Theoretical Studies on the Singlet and Triplet Cyclopropylidene–Allene System

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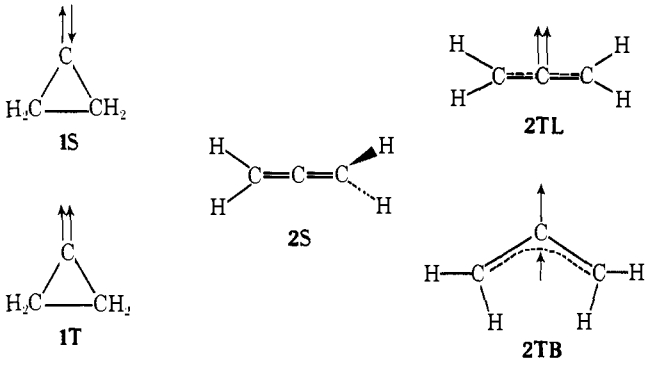
Abstract: Ab initio SCF calculations employing the STO-3G and 4-31G basis sets have been carried out with full geometry optimization on the singlet and triplet cyclopropylidene–allene systems. Triplet cyclopropylidene (**1T**) is calculated to be of lower energy than singlet cyclopropylidene (**1S**) by 8.4 kcal/mol. Triplet allene is calculated to be a bent, planar species, being 8.0 kcal/mol lower in energy than the linear, planar form. Both **1S** and **1T** undergo disrotatory ring opening, although the intimate details of the two processes differ greatly. In both cases substantial shortening of the C–C bond lengths are observed as the ring opens. Barrier heights for the ring opening of **1S** and **1T** are calculated to be 18 and 19 kcal/mol, respectively (4-31G level). The results of these calculations are significantly different from those reported previously, and the differences are discussed. The structures and ring-opening processes of **1S** and **1T** are compared with those reported for the cyclopropyl cation and radical.

Introduction

Our interest in the synthesis, structure, and chemical reactivity of allenes[2] has led us to carry out a detailed theoretical study on the structures of singlet and triplet cyclopropylidene (**1S** and **1T**, respectively) and allene (**2S** and **2T**) and their mode of interconversion as might be related to their photochemistry.[3]



Prior to the initiation of this study, two somewhat conflicting reports on **1S** and its conversion to **2S** had appeared. Using orbital symmetry diagrams Borden[4] originally suggested that **1S** opened by a monorotatory process (see Figure 1), and that **1T** should not open. In a MINDO/2 study of the reaction of ^1S carbon atoms with ethylene in which **1S** is initially formed, the calculations of Dewar and co-workers[5] indicated that in the process of opening of **1S** to **2S** methylene "rotation takes place only in the final stages of the reaction, the original unrotated geometry being retained in the transition state". The barrier height for the conversion of **1S** to **2S** was calculated to be 50 kcal/mol, although the authors acknowledged that this value was undoubtedly high because of the inability of MINDO/2 to accurately calculate the strain energies of small-ring compounds. In a later study using a newer version of MINDO/2 the barrier height for the conversion of **1S** to **2S** was calculated to be 13.7 kcal/mol.[6]

During the course of the present study, the results of a Simplex–INDO study on the singlet and triplet energy surfaces of the cyclopropylidene–allene system appeared,[7] certain of the results of which were inconsistent with those obtained in our calculations using STO-3G and 4-31G ab initio molecular orbital techniques.[8] Because of substantial differences between the Dillon and Underwood results[7] and ours, which will be discussed in later sections of this paper, the calculations were carried to completion. Very late in our study, ab initio calculations, including correlation energy corrections, on the geometry and rotational processes in singlet and triplet excited states of allene appeared[9] which supported our results of STO-3G and 4-31G geometry optimization calculations. The following sections describe our results obtained by using the ab initio program Gaussian 70[8] along with a comparison with the results of previous calculations.

Results and Discussion

Singlet Cyclopropylidene. The STO-3G fully geometry optimized C_{2v} structure of singlet cyclopropylidene (**1S**) is shown in Figure 2,[10] along with the STO-3G and 4-31G total energies. **1S** lies in a fairly deep energy well (~18 kcal/mol at the 4-31G level relative to the transition state for ring opening; see Figure 5), and is higher in energy than triplet cyclopropylidene (**1T**) at its equilibrium geometry by 8.4 kcal/mol and is higher than **2S** by 74.2 kcal/mol. These results are in distinct contrast to those reported by Dillon and Underwood,[7] who claim that "there is no energy minimum at the point which corresponds to cyclopropylidene", and, furthermore, that **1S** is of *lower* energy than **1T**. It is not obvious whether Dillon and Underwood's lack of finding an energy minimum corresponding to **1S** is due to the type of calculations used (INDO) or to differences between the present STO-3G optimized geometry of **1S** (Figure 2) and that assumed by Dillon and Underwood[7] (C–C bond lengths of 1.31 Å, C_1–C_2–C_3 bond angle of 60°, and with completely planar methylene groups).[11] The report that **1S** is of lower energy than **1T** (by 22 kcal/mol) is, however, not due to differences in geometry; it is the result of the type of calculations (INDO) employed. Our INDO calculations on the reported geometries of **1S** and **1T**, and on the STO-3G optimized geometries determined in this study, indicate that the INDO method does incorrectly predict that the singlet is of lower energy than the triplet. This inversion of relative energies is not unexpected in CNDO- and INDO-type calculations.

