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Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XI. Geometries and Energies of $C_3H_7^+$ Cations[1a]

L. Radom,[1b] J. A. Pople,*[1b] V. Buss,[1c,d] and P. v. R. Schleyer[1d]

Contribution from the Departments of Chemistry, Carnegie-Mellon University, Pittsburgh, Pennsylvania 15213, and Princeton University, Princeton, New Jersey 08540. *Received June 2, 1971*

Abstract: *Ab initio* molecular orbital theory has been used to study the geometries and energies of nine $C_3H_7^+$ cations. Optimized geometries for these species were determined using the minimal STO-3G basis set. The parent hydrocarbon, propane, is revealed to be a poor model for the carbon skeletons of the 2-propyl cation (IX), and for two conformations (I and II) of the methyl-staggered 1-propyl cation. The methyl-eclipsed 1-propyl cation (III) has a most peculiar structure with an 83.4° CCC bond angle, and quite unequal C–C bond lengths. This form, which alternatively can be regarded as a distorted corner-protonated cyclopropane, emphasizes the arbitrary nature of the division of carbocations into "classical" and "nonclassical" categories. The approximately one-electron C···C bonds in the corner-protonated (IV and V) and edge-protonated (VI) cyclopropanes have unusual lengths, 1.80–1.85 Å; lengthening is also observed for the C···H bonds in VI (1.32 Å). Relative energies were obtained by carrying out single calculations with the extended 4-31G basis set at the STO-3G optimized geometries. Only two potential minima in the $C_3H_7^+$ energy surface were found. These correspond to the 2-propyl cation (IX) and, oddly enough, to the distorted corner-protonated species (III) for which there is no precedent in the literature. However, the energy surface is indicated to be quite flat; only 0.5 kcal mol^{-1} separates III from IV, V, and I. Face-protonated cyclopropane (VII) is a very unstable structure. The popularly invoked edge-protonated cyclopropane (VI) is found to be the *second least stable* structure, lying about 10 kcal mol^{-1} in energy above III. This suggests that there should be an appreciably higher barrier for 1,3-hydride shifts compared with 1,2-methyl shifts in the 1-propyl cation, contrary to experimental findings. Possible reasons for this discrepancy are explored. Otherwise, the calculations are in good agreement with the available experimental evidence, *e.g.*, the 17 kcal mol^{-1} energy difference between the 1- and 2-propyl cations. Carbon 1s orbital energies were calculated for comparison with X-ray photoelectron spectral data of carbonium ions. Classical carbocations, such as I, show large differences in the 1s energies, but these differences are quite small in the symmetrically bridged structures IV and VI. The X-ray photoelectron spectrum of the 2-norbornyl cation is interpreted on this basis as favoring the symmetrical, corner-protonated structure.

There has been considerable recent interest in the structures and stabilities of $C_3H_7^+$ cations, both from an experimental and theoretical viewpoint.[2] Although both semiempirical[3–8] and *ab initio*[9–11] molecular

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[1] (a) A preliminary account of part of this work has been given in L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971). (b) Carnegie-Mellon University. (c) Princeton University Fellow, 1968–1969; American Cyanamid Fellow, 1969–1970. (d) Princeton University.

[2] For recent reviews, see (a) C. J. Collins, *Chem. Rev.*, **69**, 541 (1969); (b) C. C. Lee, *Progr. Phys. Org. Chem.*, 7, 129 (1970); (c) J. L. Fry and G. J. Karabatsos in "Carbonium Ions," Vol. 2, G. A. Olah and P. v. R. Schleyer, Ed., Interscience, New York, N. Y., 1970, Chapter 14.

[3] R. Hoffmann, *J. Chem. Phys.*, **40**, 2480 (1964).

[4] R. Sustmann, J. E. Williams, M. J. S. Dewar, L. C. Allen, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 5350 (1969).

[5] H. Fischer, H. Kollmar, H. O. Smith, and K. Miller, *Tetrahedron Lett.*, 5821 (1968).

[6] H. Kollmar and H. O. Smith, *ibid.*, 1833 (1970).

[7] H. Kollmar and H. O. Smith, *Angew. Chem., Int. Ed. Engl.*, **9**, 463 (1970).

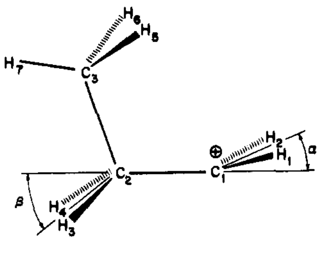

Figure 1. Methyl-staggered 1-propyl cation (I).

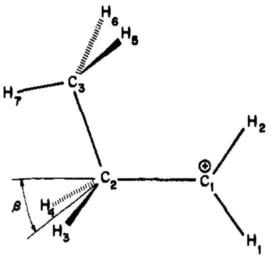

Figure 2. Methyl-staggered 1-propyl cation (II).

orbital calculations have been applied to the problem, there has been no extensive geometry optimization at the *ab initio* level. We believe that geometry optimization is critical for most of these species if reliable estimates of the relative energies of the different structural isomers are to be obtained, since many of the bond lengths and angles have unusual values. Again, there are serious reservations on the current use of semiempirical techniques with charged species and, in particular, these methods may artificially favor cyclic over open structures.[4]

We have therefore felt it desirable to perform *ab initio* molecular orbital calculations *with* geometry optimization on certain well-defined $C_3H_7^+$ structures. Complete geometry optimizations (subject only to specified symmetry restrictions) have been carried out for various forms of the methyl-staggered 1-propyl cation, methyl-eclipsed 1-propyl cation, 2-propyl cation and corner-, edge-, and face-protonated cyclopropanes and a partial optimization for the H-bridged form of the propyl cation. The geometries and energies of these cations are reported and discussed in this paper.

Method. Standard LCAO-SCF molecular orbital theory is used. The molecular orbitals ψ_i are taken as linear combinations of basis functions ϕ_μ

$$\psi_i = \sum_\mu c_{\mu i}\phi_\mu$$

Solution of the Roothaan equations[12] then leads to the coefficients $c_{\mu i}$ and the total energy for each nuclear configuration considered.

We make use of two basis sets ϕ_μ in this work. The first (STO-3G)[13] closely simulates a minimal basis (1s, 2s, 2p for C, 1s for H) set of Slater-type atomic orbitals. The standard exponents used here and full details of the STO-3G basis set are given in ref 13. This basis has already produced *geometries* in excellent agreement with experiment for a large number of neutral acyclic and cyclic molecules.[14-17] We have therefore used the STO-3G basis to determine optimized geometries for all the species considered here.

