from the middle represents a process which destroys the mirror plane of symmetry. Primes denote enantiomeric structures. Numbers not in parentheses are best estimated relative energies (kJ mol^{-1}). Numbers in parentheses are relative energies calculated at the RHF/3-21G level: stable structures (\bullet); transition structures ($+$). See the text for a discussion.

C_s symmetry but corresponds to an *unrotated* deformation of **2**. At 105° the energy is 59 kJ mol^{-1} lower than that of **8** which has almost the same $C_1C_2C_3$ angle, 104.9° . The structure which is obtained if the $C_1C_2C_3$ angle is fixed at 100° but without any other constraints is labeled **11** and is shown in Figure 2. The two lines pass at a $C_1C_2C_3$ angle of 97° with an energy of 73 kJ mol^{-1} relative to **1**. At the 6-31G* level, the chiral structure **10** (Figure 2) is found through full optimization to be a stationary point 72 kJ mol^{-1} higher in energy than **1**. Vibrational frequency analysis confirms that **10** is a transition structure. **10** is unsymmetrically disrotated, with rotation by 44° about C_1C_2 and rotation by 23° about C_2C_3 out of the $C_1C_2C_3$ plane. The $C_1C_2C_3$ angle in **10** is 96.2° . At a $C_1C_2C_3$ angle of 95° a disrotatory angle of 35° at both ends is achieved. To reach the transition structure, one of the two methylene groups continues to rotate in the same direction while the other *reverses* its sense of rotation. The unique coordinate corresponds to a strong conrotatory motion of both groups. Our best estimate for the barrier hindering the conversion **1** \rightarrow [**10**] \rightarrow **2** is 48 kJ mol^{-1} (Table IV).

The complete description of the conversion of **1** to **2** is shown in Scheme I. The four substitution positions of **1** are labeled to distinguish the four possible stereoisomers. The mechanism is expounded with one of these, **1a**. Except for the relative energies in the INDO study,¹⁰ the mechanism is substantially the same as found by Pasto and co-workers¹¹ and by Dillon and Underwood.¹⁰ The ring **1a** opens initially by a disrotatory motion in two possible directions up to the point where the reaction channel in each direction branches. The branching points, which we have not located precisely, are labeled **7a** and **7b** for the purpose of discussion as we expect them to resemble **7** (Figure 1). At points **7a** and **7b**, the rotation about one of the bonds (C_1C_2 or C_2C_3) reverses while the rotation about the other continues. At this point the symmetry is broken. The energy continues to rise until the asymmetric transition structure **10** is reached. With maximal labeling, four such structures may be distinguished as shown in Scheme I. Beyond the transition structure (**10**) in each of the