In **1S** the nonbonded pair of electrons is highly localized on C_2 in an in-plane sp hybrid orbital in the highest occupied molecular orbital (HOMO) (see Figure 3).[12] The lowest unoccupied molecular orbital (LUMO) consists almost entirely of the out-of-plane 2p AO on C_2.

Singlet Cyclopropylidene to Allene Interconversion. The mode of conversion of **1S** to ground state, singlet allene (**2S**) has been investigated using complete geometry optimization STO-3G calculations at 10° intervals of the C_1–C_2–C_3 bond angle from 70 to 110° and selected higher angles. At 70, 80, and 90° the optimized geometries[13] (see Table I) represent a

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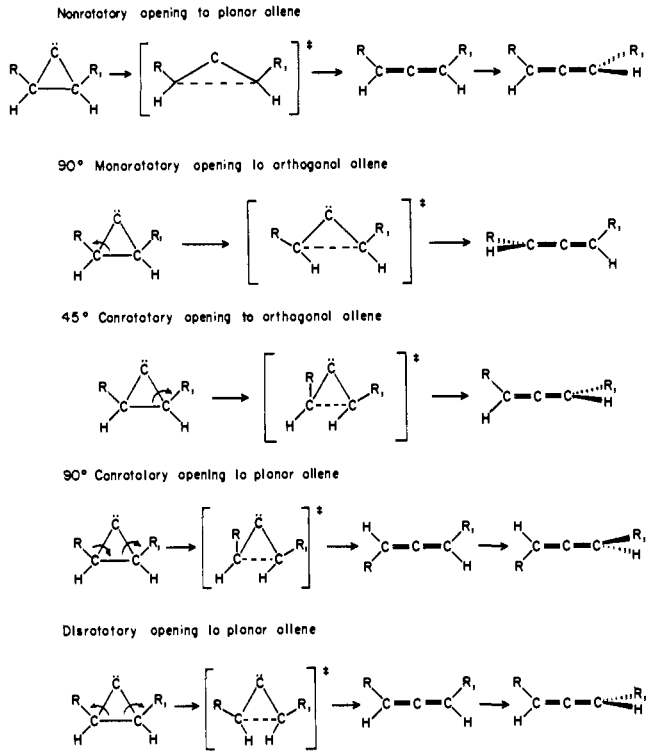


Figure 1. Rotatory ring-opening processes for conversion of **1S** and **1T** to planar or orthogonal allene.

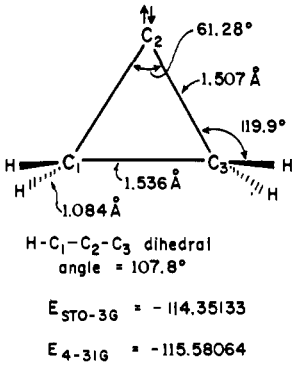


Figure 2. STO-3G geometry optimized structure of singlet cyclopropylidene and STO-3G and 4-31G energies.

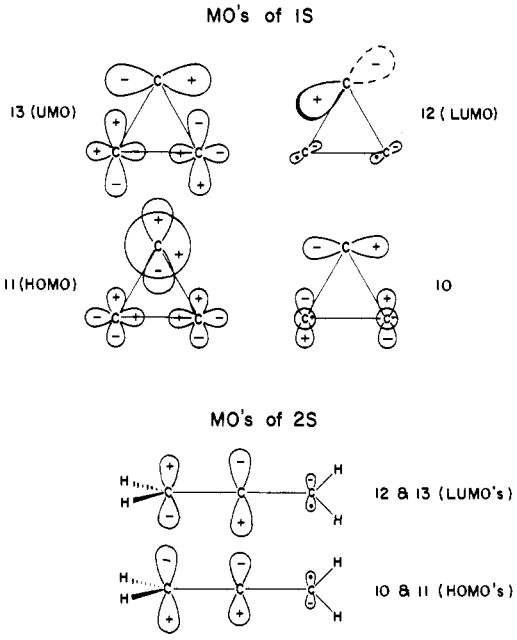


Figure 3. MOs of **1S** and **2S.**

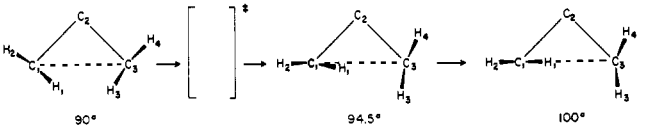


Figure 4. Geometries of the singlet species near the transition state for ring opening of **1S.** For structural parameters, see Table I.

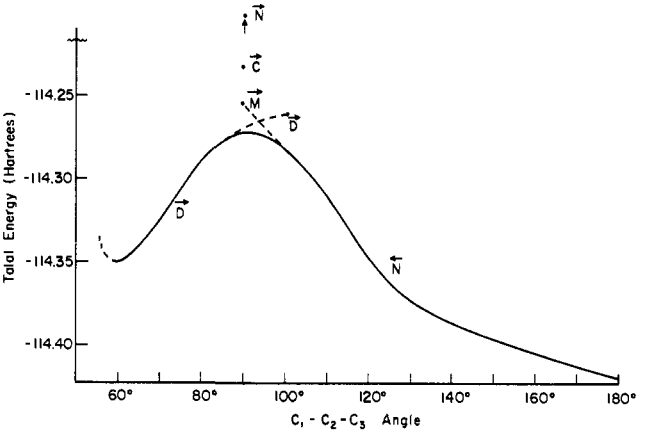


Figure 5. Minimum energy surface for the conversion of **1S** to **2S.** Points labeled $\tilde{D}$, $\tilde{M}$, $\tilde{C}$, and $\tilde{N}$ are the energies of the structures formed by **D, M, C,** and **N** ring-opening processes from **1S,** the $\tilde{N}$ point being off scale. The points labeled $\tilde{N}$ are the energies of the nonrotatory ring closing process from **2S.**