The second basis is the extended 4-31G basis set.[18] Here, the valence atomic orbitals are split into inner and outer parts and this feature gives the 4-31G basis built in flexibility with regard to the size and anisotropy of the electron distribution around each nucleus. This basis set (which is computorially more expensive than STO-3G) is the more successful in comparing the *energies* of isomeric systems.[15-20] We have therefore applied the 4-31G basis to the STO-3G optimized geometries to study the relative energies of the $C_3H_7^+$ species. This procedure has previously been used for the complete set of C_1 and C_2 hydrocarbons and their cations[15] and for C_3 neutral hydrocarbons.[16]

For each structure considered, we obtain the optimized geometry by specifying a symmetry that defines the particular structure and then minimizing the energy with respect to all remaining geometric parameters. The optimized geometries so determined are local potential minima for the specified symmetries.

Equilibrium Geometries[21]

Methyl-Staggered 1-Propyl Cation (I, II). We have considered two forms of the methyl-staggered 1-propyl cation. The first (I) is shown in Figure 1 and has its CCC plane bisecting the HC_1H angle. In the second conformation (II, Figure 2), the HC_1H angle lies in the CCC plane. All the geometric parameters in both these structures of C_s symmetry have been optimized.

Results for I are shown in Table I. It is generally assumed that the structures of "classical" carbonium ions resemble the structures of the parent hydrocarbons except for changes at the carbonium center. Our calculations reveal, however, that substantial differences are to be expected. In particular, the C_1–C_2 bond length is about 0.07 Å shorter in the 1-propyl cation (1.474) than in propane (1.541)[22] while the C_2–C_3 length is 0.05 Å longer. The CCC bond angle in the 1-propyl cation (101.5°) is about 11° smaller than in propane (112.4°). The distortions in this cation, relative to propane, correspond to movement toward a methyl-bridged species.

Also included in Table I are the theoretical geometric parameters for the corresponding conformation of the ethyl cation[22] (methyl group at C_3 in Figure 1 replaced by H). The two geometries are very similar but some small changes are evident. The C_1–C_2 bond length,

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[8] H. Kollmar and H. O. Smith, *Theor. Chim. Acta*, 20, 65 (1971).

[9] J. P. Petke and J. L. Whitten, *J. Amer. Chem. Soc.*, 90, 3338 (1968).

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[15] W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, 93, 808 (1971).

[16] L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.*, 93, 5339 (1971).

[17] W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *ibid.*, 93, 6377 (1971).

[18] R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 54, 724 (1971).

[19] W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, 92, 4796 (1970).

[20] L. Radom, W. J. Hehre, and J. A. Pople, *ibid.*, 93, 289 (1971).

[21] All bond lengths in this paper are in angströms and angles in degrees.

[22] Comparisons are made throughout this paper with corresponding results for propane, cyclopropane, and the ethyl cations and refer to the calculations in ref 16, 16, and 15 respectively.

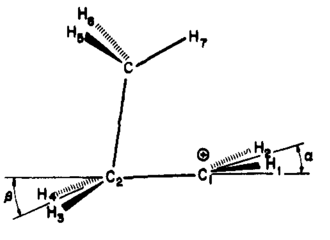

Figure 3. Methyl-eclipsed 1-propyl cation (III).

further reduced in the 1-propyl cation, is consistent with a small increase in the degree of double bond character in this bond.[10,23] There is increased nonplanarity at the carbonium center producing a more staggered-like structure.

Table I. Geometries[a–c] of Methyl-Staggered 1-Propyl Cation (I) and Ethyl Cation

	Methyl-staggered 1-propyl cation (I)	Ethyl cation[d]
C_1–C_2	1.474	1.484
C_2–C_3	1.592	
C_1–H_1	1.113	1.115
C_2–H_3	1.091	1.091
C_3–H_5	1.088	
C_3–H_7	1.089	
(C_1–C_3)	2.376	
$C_1C_2C_3$	101.5°	102.2°
$H_1C_1H_2$	116.5°	116.7°
$H_3C_2H_4$	112.5°	113.6°
$H_5C_3H_6$	110.6°	
$C_2C_3H_7$	104.9°	
$C_2C_3H_{56}$	129.7°	
α	5.4°	2.9°
β	48.1°	46.6°

[a] All distances in this paper are in ångströms. [b] The notation H_{AB} is used throughout this paper to denote a point on the bisector of H_ACH_B. [c] Some nonindependent geometric parameters of interest are included in parentheses in this and subsequent tables. [d] H at C_3 in Figure 1 from ref 15.

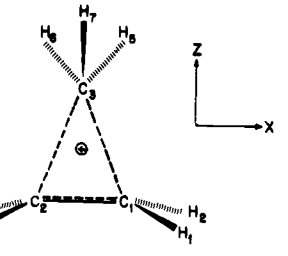

Figure 4. Corner-protonated cyclopropane (IV). θ, θ′ are angles between C_1–H_1, C_1–H_2, respectively, and the *XZ* plane; ϕ, ϕ′ are angles between the *XZ* projections of C_1–H_1, C_1–H_2, respectively, and the *X* axis.

The geometry of the cis conformation II is included in Table II and again compared with the appropriate conformation of the ethyl cation (methyl group at C_3 in Figure 2 replaced by H). Changing the conformation at C_1 produces interesting structural variations in the remainder of the molecule. The C_2–C_3 bond is no longer lengthened but is the same as in propane (1.541 Å). The C_1–C_2 bond is about as long as in the corresponding conformation of the ethyl cation and longer than in I. Both these bond lengths reflect the elimination of the C–C hyperconjugation in II.[10,23] Finally the CCC bond angle widens substantially to a value (115.7°) even larger than in propane.

Table II. Geometries of Methyl-Staggered 1-Propyl Cation (II) and Ethyl Cation

	Methyl-staggered 1-propyl cation (II)	Ethyl cation[a]
C_1–C_2	1.492	1.488
C_2–C_3	1.541	
C_1–H_1	1.115	1.115
C_1–H_2	1.115	1.115
C_2–H_3	1.103	1.101
C_3–H_5	1.087	
C_3–H_7	1.086	
(C_1–C_3)	2.569	
$C_1C_2C_3$	115.7°	112.9°
$C_2C_1H_1$	120.7°	120.6°
$C_2C_1H_2$	122.8°	122.7°
$H_3C_2H_4$	104.2°	105.9°
$H_5C_3H_6$	109.4°	
$C_2C_3H_7$	108.6°	
$C_2C_3H_{56}$	127.5°	
β	65.9°	60.9°

[a] H at C_3 in Figure 2. From ref 15.