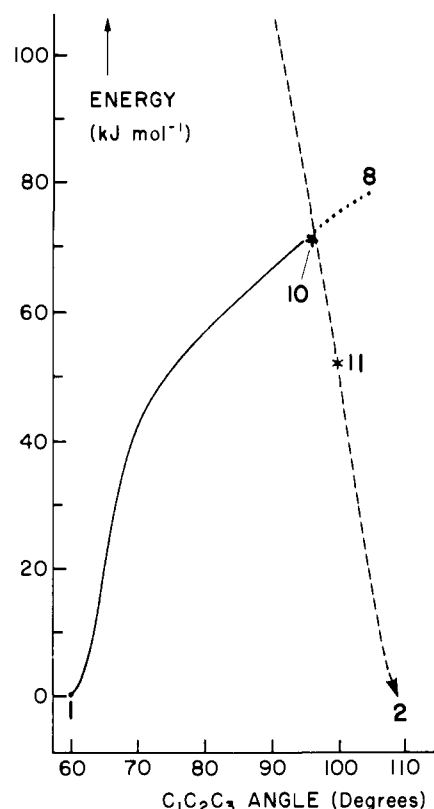
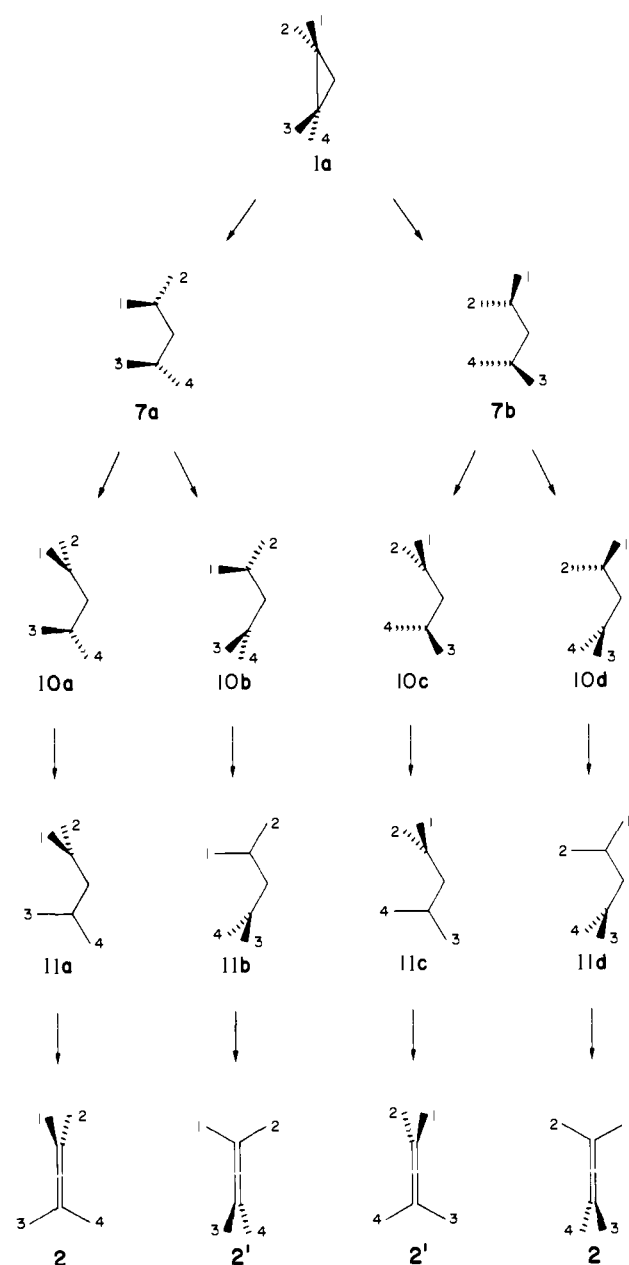


Figure 4. The singlet cyclopropylidene (**1**) \rightarrow allene (**2**) conversion: variation of the total energy at the RHF/6-31G* level as a function of the CCC angle. Structures on the solid and dotted lines have C_s symmetry and arise from disrotatory motion of the methylene groups. Structures on the dashed line have C_s symmetry and arise from nonrotatory bending at C_2 . The structures on the dotted line are unstable with respect to conrotatory motion of the methylene groups.

four channels, rotation about both bonds continues rapidly (relative to the rate of the $C_1C_2C_3$ angle opening) until the nonrotatory channel (in which structures have C_s symmetry) is joined. This point also we have not located exactly but have called it **11** as it should roughly resemble structure **11** (Figure 2). The four possible structures resulting from **10a**–**10d** are labeled **11a**–**11d**. Structures **11a** and **11d** are both in channels which lead to the same enantiomeric form of allene, labeled **2** in Scheme I. Structures **11b** and **11c** are in channels which lead to the other enantiomer, **2'**. The complete graph of the cyclopropylidene \rightarrow allene conversion is shown in Figure 5. Structure **1b** is the stereoisomer of **1a** with positions 3 and 4 interchanged. Primes denote enantiomeric structures. Note that 16 isomeric transition structures **10a**–**10h'** are possible due to the asymmetry of **10**.