disrotatory (**D**) ring-opening process, the disrotation of the methylene groups occurring synchronously with opening of the C_1–C_2–C_3 bond angle. During this **D** process, the two methylenes develop considerable nonplanarity (see Figure 4). The rate of inward rotation of H_1 and H_3 lags considerably behind the outward rotation of H_2 and H_4. Inspection of the Mulliken overlap populations reveals that this effect is not due to an antibonding repulsion between H_1 and H_3, but arises from antibonding repulsions between the **1S** AO on the hydrogens and the AOs on the opposing carbon atoms.

At 100° the lowest energy structure has a distorted perpendicular geometry (see Figure 4) derived by an apparent monorotatory (**M**) process from **1S**[14] (or conversely via a nonrotatory (**N**) process from **2S** to **1S**). As in the 90° **D** structure, the distortion of the perpendicular methylene in the 100° structure arises from repulsive antibonding interactions between the **1S** AOs on H_3 and H_4 and the AOs on C_1 and not from between H_3 and H_4 with H_1. As the C_1–C_2–C_3 bond angle increases the distortion of the methylene decreases, ultimately becoming planar (see Table I).

The lowest energy **D** structure at 100°, optimized by maintaining a vertical plane of symmetry, is of considerably higher energy than the **M** (from **1S**) structure at 100° (see Figure 5). Unconstrained optimization of the H–C–C–C dihedral angles in the **D** structure resulted in a smooth conversion to the 100° **M** (from **1S**) structure indicating that the 100° **D** structure does not lie in an energy minimum. Similarly, a 90° **M** (from **1S**) structure is of much higher energy than the 90° **D** structure, and similarly does not lie in an energy minimum. It must be concluded, therefore, that the **D** (from **1S**) and **N** (from **2S**) energy valleys are not separated by an energy maximum but must intersect between C_1–C_2–C_3 bond angles of 90 and 100°.

Table I. Singlet C_3H_4 Geometries and Energies at Selected C_1-C_2-C_3 Bond Angles

C_1-C_2-C_3 bond angle	bond lengths						bond angles				dihedral angles				energy,[a] hartrees
	C_1-C_2	C_2-C_3	H_1-C_1	H_2-C_2	H_3-C_3	H_4-C_3	$H_1C_1C_2$	$H_2C_1C_2$	$H_3C_3C_2$	$H_4C_3C_2$	H_1C_1-C_2C_3	H_2C_1-C_2C_3	H_3C_3-C_2C_1	H_4C_3-C_2C_1	
61.3	1.507	1.507	1.084	1.084	1.084	1.084	119.9	119.9	119.9	119.9	−107.8	107.8	107.8	−107.8	−114.351 33 (−115.580 25)
70	1.456	1.456	1.079	1.088	1.079	1.088	118.7	117.8	118.7	117.8	−101.8	108.8	101.8	−108.8	−114.321 55
80	1.418	1.418	1.083	1.088	1.083	1.088	128.1	117.4	128.1	117.4	−62.0	125.2	62.	−125.2	−114.287 11
90	1.402	1.402	1.091	1.092	1.091	1.092	127.3	119.0	127.3	119.0	−42.6	133.3	42.6	−133.3	−114.270 14
94.5	1.366	1.390	1.084	1.087	1.098	1.099	128.0	120.2	124.7	122.1	−3.3	86.2	82.3	−106.4	−114.271 72 (−115.551 78)
100	1.343	1.375	1.081	1.087	1.096	1.096	125.9	121.7	123.0	123.0	0.0	180.0	96.7[b]	−95.7[b]	−114.288 82
110	1.331	1.356	1.080	1.085	1.093	1.093	123.8	123.0	122.4	122.4	0.0	180.0	97.9	−97.9	−114.321 35
130	1.307	1.323	1.083	1.083	1.087	1.087	122.3	122.3	122.3	122.3	0.0	180	97.4	−97.4	−114.372 22
180	1.289	1.289	1.082	1.082	1.082	1.082	121.9	121.9	121.9	121.9	0.0	180	90.0	−90.0	−114.421 73 (−115.698 42)

[a] Nonparenthesized energies are calculated by STO-3G and parenthesized values by 4-31G calculations. [b] Not symmetry coupled when optimized. See ref 13.