Methyl-Eclipsed 1-Propyl Cation (III). The methyl-eclipsed 1-propyl cation (III, Figure 3) has C_s symmetry and the geometric parameters in Table III. Structure III differs from the methyl-staggered 1-propyl cation (I) in several ways. Rotation of the methyl group in I is accompanied by substantial changes in the carbon skeleton. Thus, the CCC angle is smaller (83.4° *vs.* 101.5°) giving a much closer approach to a methyl-bridged arrangement. This is accompanied by changes in C–C lengths. The C_2–C_1^+ bond to the carbonium center is further shortened (1.439 *vs.* 1.474) while the C_2–C_3 bond is further lengthened (1.632 *vs.* 1.592). Despite the closer approach of C_3 to C_1, the CH_2^+ group at C_1 is still bent upward toward C_3 although not quite as much as in I. There is weak but significant bonding between C_1 and C_3 and also C_1 and H_7 in III so this structure could alternatively be regarded as a *distorted corner-protonated cyclopropane.*

Table III. Geometry of Methyl-Eclipsed 1-Propyl Cation (III)

C_1–C_2	1.439	$C_1C_2C_3$	83.4°
C_2–C_3	1.632	$H_1C_1H_2$	117.5°
C_1–H_1	1.105	$H_3C_2H_4$	114.5°
C_2–H_3	1.088	$H_5C_3H_6$	113.1°
C_3–H_5	1.088	$C_2C_3H_7$	116.6°
C_3–H_7	1.102	$C_2C_3H_{56}$	121.4°
(C_1–C_3)	2.048	α	4.2°
		β	34.3°

Corner-Protonated Cyclopropane (Methyl-Bridged Form of the Propyl Cation) (IV, V). Corner-protonated cyclopropane is taken by definition to have the bridging carbon equidistant from the other two carbon atoms. Geometry optimization has been carried out for two conformations, IV (Figure 4) and V (Figure 5), both having C_s symmetry, leading to the results given in Table IV.

The long bridging C–C distances (1.803) should be noted. A comparison of these structures with the H-bridged form of the ethyl cation (methyl group at C_3

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(23) L. Radom, J. A. Pople, and P. v. R. Schleyer, unpublished results.

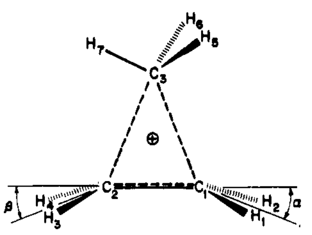


Figure 5. Corner-protonated cyclopropane (V).

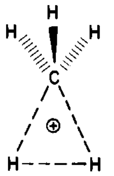
replaced by H) shows that the C_1–C_2 bond lengths are similar (1.399 *vs.* 1.403 in $C_2H_5^+$). These bond lengths are between normal single (1.54 for ethane) and double (1.31 for ethylene) bond values and are close to the value for benzene (1.39).[14] There is increased bending of the CH_2 plane (average values of around 11° compared with 2.5° in $C_2H_5^+$).

Table IV. Geometries of Corner-Protonated Cyclopropanes (IV and V)[a]

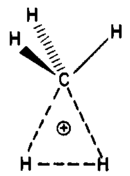
IV	C_1–C_2	1.399	$H_5C_3H_6$	105.4°
	C_2–C_3	1.803	$0\,C_3H_7$	109.5°
	C_1–H_1	1.093	$0\,C_3H_{56}$	123.0°
	C_1–H_2	1.093	θ	58.2°
	C_3–H_5	1.094	θ'	58.9°
	C_3–H_7	1.085	ϕ	15.3°
	(C_3–0)	1.661	ϕ'	6.4°
			($C_1C_2C_3$)	67.2°
V	C_1–C_2	1.399	$H_5C_3H_6$	113.9°
	C_2–C_3	1.803	$0\,C_3H_7$	107.7°
	C_1–H_1	1.092	$0\,C_3H_{56}$	129.3°
	C_2–H_3	1.094	$H_1C_1H_2$	117.3°
	C_3–H_5	1.088	$H_3C_2H_4$	117.5°
	C_3–H_7	1.098	α	11.4°
	(C_3–0)	1.661	β	11.0°
			($C_1C_2C_3$)	67.2°

[a] For convenience in defining certain parameters, the point 0 is taken at the midpoint of C_1–C_2.

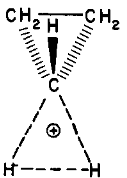
The most stable conformations of CH_5^+ (IV′, V′) have been shown[15,17,24] to have structures which correspond approximately to a methyl cation bonded to a hydrogen molecule. Our structures (IV, V) for corner-protonated cyclopropane are analogous to these, the hydrogen molecule fragment being replaced by ethylene. Alternative analogous structures (IV″, V″) for $C_3H_7^+$ can be postulated[25] which correspond to a cyclopropyl cation bonded to a hydrogen molecule. Structure IV″ has the same symmetry as IV so unless the potential surface in the vicinity of these structures has a *double* minimum (which is quite unlikely), our calculations indicate that IV″ should collapse directly to IV. We believe that both IV″ and V″ are likely to be considerably less stable than IV and V.



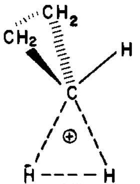
IV′



V′



IV″



V″

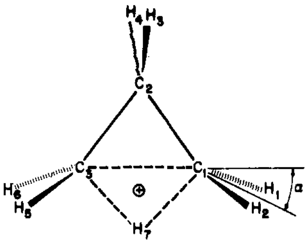


Figure 6. Edge-protonated cyclopropane (VI).

Edge-Protonated Cyclopropane (VI). This species (Figure 6) has C_{2v} symmetry and the calculated geometry shown in Table V. The C_2–C_1 and C_2–C_3 bond lengths (1.516) are close to the optimized C–C bond lengths (1.502) calculated for cyclopropane itself.[22] On the other hand, the C_1–C_3 bond is considerably longer. The values of the C_1–C_3 distances for this cation are consistent with data on corner-protonated cyclopropane and the H-bridged form of the ethyl cation and suggest that C–C and C–H bonds with approximately one electron have lengths which are typically about 1.80–1.85 and 1.30–1.35 Å, respectively. A partial optimization of the geometry of edge-protonated cyclopropane has been previously carried out by Petke and Whitten[9] with similar conclusions.