With the complete mechanism of the isomerization **1** \rightarrow **2** in hand, the question of chiral discrimination may be addressed. Referring to Scheme I, we see that four channels are available to convert **1** to **2** and **2'**. If **1a** is an anti-disubstituted cyclopropylidene with substituents in the 1- and 4-positions, then not much preference will be shown for either of channels **1a** \rightarrow **7a** or **1a** \rightarrow **7b** since each disrotatory motion results in a large group occupying the crowded inner position which results from the initial disrotatory motion. At the branch points, however, clear steric preferences exist for the branches **7a** \rightarrow [**10a**] \rightarrow **11a** and **7b** \rightarrow [**10d**] \rightarrow **11d** since the transition structures **10a** and **10d** are less crowded than **10b** and **10c**. Each of the preferred paths leads to the same allene **2** as observed.^{5,6} If instead **1a** is a chiral syndisubstituted cyclopropylidene with substituents in the 2- and 4-positions, then a clear steric preference exists for the initial disrotatory channel **1a** \rightarrow **7a**. However, there is little distinction on steric grounds in the selection of path **7a** \rightarrow [**10a**] \rightarrow **11a** over **7a** \rightarrow [**10b**] \rightarrow **11b** since in either case the larger groups can avoid the most crowded site. As has been noted earlier,⁷ there is the possibility of electronic control in determining which carbon atom,

Scheme I



C_1 or C_3 , becomes planar and which adopts the perpendicular position in the exit channel. Experiments on the transformation of *syn*-diaryl cyclopropylidenes to 1,3-diaryl allenes in which differential steric effects were minimized by para substitution on the aromatic ring resulted, however, in low levels of stereoselection for the reaction.⁷

In summary, if the substitution pattern is anti, then the two transition structures which lead to one enantiomeric form of allene are clearly less hindered than the two which lead to the other enantiomer. Significant chiral discrimination can occur. On the other hand, if the substitution pattern is syn, then there is little steric discrimination between the transition structures which lead to the two antipodal forms of allene. In the absence of steric effects, the extent of the chiral discrimination (due to electronic factors) is quite small. That steric factors are dominant in the reaction is reinforced by the observation that tetraalkyl cyclopropylidenes do not rearrange to allenes.³³

Triplet Cyclopropylidene (3). The electronic configuration of the lowest triplet state 3 of cyclopropylidene has been given above. Our best direct estimate of the triplet-singlet (3-1) separation

(33) Moore, W. R.; Hill, J. B. *Tetrahedron Lett.* 1970, 4343, 4553.

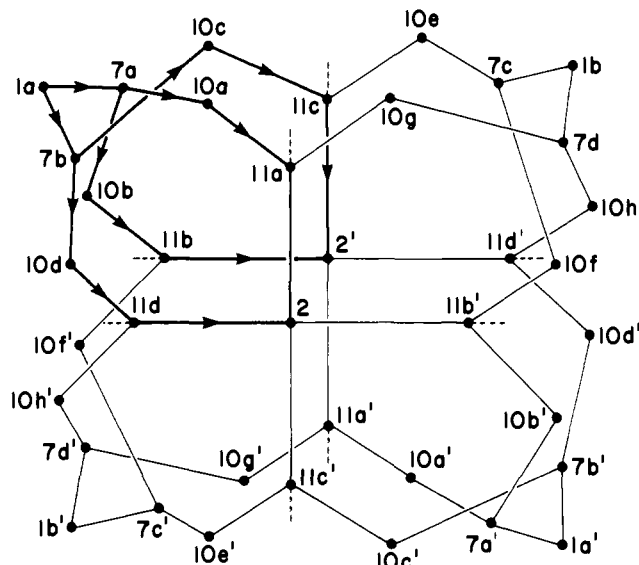
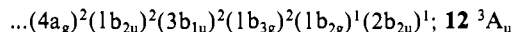


Figure 5. The complete graph of interconversions $1 \rightarrow [10] \rightarrow 2$ with maximum labeling. Structures at the branch points are approximately identified with 7 (Figure 1) and 11 (Figure 2). Primes denote enantiomeric structures. The quadrant drawn in bold corresponds to Scheme I. See text for a discussion.