Table II. Singlet Orbital Energies (Hartrees)[a]

C_1-C_2-C_3 angle	1S MO									
	4	5	6	7	8	9	10	11	12	13
61.28	−1.0930	−0.7961	−0.7065	−0.6121	−0.4924	−0.4911	−0.3963	−0.2885	0.2109	0.4882
70	−1.0887	−0.8131	−0.6939	−0.6118	−0.5145	−0.4658	−0.4248	−0.2547	0.2156	0.4319
80	−1.0792	−0.8282	−0.7131	−0.6164	−0.5302	−0.4402	−0.3978	−0.2424	0.2672	0.2882
90	−1.0576	−0.8435	−0.7088	−0.6154	−0.5414	−0.4499	−0.3537	−0.2277	0.1967	0.3270
94.5	−1.0503	−0.8446	−0.6933	−0.6050	−0.5489	−0.4639	−0.2996	−0.2624	0.1804	0.3289
100	−1.0446	−0.8483	−0.6858	−0.5979	−0.5491	−0.4802	−0.2868	−0.2841	0.1861	0.3295
120	−1.0245	−0.8625	−0.6728	−0.5787	−0.5570	−0.5130	−0.3030	−0.2962	0.2224	0.3205
130	−1.0206	−0.8726	−0.6687	−0.5731	−0.5623	−0.5264	−0.3092	−0.3045	0.2434	0.3199
140	−1.0098	−0.8779	−0.6659	−0.5668	−0.5619	−0.5331	−0.3169	−0.2992	0.2506	0.3244
180	−1.0166	−0.9005	−0.6636	−0.5671	−0.5651	−0.5651	−0.3233	−0.3233	0.3182	0.3182
	4	5	6	7	8	9	10	11	12	13
					allene MO					

[a] Arrows between columns indicate crossovers of the MOs.

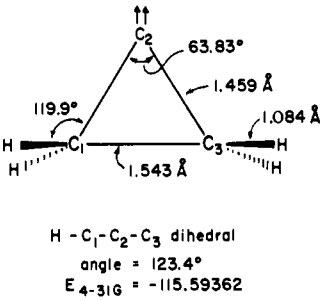


Figure 6. 4-31G geometry optimized structure of triplet cyclopropylidene **1T**.

Calculations were then carried out at an intermediate angle of 94.5° giving the fully geometry optimized structure shown in Figure 4 in which the C_1 methylene has rotated to a nearly coplanar orientation while the C_3 methylene has reversed its direction of rotation and is nearly perpendicular to the C_1-C_2-C_3 plane. The energy of this structure is slightly lower than that at 90° (0.3 kcal/mol) and we conclude that the transition state must lie between the 90 and 94.5° structures. It should be noted that the energy surface in the direction of the reaction coordinate near the transition state is rather flat, the rotational processes of the methylenes being associated with rather low dihedral angle rotational (bending) force constants (0.3-1.1 $\times 10^{-4}$ M dyn/Å).

The conversion of **1S** to **2S** therefore involves three distinct processes: (a) *initial disrotatory opening proceeding almost to the transition state;* (*b*) *a rapid transformation from the disrotatory structure to distorted monorotatory (from* ***1S****) structure between C_1-C_2-C_3 bond angles of 90 and 100°; and* (*c*) *nonrotatory conversion of the 100° structure to allene by opening of the C_1-C_2-C_3 bond angle with flattening of the out of plane methylene group.* The final 4-31G energy calculations indicate a barrier height of ~18 kcal/mol and an overall exoergicity of ~74 kcal/mol for the ring-opening process.

The transformation of the MOs of singlet cyclopropylidene to allene have been determined by correlating the character of the MO wave functions. (The energies of the MOs are listed in Table II.) Several features are noteworthy. The most dramatic changes in energy occur in those MOs of **1S** which are undergoing conversion to the π and π^* MOs of allene, those changes occurring just before and at the transition state. Several orbital crossings also occur (indicated in Table II by the arrows between columns). The ninth a_1 MO of **1S** crosses the tenth MO and shortly after the transition state becomes nearly degenerate with the 11th a_1 MO in forming the degenerate π MOs of allene. The tenth b_1 MO of **1S** crosses both the ninth and eighth MOs becoming the seventh MO in allene consistent with its becoming the $2p_z$ σ-type MO.

Overall, the ring opening of **1S** to **2S** is a net 90° monorotatory or 45° conrotatory process, the former being identical with that suggested earlier by Borden on the basis of simple orbital symmetry correlation considerations;[4] however, the more intimate details of the process are not revealed by such considerations. The nonrotatory (N) process, until after the transition state, followed by monorotation to orthogonal allene predicted by the MINDO/2 calculations[6] is not consistent with the results of the present calculations. Similarly, the initial disrotatory opening followed by reversal to a nonrotated transition state followed by a conrotatory conversion to (planar) allene as predicted by INDO calculations[7] is not in agreement with the present results.

The rotatory process described herein is fully consistent with the stereochemical aspects of the ring opening of optically active cyclopropylidenes[15] in which the direction of rotation of the methylene groups is determined by steric interactions

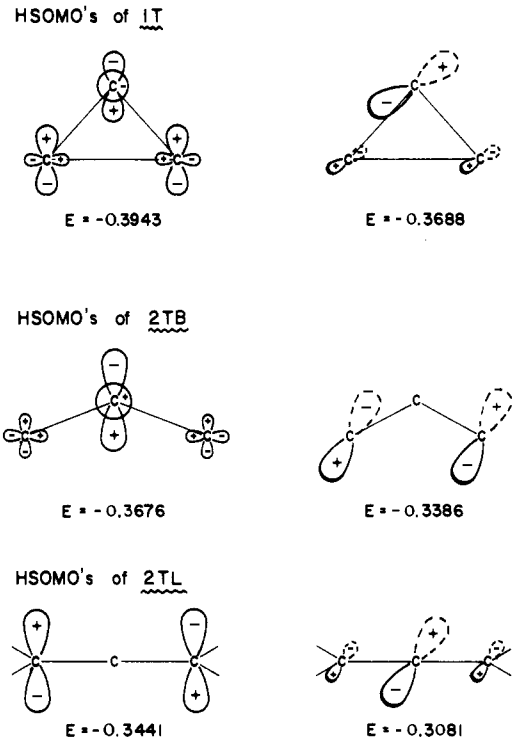
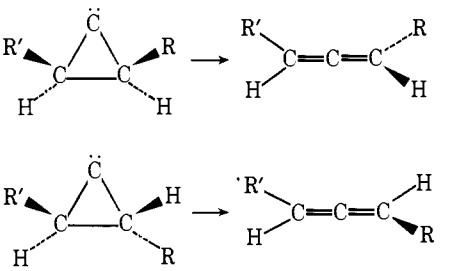