Table V. Geometry of Edge-Protonated Cyclopropane (VI)

C_1–C_2	1.516	HC_1H	117.8°
C_1–C_3	1.849	HC_2H	114.0°
C_1–H_1	1.095	α	28.6°
C_2–H_3	1.087	$C_1C_2C_3$	75.1°
C_1–H_7	1.315		

Face-Protonated Cyclopropane (VII). The optimized geometry for this species (Figure 7) of C_{3v} symmetry is given in Table VI. The C–C bonds (1.544) are longer than those in cyclopropane (1.502). In addition, the bridging C–H distance is longer than in edge-protonated cyclopropane or the H-bridged ethyl cation.

Table VI. Geometry of Face-Protonated Cyclopropane (VII)[a]

C_1–C_2	1.544	θ	51.9°
C_1–H_1	1.106	θ'	57.5°
C_1–H_2	1.089		
C_1–H_7	1.429		
(0–H_7)	1.117		

[a] 0 is the center of the CCC triangle.

H-Bridged Propyl Cation (VIII). Since the H-bridged form of the propyl cation (VIII, Figure 8) has no implied symmetry and therefore a large number of unique geometric parameters, complete geometry optimization was not attempted. Instead, the geometry was taken as that for the H-bridged form of the ethyl cation[22] in which a hydrogen atom is replaced by a regular tetrahedral methyl group (at C_3). Thus the

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(24) V. Dyczmons, V. Staemmler, and W. Kutzelnigg, *Chem. Phys. Lett.*, 5, 361 (1970).

(25) G. A. Olah, private communication.

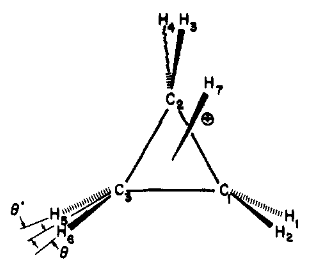

Figure 7. Face-protonated cyclopropane (VII).

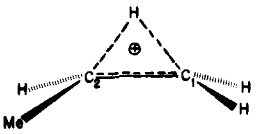

Figure 8. H-Bridged propyl cation (VIII).

bridging hydrogen was assumed to be equidistant from C_1 and C_2. The C_2–C_3 distance and $C_1C_2C_3H$ dihedral angle were then both optimized giving values of 1.533 Å and 12.0° (rotation of a C–H toward the bridging hydrogen), respectively. Although this approach is somewhat justified in view of the close correspondence between the geometries of the 1-propyl and 2-propyl cations and the analogous forms of the ethyl cation (in which a methyl group is replaced by H), it should be kept in mind that structure VIII is only partially optimized.

2-Propyl Cation (IX). Preliminary calculations on the 2-propyl cation using standard values[26] of bond lengths and angles suggest that the conformation of lowest energy has HCCC cis and CCCH cis and has C_{2v} symmetry as shown in Figure 9. Optimization of this geometry leads to the results in Table VII. Again we have included the geometry of the corresponding conformation of the ethyl cation (methyl group at C_3 in Figure 9 replaced by H) for comparison. The two geometries are very similar. The lengthening of the C–C bonds in the 2-propyl cation (1.500 *vs.* 1.488) is consistent with reduced hyperconjugation per C–C bond.[23] The CCC angle (126°) in IX is larger than the trigonal value, perhaps due to the steric effect of the methyl group. Movement of H_4 perpendicular to the CCC plane leads to an increase in calculated energy indicating the preferred planarity at the carbonium center (C_2).[4,27]

Table VII. Geometries of 2-Propyl (IX) and Ethyl Cations

	2-Propyl cation (IX)	Ethyl cation[a]
C_1–C_2	1.500	1.488
C_1–H_1	1.097	1.101
C_1–H_3	1.087	1.088
C_2–H_4	1.113	1.115
(C_1–C_3)	2.674	
$C_1C_2C_3$	126.0°	122.7°
$H_1C_1H_2$	106.6°	105.9°
$C_2C_1H_3$	112.6°	112.9°
$C_2C_1H_{12}$	119.8°	119.1°

[a] H at C_3 in Figure 9. From ref 15.

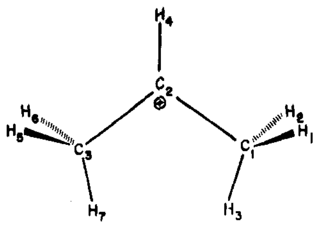

Figure 9. 2-Propyl cation (IX).

Calculated Relative Energies of the $C_3H_7^+$ Cations

The STO-3G and 4-31G energies for optimized geometries (given in the preceding section) of the $C_3H_7^+$ cations are listed in Table VIII. The broad conclusions from the STO-3G and 4-31G calculations are essentially the same. These are (1) the 2-propyl cation (IX) is the lowest energy form of $C_3H_7^+$; (2) the 1-propyl cations (I–III), corner-protonated cyclopropanes (IV, V), and H-bridged propyl cation (VIII) have similar energies; edge-protonated cyclopropane (VI) has a higher energy; and (3) face-protonated cyclopropane (VII) is a highly unfavorable geometry for $C_3H_7^+$.[28]

The most stable conformation of the methyl-staggered 1-propyl cation is predicted to be the C_s form (I) in which the CCC plane bisects the HCH angle at the carbonium center. This is favored over the other C_s conformation (II) with CCC and HCH coplanar by 1.35 (STO-3G) and 1.98 (4-31G) kcal mol^{-1}. This result agrees with previously reported calculations[10,11] in which geometry optimization was not carried out, although the magnitude of the rotational barrier is slightly lower.

Corner-protonated cyclopropane with a methyl C–H bond in a plane perpendicular to the CCC plane (IV) is very slightly favored over the conformation in which the methyl C–H lies in the CCC plane (V). The small energy difference between IV and V (0.1 kcal mol^{-1}) corresponds to the barrier to rotation of the methyl group and is compatible with low values generally observed for such sixfold barriers.

The methyl-eclipsed 1-propyl cation (III) is predicted (at the 4-31G level) to be slightly more stable than either the methyl-staggered or corner-protonated forms. We have made a moderately detailed study of the STO-3G potential surface connecting structures I, III, IV, and V. The results are shown schematically in Figure 10. The potential surface has not been investigated in detail at the 4-31G level. However, if we assume that structures I and III are also minima on this surface when C_s symmetry is maintained (*i.e.*, methyl group rotation is not permitted), a possible set of potential curves is illustrated in Figure 11.