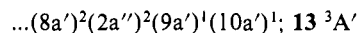
is 39 kJ mol^{-1} in favor of the singlet. The true separation is probably about 65 kJ mol^{-1} since calculations at a similar level of theory overestimate the energy separation in methylene by about 25 kJ mol^{-1} : the currently accepted separation in methylene is $35\text{--}40 \text{ kJ mol}^{-1}$ in favor of the triplet³⁴ whereas calculations comparable to ours³⁵ yield 64 kJ mol^{-1} for this energy difference.

Triplet Allene (6). The lowest triplet state of allene is 6^3A_2 , whose electronic configuration has been given above. 6 lies slightly higher (by 10 kJ mol^{-1}) than the corresponding singlet state 5. The reversal of the usual singlet-triplet order has been explained by Staemmler²⁸ to be a consequence of the effect of dynamic spin polarization on the relative correlation energies and the small value of the exchange integral.

6 is a planar structure with a $C_1C_2C_3$ angle of 137.3° . The transition structure for planar inversion at the central carbon is 12 which has D_{2h} symmetry and configuration



The barrier hindering planar inversion is 25 kJ mol^{-1} . Torsion about one of the C-C bonds of 6 yields the transition structure 13 which has C_s symmetry and the configuration



The barrier hindering rotation in 6 is calculated to be 91 kJ mol^{-1} .

Triplet Cyclopropylidene \rightarrow Triplet Allene (3 \rightarrow 6). The ring opening $3 \rightarrow 6$ is exoergic by 105 kJ mol^{-1} . Ring opening proceeds by an unsymmetrical but nonrotatory rupture of the $C_1\text{--}C_3$ bond with an activation energy of 99 kJ mol^{-1} . The transition structure for the process is 14 which has C_s symmetry. Frequency analysis of 14 indicates that the normal coordinate associated with the imaginary frequency has a' symmetry and connects 14 to 3 on one side and would connect 14 to 12 if the plane of symmetry were to be preserved. 12 lies 179 kJ mol^{-1} below 14 and is itself a transition structure for in-plane inversion of 6. Unlike 8 which lies on a topologically equivalent point on the singlet surface at the 3-21G level, more rigorous calculations do not significantly alter the position of 12 relative to 14 and 6. Since 12 converts to 6 by a process which destroys the symmetry plane which is preserved along the path $3 \rightarrow [14] \rightarrow 12$ (Figure

(34) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* 1983, 79, 5251 and references therein.

(35) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* 1976, 10, 1.

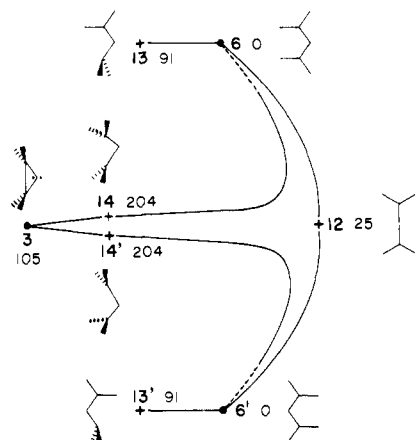


Figure 6. Schematic representation of the triplet cyclopropylidene (**3**) → allene (**6**) interconversion and the isomerization of **6** by in-plane (**6** → [**12**] → **6**) and by rotation (**6** → [**13**] → **6**). Best estimated relative energies (kJ mol^{-1}): stable structures (●); transition structures (+).