Figure 7. HSOMOs and 4-31G energies (hartrees) of **1T**, **2TB**, and **2TL**.

in the initial disrotatory opening of **1S** as illustrated in the following equations.



Triplet Cyclopropylidene (1T). The 4-31G fully optimized structure of **1T** is shown in Figure 6 (see also Table III).[16] As pointed out earlier, **1T** lies at lower energy than **1S** by 8.4 kcal/mol at the 4-31G level. The calculated unrestricted Hartree-Fock wave function of **1T** is essentially pure triplet as indicated by the $\langle S^2 \rangle$ value of 2.010 (as compared to 2.000 for a pure triplet).

The highest singly occupied molecular orbital (HSOMO) consists almost entirely (Mulliken population of 0.947) of a contribution from the $2p_y$ AO on C_2 (see Figure 7). The other unpaired electron occupies an in-plane MO with populations of 1.047 and −0.035 on C_2 and C_1 (C_3), respectively.

Triplet Allene (2T). Initial STO-3G geometry optimization calculations on triplet allene suggested that **2T** was a bent planar species. However, the calculations indicated that there were significant contributions of higher spin states to the nominal triplet wave function ($\langle S^2 \rangle = 2.189$). This initially caused concern in view of the fact that the most stable form of triplet allene had been reported by Dillon and Underwood[7] to be a linear planar species. The contribution of other spin states of similar energy, but significantly different geometry, in our calculations could have conceivably resulted in optimization to a structure not representative of triplet allene. Geometry-optimized 4-31G calculations, however, resulted in essentially the same structure but indicated a significantly lower contribution of other spin states to the wave function ($\langle S^2 \rangle = 2.130$).

Table III. Triplet Cyclopropylidene to Allene Interconversion Energies and Geometries

	bond lengths			bond angles		dihedral angles			
$\angle C_1-C_2-C_3$	C-C	H_1-C_1	H_2-C_2	$H_1-C_1-C_2$, $H_3-C_3-C_2$	$H_2-C_1-C_2$, $H_4-C_3-C_2$	$H_1-C_1-C_2-C_3$, $H_3-C_3-C_2-C_1$	$H_2-C_1-C_2-C_3$, $H_4-C_3-C_2-C_1$	4-31G energy	$\langle S^2 \rangle$
63.83 (**1T**)	1.459	1.084	1.084	119.9	119.9	−123.4	123.4	−115.593 62	2.015
78.3 (20%)	1.410	1.084	1.086	121.5	121.5	−122.6	122.6	−115.579 73	2.010
85.5 (30%)	1.402	1.084	1.084	121.9	122.2	−81.2	96.4	−115.562 74	2.010
92.7 (40%)	1.472	1.069	1.077	117.7	122.3	−47.8	156.0	−155.567 23	2.307
99.9 (50%)	1.461	1.081	1.085	118.2	122.7	−42.7	160.5	−115.592 61	2.283
107.1 (60%)	1.411	1.069	1.073	119.0	123.3	−22.2	167.4	−115.616 90	2.181
114.3 (70%)	1.408	1.081	1.082	119.3	123.3	−13.8	171.2	−115.632 45	2.168
121.5 (80%)	1.395	1.082	1.081	119.9	123.0	−3.4	176.5	−115.643 39	2.153
138.1 (**2TB**)	1.363	1.076	1.068	121.4	121.6	0.0	180.0	−115.652 22	2.130
150.0	1.351	1.085	1.082	123.5	120.5	0.0	180.0	−115.649 45	2.124
160.0	1.342	1.086	1.084	123.9	120.6	0.0	180.0	−115.644 87	2.116
170.0	1.334	1.086	1.054	124.0	121.1	0.0	180.0	−115.640 58	2.113
180.0 (**2T**)	1.356	1.086	1.086	122.2	122.2	0.0	180.0	−115.639 48	2.130

[a] Parenthesized percentages are percent ring opening from **1T** to **2TB**.

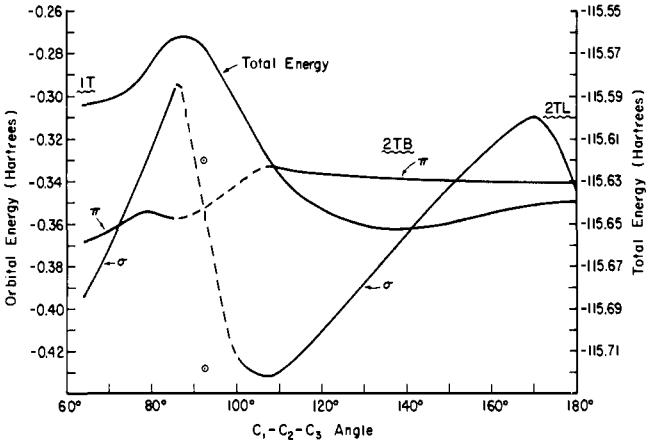


Figure 8. Minimum energy surface for conversion of **1T** to **2TB** and on to **2TL** (right energy scale in hartrees) and HSOMOs energies (left scale in hartrees).