Several interesting points are brought out by Figures 10 and 11. These concern the migration of the methyl group in 1,2-methyl shifts. If C_s symmetry is maintained, a 1,2-methyl shift converts I not to its mirror image, but to $\overline{\text{III}}$, the mirror image of III (solid line in Figures 10 and 11). However, if methyl rotation is allowed, the lowest energy path for conversion of I to its mirror image $\overline{\text{I}}$ passes through the corner-protonated form IV as a transition state. This is suggested by the

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[26] From J. A. Pople and M. Gordon, *J. Amer. Chem. Soc.*, **89**, 4253 (1967), together with C^+–C = 1.49, C^+–H = 1.12.

[27] J. E. Williams, R. Sustmann, L. C. Allen, and P. v. R. Schleyer, *ibid.*, **91**, 1037 (1969).

[28] Carbon analogs of face-protonated cyclopropanes have been investigated recently and are also highly unfavorable energetically: R. C. Bingham, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, **92**, 3471 (1970); S. A. Sherrod, R. G. Bergman, G. J. Gleicher, and D. Morris, *ibid.*, **92**, 3469 (1970).

Table VIII. Energies of $C_3H_7^+$ Cations

Cation	STO-3G Total (hartrees)	STO-3G Rel (kcal mol^{-1})	4-31G Total (hartrees)	4-31G Rel (kcal mol^{-1})
2-Propyl (IX)	−116.02765	0	−117.20864	0
Methyl-eclipsed 1-propyl cation (III)	−115.99500	20.5	−117.18167	16.9
Corner-protonated cyclopropane (IV)	−115.99130	22.8	−117.18109	17.3
Methyl-staggered 1-propyl cation (I)	−115.99631	19.7	−117.18092	17.4
Corner-protonated cyclopropane (V)	−115.99117	22.9	−117.18091	17.4
H-Bridged propyl cation (VIII)	−115.98959	23.9	−117.17957	18.2
Methyl-staggered 1-propyl cation (II)	−115.99416	21.0	−117.17776	19.4
Edge-protonated cyclopropane (VI)	−115.98450	27.1	−117.16541	27.1
Face-protonated cyclopropane (VII)	−115.77102	161.0	−116.98612	139.6

dashed curves in Figures 10 and 11. It should be noted that the lowest energy path in the STO-3G surface (Figure 10) connects methyl *staggered* forms (I, $\bar{\text{I}}$), whereas the suggested 4-31G surface connects methyl *eclipsed* forms (III, $\overline{\text{III}}$).

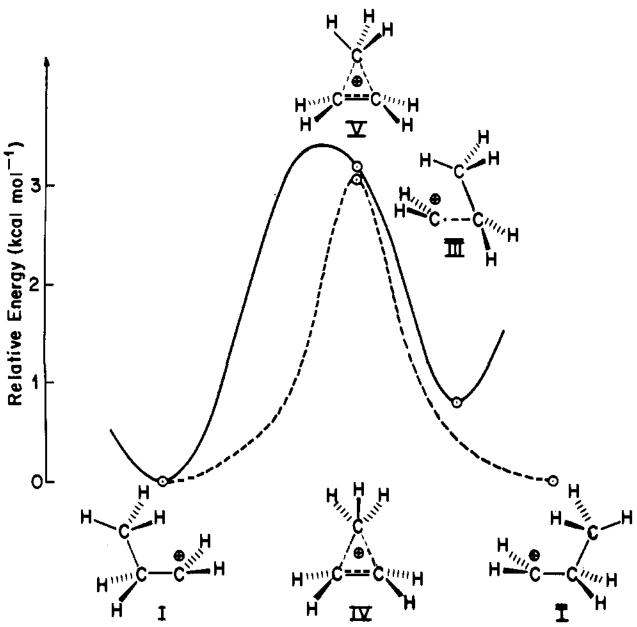

Figure 10. STO-3G potential functions for 1,2-methyl shifts: (——) C_s symmetry maintained (I → V → $\overline{\text{III}}$); (- - -) methyl rotation permitted (I → IV → $\bar{\text{I}}$).

Our calculated energies for edge-protonated cyclopropane (VI) are somewhat higher than for the 1-propyl cations or corner-protonated cyclopropanes. In order to test whether this species is located at a saddle point or local potential minimum on the STO-3G surface, calculations were performed on a structure in which the bridging hydrogen was moved off-center. The ratio of the length of the projection of the bridging C–H bond on the C–C bond was held constant at 0.475 (this ratio is, of course, 0.5 in edge-protonated cyclopropane itself) and the remaining parameters were optimized. The resultant energy was lower than that calculated for edge-protonated cyclopropane indicating that the latter lies at a saddle point. A 1,3-hydride shift in the 1-propyl cation proceeding *via* an edge-protonated cyclopropane transition state requires 7 (STO-3G)–10 (4-31G) kcal mol^{-1}.

The geometry of the H-bridged propyl cation VIII (considered as the transition state or intermediate in the conversion of the 1-propyl cation to the 2-propyl cation) is not determined at all by symmetry since the structure has no reflection plane. Our approximation to this species is a structure based on the H-bridged ethyl cation in which one of the hydrogens is replaced by a methyl group. The energies of this species suggest that a 1,2-hydride shift [calculated[15] to require 11.4 (STO-3G) and 6.8 (4-31G) kcal mol^{-1} in the ethyl cation] is facilitated by β-methyl substitution. Our estimates of this activation energy for the 1-propyl cation to 2-propyl cation interconversion are 4 (STO-3G) and 1 (4-31G) kcal mol^{-1}.

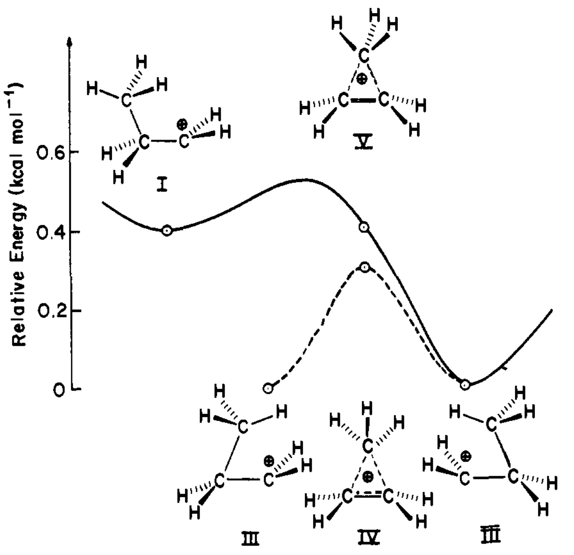

Figure 11. 4-31G potential functions for 1,2-methyl shifts: (——) C_s symmetry maintained (I → V → $\overline{\text{III}}$); (- - -) methyl rotation permitted (III → IV → $\overline{\text{III}}$).