6), it cannot lie on the lowest energy path from **14** to **6**. Rather, at some point between **14** and **6** before **12** is reached, torsion at one or both methylene groups must set in. It is of interest to note that if only one of the methylene groups rotates through 90° then **14** would convert to **13**. As **13** itself is a transition structure for geometric isomerization of **6**, it also cannot lie on the reaction coordinate **3** → [**14**] → **6**. As a consequence, each of the methylene groups must ultimately rotate through an angle of 90° but in an unsymmetrical fashion. By allowing the geometry to relax without symmetry constraints from **14** to **6**, it is apparent that the single most important factor is the relaxation of the $C_1C_2C_3$ angle. As a consequence, the $C_1C_2C_3$ bond system becomes almost linear (close to structure **12**) before rotation and rebending allow the equilibrium geometry **6** to be attained.

The preceding description of the conversion **3** → **6** is substantially different from that found by Pasto and co-workers,¹¹ who may have restricted their investigation to structures with C_s symmetry. Although they guessed that the $C_1C_2C_3$ angle of their transition structure was close to 88° , the value found for **14**, they found a rapid disrotatory motion around the transition structure to give a nonplanar structure followed by gradual flattening of the methylene group while ring opening continued to **6**. Their estimated barrier at the 4-31G level, 80 kJ mol^{-1} , is somewhat higher than that found in this investigation at the 3-21G level, 64 kJ mol^{-1} , or at the 6-31G level, 69 kJ mol^{-1} . Our best estimate for the barrier after inclusion of polarization functions and correction for changes in correlation energies and zero-point vibrational energies is 99 kJ mol^{-1} . Thus the conversion of cyclopropylidene to allene on the triplet potential energy surface is substantially more hindered than that on the singlet surface, the latter barrier being 48 kJ mol^{-1} .

Concluding Remarks

Ab initio calculations with gradient techniques and inclusion of correlation have revealed the detailed mechanisms of the cyclopropylidene → allene conversion on both the singlet and triplet potential energy surfaces. The singlet reaction has an activation energy of 48 kJ mol^{-1} . The reaction coordinate branches prior to passage over chiral and enantiotopic transition structures. Elucidation of the transition structures (**10** and **10'**) has enabled a rationale to be presented for the high degree of stereoselectivity on the basis of steric factors observed for the conversion of anti-substituted cyclopropylidenes to allenes, and for the very low degree of stereoselectivity observed in the case of syn substitution. The analogous reaction of triplet cyclopropylidene is hindered by a higher barrier, 99 kJ mol^{-1} . Here the transition structure (**14**) is reached by means of a nonrotatory but unsymmetrical rupture of the bond opposite to the carbene site.

Registry No. Cyclopropylidene, 2143-70-6; allene, 463-49-0.

Generalization of the Born Equation to Nonspherical Solvent Cavities

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Abstract: Solvent effects on the methylamine-acetic acid complex are studied by embedding the molecule in a spheroidally shaped cavity and employing the generalized Born equation. The solvent effect is found to stabilize the zwitterion but not enough to make it more stable than the neutral complex.

I. Introduction

Lack of agreement between gas-phase calculations and experimental solution data is probably due to the solute-solvent interaction. For a charged solute in a polar solvent the Born equation¹ approximates this interaction by placing the solute molecule in a spherical solvent cavity. The ion is idealized as a point particle at the center of a sphere. The solvent is treated as a continuum whose electrical properties are embodied in its dielectric constant, ϵ . The electrostatic hydration energy is then given by

$$U = -\frac{Q^2}{2a} \left[1 - \frac{1}{\epsilon} \right] \quad (1)$$

where Q is the solute's net charge and a is the radius of the spherical cavity. This formula has been applied to numerous problems of practical interest in the literature.² Two sources of error in this expression are first that the solute molecule, in reality, consists of a distribution of charge corresponding to the distorted atomic charge clouds positioned around the atomic locations in

(1) Born, M. *Phys. Z.* **1920**, *1*, 45.

(2) See, for example: Aue, B. H.; Webb, H. M.; Bowers, M. T. *J. Am. Chem. Soc.* **1976**, *98*, 318.

[†] City College of the City University of New York.

* John Jay College of the City University of New York.