Table IV. 4-31G Orbital Energies during Ring Opening of **1T** to **2TB** and on to **2TL**[a]

extent of ring opening, %	$C_1-C_2-C_3$ bond angle, deg	HSOMO	LSOMO
0 (**1T**)	63.83	−0.3688 (p_y)	−0.3943 (σ)
20	78.3	−0.3306 (σ)	−0.3542 (p_y)
30	85.5	−0.2958 (σ)	−0.3575 (p_y)
40	92.7	−0.3307	−0.4283
50	99.9	−0.3413 (p_y)	−0.4230 (σ)
60	107.1	−0.3324 (p_y)	−0.4324 (σ)
70	114.3	−0.3354 (p_y)	−0.4214 (σ)
80	121.5	−0.3365 (p_y)	−0.4073 (σ)
100 (**2TB**)	138.1	−0.3386 (p_y)	−0.3676 (σ)
$C_1-C_2-C_3$ angles in **2T**, deg			
150		−0.3404 (p_y)	−0.3434 (σ)
160		−0.3234 (σ)	−0.3404 (p_y)
170		−0.3096 (σ)	−0.3412 (p_y)
180		−0.3081 (p_y)	−0.3441 (σ)

[a] Orbital energies are given in hartrees. The dominant character of the orbitals is indicated in parentheses.

During the final stages of these calculations the results of an unrestricted Hartree-Fock 6-31G calculation including correlation energy corrections appeared also indicating that the lowest energy form of **2T** had a bent planar structure.[9] Our value of 138.1° for the $C_1-C_2-C_3$ bond angle in **2T** is quite close to that of 135.4° found in the more extensive calculations,[9] with the bent structure being lower in energy than the linear structure. The result reported by Dillon and Underwood[7] was obtained using the INDO technique which does, in fact, incorrectly predict that a linear planar structure is lower in energy than the bent planar form of **2T**.

The HSOMO of **2TB** is a nonbonding π allyl-type MO (see Figure 7), while the second SOMO is an in-plane MO with dominant contribution from the AOs on C_2. The Mulliken populations on C_1, C_2, and C_3 are 0.70, −0.40 and 0.70 for the HSOMO and 0.11, 0.77, and 0.11 for the second SOMO, respectively. The linear planar allene triplet lies 8.0 kcal/mol higher in energy (4-31G level). The SOMOs are illustrated in Figure 7, the HSOMO being an antibonding allyl-type MO perpendicular to the plane of the molecule, while the second SOMO is an in-plane, nonbonding allyl-type MO.

Interconversion of 1T and 2T. The energy surface connecting **1T** and planar, bent triplet (**2TB**) was calculated at 10% intervals between 20 and 80% ring opening, and at 150, 160, and 170° for the conversion of **2TB** to the linear, planar form **2TL** and is shown in Figure 8.[16] Although the total energy surface is smooth and appears normal, a detailed analysis of the character and energies of the SOMOs shows a dramatic discontinuity between 30 and 50% ring opening (85.5 and 99.9°, respectively) (see Figure 8 and Table IV). The in-plane σ SOMO initially rapidly decreases in energy up to 85.5° owing

to a decrease in the bonding between C_1 and C_3 as the ring opens. At 99.9°, however, it is at considerably lower energy. At 92.7° (40% ring opening) the character of the SOMOs is highly mixed, showing neither dominant σ nor π character. Furthermore, the energies of the SOMOs (indicated by ⊙ in Figure 8) are not close to those expected for the σ- and π-type SOMOs. These results appear to be due to mixing of the σ- and π-type SOMOs which are accidentally nearly degenerate at 92.7° at which point the calculations were carried out. (The dashed lines in Figure 8 show the correlations between the σ- and π-type MOs.) Although this mixing greatly affects the character and energies of the SOMOs, it does not affect the total energy of the system.

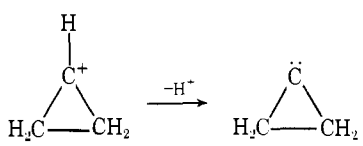
Another discontinuity which occurs in this same region, but which is not related to that discussed above, is observed in the values of $\langle S^2 \rangle$. The value of $\langle S^2 \rangle$ remains constant at ~2.010 up to 85.5° indicating a nearly pure triplet wave function. At 92.7° the value of $\langle S^2 \rangle$ is 2.307[16] which steadily decreased to 2.130 at **2TB.** Full geometry optimization using both the STO-3G and 4-31G basis sets gives essentially identical structures, even though the $\langle S^2 \rangle$ values are significantly different (2.540 and 2.307, respectively). We therefore believe that the calculations provide a valid description of the triplet geometry. The only significant effects that removal of the spin contamination might have would be to possibly push the transition state to a slightly higher C_1-C_2-C_3 angle and to make small changes in the shape of the energy curve just beyond the transition state.