In summary, our 4-31G calculations suggest that the $C_3H_7^+$ energy surface has two local minima, the 2-propyl cation (IV) and a species (III), which may either be described as a distorted corner-protonated cyclopropane or distorted 1-propyl cation. 1,2-Methyl shifts in III occur *via* a corner-protonated cyclopropane transition state (IV) and require little activation energy (0.4 kcal mol^{-1}). The calculations indicate that more energy is required for 1,3-hydride shifts in III. These occur *via* an edge-protonated cyclopropane transition state (VI) with an activation energy of approximately 10 kcal mol^{-1}. 1,2-Hydride shifts in the 1-propyl cation (I) should occur easily, the approximate activation energy being 1 kcal mol^{-1}.

It should be emphasized that these are theoretical predictions applying to the gas phase. They are, of course, subject to the inherent limitations of the theoretical method and may involve errors of a few kilocalories per mole. In particular, for the neutral molecules which have previously been studied by *ab initio* molecular orbital theory using extended[29] basis sets, it has always been found that the energies of cyclic relative to acyclic molecules are overestimated.[16,19,30,31] Moreover, with the limited amount of data currently available, it seems that this deviation is largest when the cyclic system is most compressed.[16] For cyclopropane compared with propene, the error is 6 kcal mol^{-1}. We suggest that for the cations reported here, this type of error is likely to be most serious for the edge protonated cyclopropane (VI) and is probably less than 6 kcal mol^{-1}.

Carbon 1s Orbital Energies

Techniques have recently been developed for measuring the X-ray photoelectron spectra (ESCA) of carbonium ions.[32] The measured 1s binding energies may provide information on structure and bonding in these cations which usefully supplements that available from other physical methods.

Calculated[33] (STO-3G) and experimental[32] carbon 1s orbital energy differences between methyl and cationic carbons for the *tert*-butyl cation are in moderate agreement. We report here the 4-31G calculated 1s orbital energies for the $C_3H_7^+$ cations (Figure 12).

The 1s energies of the "classical" carbon atoms carrying a formal positive charge (315.45–315.88 eV) in I, II, and IX are notably higher than the orbital energies of all other types of carbons. The shifts are so large (2–5 eV) that identification of such classical cations despite the present experimental resolution limitations of the method[32] should be a simple matter. In contrast, the 1s energies of the various kinds of carbons in the symmetrically bridged species IV and VI are similar, differing by only 1–2 eV. The 1s orbital energy spread in III and VIII is somewhat larger (~3 eV).

Our calculations thus indicate that the X-ray photoelectron method should have considerable potential for differentiating between classical and nonclassical (bridged) carbocation structures (*vide infra*).[34] There is, however, no exact correlation between our calculated 1s orbital energies with calculated atomic charges. While higher 1s energies are often associated with carbons that carrry a formal positive charge (as in I, II, and IX), this is not always the case. For example, the carbon 1s orbital energies in corner- (IV) and edge- (VI) protonated cyclopropanes are quite similar, whereas the atomic charge distributions are quite different.

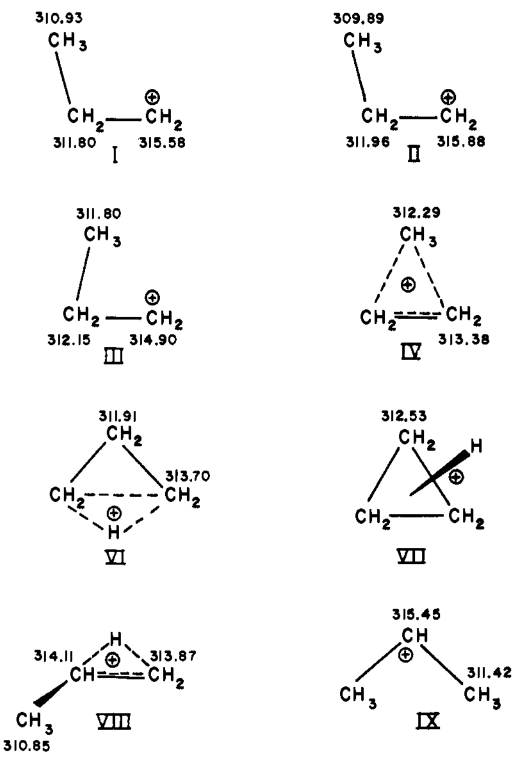

Figure 12. Carbon 1s orbital energies (4-31G, eV) for $C_3H_7^+$ cations.

Previous Theoretical Work

Most of the previously reported theoretical work on the $C_3H_7^+$ isomers has been carried out with a minimal amount of geometry variation.[3,4,9] These studies suffer from the fact that the conclusions drawn regarding the relative energies depend on the assumed geometries of the cations. From the results reported earlier in this paper, it may be seen that many of the bond lengths and angles have unusual values. It is clear that in the absence of geometric data on very similar systems, optimization of all geometric parameters is highly desirable.

The only previous *ab initio* study of the relative energies of structural isomers of $C_3H_7^+$ is that of Petke and Whitten.[9] With limited geometry variation, they found that edge protonation in cyclopropane was much more favorable than face protonation. In addition, they found that their calculated energy increased when the bridging hydrogen in edge-protonated cyclopropane was moved off center, thus concluding that this structure is located at an energy minimum. Our experience has shown that such a test for an energy minimum is invalid unless the displacement is accompanied by careful optimization of the remaining geometric parameters. In particular, we find here that distortion from the symmetric edge-protonated structure leads to an energy *lowering* when variation in other geometric parameters is carried out indicating that this is *not* an energy minimum (*vide supra*).

CNDO and INDO studies of the $C_3H_7^+$ cations in which geometry optimization has been carried out have recently been reported by Kollmar and coworkers.[5–8] The geometries they obtain are similar to those found

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(29) This statement does not always apply to *minimal* basis set calculations (see, *e.g.*, ref 16) since an additional effect (the poor description of double and triple bonds compared with single bonds) is involved. It *does* apply in these cases if cyclic molecules are compared with acyclic molecules containing the *same* types of bonds.[19]

(30) S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, 14, 305 (1969).

(31) L. C. Snyder and H. Basch, *J. Amer. Chem. Soc.*, 91, 2189 (1969).

(32) G. A. Olah, G. D. Mateescu, L. A. Wilson, and M. H. Gross, *ibid.*, 92, 7231 (1970).

(33) L. Radom, J. A. Pople, and P. v. R. Schleyer, unpublished results.