The ring opening of **1T** to **2TB** occurs initially via an essentially nonrotatory process which rapidly changes to a disrotatory process in, or very shortly after, the transition state. The barrier height for this process is estimated to be ~19 kcal/mol (4-31G level) and occurs near 88°, or ~33% ring-opened structure. As the **N** process approaches the transition state the methylenes approach nearly planar configurations. After entering the disrotatory phase the methylenes become distinctly nonplanar, the rotation of the inner hydrogens lagging behind that of the outward rotating hydrogens (see Figure 9). As in the disrotatory opening of **1S,** this nonplanarity is due to repulsive interactions between the **1S** AOs on H_1 (or H_3) and the AOs on C_3 (or C_1). As the C_1-C_3 distance increases during the ring-opening process this repulsion decreases and the methylenes become planar.

The opening of **1T** therefore occurs in basically three phases: (*a*) *a nonrotatory process up to the nearly planar transition state with a* C_1-C_2-C_3 *bond angle of almost 90°;* (*b*) *a rapid disrotatory motion around the transition state to give a nonplanar structure; and* (*c*) *ring opening with gradual flattening of the methylenes to give the bent planar triplet allene.* The 4-31G energy calculations indicate a barrier height of ~19 kcal/mol and an overall exoergicity of ~37 kcal/mol for the ring-opening process.

Although the much cruder INDO calculations[7] also predict a nonrotatory process up to 90°, further details of the transformation are quite inconsistent with the present results. The INDO results indicate disrotation between 90 and 105° to produce an all-planar transition state at about 105° with a barrier height of 74 kcal/mol, proceeding to planar-linear triplet allene, with an overall *endoergicity* of 35 kcal/mol!

Comparison of 1S and 1T with the Cyclopropyl Cation and Radical. It is interesting to compare the structures, mode of ring opening, and the activation energies for the ring opening of **1S** and **1T** with the results reported for the cyclopropyl



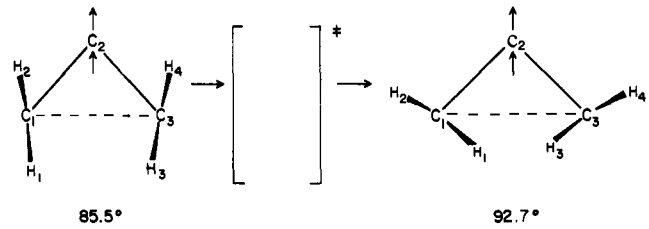


Figure 9. Geometries of the triplet species near the transition state.

cation and radical.[17] **1S** can be considered to be derived from the cyclopropyl cation by removal of a proton from the cationic center, the electrons which were previously considered to be associated with the C-H bond becoming the nonbonding pair of electrons in **1S.** Thus, the MOs of the two species should be very similar. In keeping with this notion, both systems undergo disrotatory ring opening in which the disrotation of the methylene groups occurs synchronously with the ring-opening process. The barrier height for ring opening of the cyclopropyl cation has been calculated[17] to be 1.3 kcal/mol (double ζ basis with limited configuration interaction)[18] compared to our result of 18 kcal/mol for **1S.**[19] The optimized bond lengths in the cyclopropyl cation are calculated to be 1.40 Å, considerably shorter than those in **1S** of 1.507 Å for C_1-C_2 and C_2-C_3. (It must be recognized, however, that bond lengths calculated by the STO-3G method are slightly longer than experimentally observed bond lengths. Nonetheless a significant difference still exists.)

In **1T,** an electron has been transferred from the in-plane σ MO to the vacant 2pπ AO on C_2 of **1S** resulting in a shortening of the C_1-C_2 and C_2-C_3 bonds to 1.459 Å. This shortening can be rationalized on the basis of a decrease in the dominant repulsion between the nonbonded (single) σ electron on C_2 and the electrons of the C_1-C_2 and C_2-C_3 bonds. **1T** can be related to the cyclopropyl radical by removal of a hydrogen atom from the latter, and, thus again, similarities between the two systems should exist. Both **1T** and the radical are predicted to undergo overall disrotatory ring opening. However, in contrast to **1S** and the cation, the ring opening and disrotation of the methylenes in **1T** and the radical do not occur synchronously. The initial ring opening of **1T** and the radical occurs in a nonrotatory manner with the disrotation process beginning at, or shortly after, the transition state. Assuming that the MOs of the radical are very nearly the same as those of the cation (application of Koopman's theorem)[20] the activation energy for opening of the radical has been calculated[17] to be 35 kcal/mol compared to our result of 19 kcal/mol for the opening of **1T.**