(34) G. A. Olah, *J. Amer. Chem. Soc.*, submitted for publication, and private communication.

here except that bridging C–H and C–C distances are consistently shorter than our values. However, their relative stabilities disagree with our results in several instances. For example, the CNDO work[6] predicts the lowest energy form of $C_3H_7^+$ is edge-protonated cyclopropane (VI) which is 11 kcal mol^{-1} more stable than the corner-protonated form (IV) and 14 kcal mol^{-1} more stable than the 2-propyl cation (IX). Again, the H-bridged propyl cation (VIII) is calculated by CNDO[5] to be 19 kcal mol^{-1} more stable than the 1-propyl cation (I) which differs considerably from our result. It is possible that this preference for cyclic structures is (partially at least) an artifact of the method used[4,35] since the same CNDO and INDO calculations are not successful in predicting the relative energies of *neutral* cyclic and acyclic molecules.[36] In addition, they predict the H-bridged form of the ethyl cation to be more stable than the classical cation[7] in contrast to the results of several *ab initio* calculations.[4,15,37–39]

The various theoretical methods all agree that face-protonated cyclopropane (VII) is highly unfavorable[3–6,9] and also they give similar differences in energy between the 1-propyl and 2-propyl cations.[4,6]

Effect of Methyl Substitution on Cation Stabilities

The energy difference between the 1-propyl and 2-propyl cations derived from a recent electron impact study[40] is 16 kcal mol^{-1}. This is close to both our STO-3G (19.7 kcal mol^{-1}) and 4-31G (17.4 kcal mol^{-1}) values for the I–IX energy difference.

It is of considerable interest to examine the energies of the 1-propyl, 2-propyl, and H-bridged propyl cations and their C_2 analogs in terms of the effect of methyl substitution on the stabilities of cations. Firstly, we discuss substitution in the methyl cation itself. The energy change in the hydride transfer reaction (eq 1)

$$R^+ + CH_4 \longrightarrow RH + CH_3^+ \qquad (1)$$

is useful in this respect. For example, when R is CH_3CH_2 the energy change in (1) shows how much the methyl cation is stabilized by methyl substitution (to give the ethyl cation) relative to the stabilization of methane to give ethane. Some results for various R are given in Table IX.

Table IX. Energy Changes (kcal mol^{-1}) for the Reaction $R^+ + CH_4 \rightarrow RH + CH_3^+$

	Calcd[a]		
R	STO-3G	4-31G	Exptl[b]
Ethyl	30.9	29.9	40
1-Propyl (I)	35.9	35.0	46
2-Propyl (IX)	55.6	52.4	62

[a] Throughout this paper, total energies for the C_1 and C_2 molecules and ions are from ref 15 and for C_3 molecules from ref 16. [b] These values and those in Table X are calculated from $\Delta H_f°$ (298°) values without vibrational or temperature corrections. $\Delta H_f°$ (298°) values for cations are from ref 40, for neutral molecules as quoted in ref 19.

The STO-3G and 4-31G values are in close agreement but are consistently lower (by about 10 kcal mol^{-1}) than the experimental. Ethyl substitution on the methyl cation (to give the 1-propyl cation) leads to a small additional stabilization compared to methyl substitution. Dimethyl substitution (to give the 2-propyl cation) leads to considerably more stabilization but less than twice the monomethyl value.

A second important consideration is the effect of methyl substitution on the open and H-bridged forms of the ethyl cation given by the energy change in eq 2.

$$C_3H_7^+ + C_2H_6 \longrightarrow C_3H_8 + C_2H_5^+ \qquad (2)$$

Both the STO-3G and 4-31G calculations predict the heats of this reaction quite well (Table X). Methyl substitution at the α carbon (giving the 2-propyl cation) has a greater stabilizing effect than substitution in the H-bridged ethyl cation, which, in turn, is more favorable than β substitution (to give the 1-propyl cation). Thus, as the site of methyl substitution moves away from the positive carbon, the stabilization due to substitution decreases. These results may provide a useful indication of the effect of methyl substitution on the stabilities of open and bridged cations in general.

Table X. Energy Changes (kcal mol^{-1}) for the Reaction $C_3H_7^+ + C_2H_6 \rightarrow C_3H_8 + C_2H_5^+$

		Calcd		
$C_3H_7^+$	$C_2H_5^+$	STO-3G	4-31G	Exptl
2-Propyl (IX)	Ethyl	24.7	22.5	22
H-Bridged propyl (VIII)	H-Bridged ethyl	12.2	11.1	
1-Propyl (I)	Ethyl	5.0	5.1	6

Proton Affinities

Proton affinities, *i.e.*, heats of the reaction

$$C_3H_7^+ \longrightarrow C_3H_6 + H^+$$

may be calculated for various $C_3H_7^+$–C_3H_6 pairs. The proton affinities for the process involving the most stable of these two forms, *i.e.*, the 2-propyl cation and propene, respectively, are 230.5 (STO-3G), 190.8 (4-31G), and 179 (experimental) kcal mol^{-1}. The calculated quantities are greater than the experimental as was observed previously[15] for the C_2 hydrocarbons and their cations.

Taking C_3H_6 as cyclopropane shows that the protons in all the protonated cyclopropanes are bound with respect to cyclopropane. The numerical values are 206.3 (STO-3G) and 187.1 (4-31G) kcal mol^{-1} for the distorted corner-protonated form (III), 203.9 (STO-3G) and 186.6 (4-31G) kcal mol^{-1} for corner-protonated cyclopropane (IV), 199.8 (STO-3G) and 176.9 (4-31G) kcal nol^{-1} for edge-protonated cyclopropane (VI), and 65.8 (STO-3G) and 64.4 (4-31G) kcal mol^{-1} for face-protonated cyclopropane (VIII). These are slightly higher than the values obtained from a previous *ab initio* study[9] but much lower than semiempirical results.[4,5]

Gas Phase Experimental Studies

In addition to the electron impact work[40] referred to above, relevant gas-phase radiolysis studies have been

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(35) E. I. Snyder, *J. Amer. Chem. Soc.*, **92**, 7529 (1970).

(36) H. Fischer and H. Kollmar, *Theor. Chim. Acta*, **13**, 213 (1969).

(37) J. E. Williams, V. Buss, L. C. Allen, P. v. R. Schleyer, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 2141 (1970).

(38) G. V. Pfeiffer and J. G. Jewett, *ibid.*, **92**, 2143 (1970).

(39) D. T. Clark and D. M. J. Lilley, *Chem. Commun.*, 549 (1970).