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(1) The research described herein was supported in part by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1845 of the Notre Dame Radiation Laboratory.
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of 58.3°, C_1–C_2 bond length of 1.530 Å, C–H bond length 1.081 Å, and ∠H–C–H angles of 113.8°.
(11) Dewar and co-workers derived C_1–C_2 and C_2–C_3 bond lengths of 1.428 Å, C_1–C_2–C_3 bond angle of 62.6°, C_2–C_1–H bond angles of 119.7°, and H–C–C–C dihedral angles ~110° using the Simplex–MINDO/2 procedure (see ref 6).
(12) This MO description is different from that implied in ref 6 in which the nonbonded pair of electrons is depicted as occupying a 2p AO on C_2.
(13) In the geometry optimization calculations at 90° each H–C–C bond angle and H–C–C–C dihedral angle was optimized individually producing a structure with perfect C_s symmetry. Final calculations at 90°, as well as those at 70 and 80°, were carried out by coupling symmetry related bond lengths, bond angles and dihedral angles.
(14) At 100° the H–C bond lengths, H–C–C bond angles, and H–C–C–C dihedral angles were individually optimized. After two complete cycles of optimization, the predicted geometry was approaching that with a plane of symmetry coincident with the C_1–C_2–C_3 plane. Instead of cycling further, the H_3–C_3 and H_4–C_3 bond lengths, H_3–C_3–C_2 and H_4–C_3–C_2 bond angles, and the H_3–C_3–C_2–C_1 and H_4–C_3–C_2–C_1 dihedral angles were symmetry coupled and optimized. This latter procedure was used at angles of 120–180°.
(15) For a thorough review of the stereochemical aspects of the ring opening of cyclopropylidenes see ref 7.
(16) Although in general the structures were optimized using the STO-3G minimal basis set, the results of the STO-3G calculations on the triplet energy surface indicated considerably greater contributions of higher spin states to the triplet wave function than in the 4-31G extended basis set as indicated by the value of $\langle S^2 \rangle$, particularly from 40% ring opening to allene. Therefore, 4-31G geometry optimization calculations were carried out on **1T**, at 40% ring opening, and for bent planar allene. The geometries resulting from these calculations, however, were only negligibly different from the STO-3G optimized structures, and geometry optimization at the other points on the triplet surface were carried out using the STO-3G basis set with the final energies being calculated using the 4-31G extended basis set.
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(19) Because of the small effect of incorporation of CI on the energies in the cyclopropyl cation calculations it was not considered worthwhile to incorporate CI into the present calculations.
(20) The application of Koopmans' theorem to the cation and radical pair in ref 17 assumes that the two species have identical structures, i.e., planar cation and radical centers. However, in the case of the cyclopropyl radical, EPR[21] and stereochemical studies[22] involving the cyclopropyl radical have been interpreted in terms of a nonplanar radical center with a low energy barrier to inversion. This does not invalidate the comparisons made between **1T** and the cyclopropyl radical as during the ring opening of the cyclopropyl radical planarity must be achieved along the reaction coordinate. Such a change in geometry would result in an increase in the activation energy for ring opening of the radical over that calculated on the basis of a planar radical in ref 17.
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Ab Initio Molecular Orbital Study of the Geometries, Properties, and Protonation of Simple Organofluorides[1]

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Abstract: SCF calculations with minimal, STO-3G, and extended, 4-31G, basis sets have been used to study the geometries and properties of the simple alkyl fluorides, HF to *t*-BuF, and vinyl fluoride. Particular emphasis is placed on examining the corresponding protonated fluorides in order to better understand the gas-phase behavior of these species as well as to provide insight into the solvation of carbonium ions in a superacid medium such as liquid HF. In contrast to an earlier study of alkyl chlorides, computed properties for the protonated fluorides are poorly described with the minimal basis set calculations. This necessitates limited geometry optimization at the 4-31G level to obtain reasonable agreement with experimental proton affinities and carbonium ion–FH dissociation energies (ΔE_s). The small ΔE_s values (<8 kcal/mol) for protonated isopropyl and *tert*-butyl fluorides account for the inability to observe these ions in ICR experiments and provide evidence for the weak solvation of secondary and tertiary carbonium ions in superacid solutions. It is also found that an HF binds to bisected ethyl cation more strongly than the bridged ethyl cation by 4 kcal/mol. Although this is consistent with previous work, the conclusion could be modified by a more sophisticated theoretical treatment. As an exception, vinyl fluoride is predicted to protonate on carbon rather than fluorine; the reason is illuminated by a simple frontier orbital analysis. Various correlations involving the properties of the fluorides are noted, while differences in the behavior of chlorides and fluorides can usually be ascribed to the greater basicity and weaker electronegativity of chlorine.

The current interest in chemistry in the gas phase[2] and in superacid media[3] prompted a series of theoretical studies on the properties and protonation of alkyl chlorides.[4] Both semiempirical and ab initio molecular orbital calculations were used to explore the origins of variations in proton affinities and in the interactions between carbonium ions and HCl. The present work extends the analyses to alkyl fluorides and their protonated analogues. This order of presentation may at first seem unusual; however, it resulted from the fact that neither semiempirical nor ab initio calculations with minimal basis sets yield adequate descriptions of protonated fluorides, whereas both approaches are suitable for the study of neutral and protonated alkyl chlorides.[4] As discussed below, greater sophistication is necessary in the ab initio calculations to obtain energetic results in reasonable agreement with experiment for protonated alkyl fluorides.

The detailed purposes of this paper are: (1) to examine the structures and thermodynamic stability of protonated alkyl fluorides in the gas phase; (2) to determine the extent of interaction between various carbonium ions and HF as a primitive model for solvation in a superacid medium; and (3) to seek out correlations involving the properties of the fluorides and to compare the results with similar data for chlorides. The molecules treated are the simple alkyl fluorides, HF to *t*-BuF, vinyl fluoride, and their protonated derivatives. The method of analysis employs single determinant, ab initio molecular orbital calculations with both a minimal STO-3G[5a] basis set and the extended, split-valence 4-31G[5b] basis. The computations were performed using the GAUSSIAN/74 program[6] on the CDC/6500 system at Purdue.

Several significant findings were made in the course of this research. Consistent with other studies of the protonation of bases containing first-row elements,[7] the protonated fluorides are much too bound at the STO-3G level which is witnessed by proton affinities (PAs) that are too high by 40–60 kcal/mol. The consequent errors in the geometries of the ions cause

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