(40) F. P. Lossing and G. P. Semeluk, *Can. J. Chem.*, **48**, 955 (1970).

carried out.[41] These have shown that 1-propyl cations formed from *n*-butane rearrange within 10^{-10} sec to the 2-propyl cation or a protonated cyclopropane (c-$C_3H_7^+$), the former being favored under all conditions. The fact that there are at least two distinct $C_3H_7^+$ species was concluded, for example, from the reactions with *n*-butane.

$$CD_3CDCD_3^+ + n\text{-}C_4H_{10} \longrightarrow CD_3CDHCD_3 + C_4H_9^+$$

$$c\text{-}C_3D_7^+ + n\text{-}C_4H_{10} \longrightarrow CD_3CD_2CD_2H + C_4H_9^+$$

Formation of cyclopropane with ammonia suggested a protonated cyclopropane type structure for c-$C_3H_7^+$.

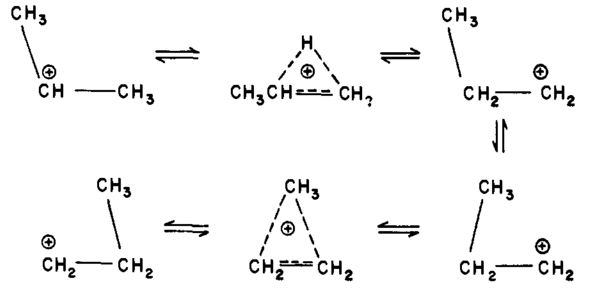
$$c\text{-}C_3H_7^+ + NH_3 \longrightarrow c\text{-}C_3H_6 + NH_4^+$$

All of these results are consistent with our calculations, the c-$C_3H_7^+$ cation corresponding to III. The additional observation that hydrogen scrambling in c-$CD_3CH_2CH_2^+$ (requiring 1,3-hydride shifts through an edge-protonated cyclopropane VI transition state) occurs easily suggests that our relative energy for edge-protonated cyclopropane is too high.

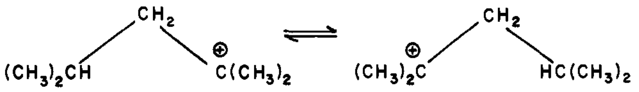
The observation that there is retention of the cis or trans configuration in the gas-phase tritiation of *cis*- and *trans*-1,2-dimethylcyclopropane has recently been proposed as evidence for the intermediacy of a protonated cyclopropane in this reaction.[42]

Experimental Data in Solution

Saunders and Hagen[43] have determined the activation energy for exchange of protons in the 2-propyl cation in SbF_5-based media to be 16.4 kcal mol^{-1}. Subsequent studies[44,45] have shown that scrambling of carbon atoms also occurs with the same activation energy. The results may be interpreted in terms of 1,2-hydride shifts and 1,2-methyl shifts as shown below (although some concerted process cannot be eliminated). Our 4-31G calculated relative energies for the possible intermediates (or transition states) are all similar (16.9–18.2 kcal mol^{-1}) and in good agreement with the observed activation energy. The additional agreement of both of these values with the gas-phase 1-propyl–2-propyl cation energy differences (see above) is noteworthy and suggests that isomeric carbonium ions may be solvated to comparable extents.[46]



Recent nmr studies[45,47] of the 2,4-dimethylpentyl cation have indicated activation energies for the 1,3-hydride shift of 9–10 and 6.5 kcal mol^{-1}.



These compare with our value of about 10 kcal mol^{-1} for the process in the analogous $C_4H_7^+$ cations. However, the effect of the methyl substituents on the activation energy has not been investigated in detail at this stage.

An unresolved problem is the nature of the "protonated cyclopropane" intermediate which appears to be involved in several types of reactions.[2,48] Experimental data have generally been interpreted in terms of edge-protonated cyclopropanes although, in most cases, corner-protonated cyclopropane is a viable alternative.

We find (at the 4-31G level) that edge-protonated cyclopropane (VI) has a relatively high energy, is not located at an energy minimum, and is therefore an unlikely candidate for a protonated cyclopropane intermediate. The theory suggests that the corner-protonated cyclopropanes (IV, V) are also not energy minima but since the energy differences between these structures (IV, V) and III are very small, they should not be completely ruled out as possible intermediates. We *do* find a potential minimum for the methyl-eclipsed 1-propyl cation (distorted corner-protonated cyclopropane, III) and suggest that *this* may be the intermediate in reactions involving so-called protonated cyclopropanes.

Previously, these reactions were discussed in terms of "classical" or symmetrical "nonclassical" cations and attempts were made to distinguish between these possibilities. The structure of III emphasized the arbitrary nature of division of cations into "classical" or "nonclassical" categories. Ordinarily, the structures of "classical" cations have been assumed to be similar in carbon skeleton to those of the parent hydrocarbons despite the fact that cations, as highly electron-deficient species, might well prefer quite different geometries. This is illustrated by many of the theoretical structures presented in this paper. III, in particular, is clearly intermediate between a "classical" structure and a "nonclassical" structure with the bridging group halfway across the C–C bond.

The available experimental data can be interpreted in terms of the distorted corner-protonated cyclopropane III as an intermediate. Two examples will be discussed.

When cyclopropane is solvolyzed in D_2SO_4, before equilibrium is reached the deuterium distribution in the 1-propanol product is[2,49–52] [$CH_2DCH_2CH_2OH$] > [CH_3CH_2CHDOH] > [CH_3CHDCH_2OH]. The reaction scheme shown in Figure 13, written in terms of methyl-eclipsed 1-propyl cations, is consistent with this ordering. However, the observation of significant amounts of CH_3CH_2CHDOH and CH_3CHDCH_2OH does suggest that our estimate of 10 kcal mol^{-1} for the energy of edge-protonated cyclopropane (VI) relative

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(41) S. G. Lias, R. E. Rebbert, and P. Ausloos, *J. Amer. Chem. Soc.*, **92**, 6430 (1970).

(42) F. Cacace, A. Guarino, and M. Speranza, *ibid.*, **93**, 1088 (1971).

(43) M. Saunders and E. L. Hagen, *ibid.*, **90**, 6881 (1968).

(44) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

(45) M. Saunders, private communication.

(46) See footnote 9 in J. L. Fry, J. M. Harris, R. C. Bingham, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **92**, 2540 (1970).

(47) D. M. Brouwer and J. A. Van Doorn, *Recl. Trav. Chim. Pays-Bas*, **88**, 573 (1969).

(48) For recent papers on this subject, see also (a) C. C. Lee and W. K.-Y. Chwang, *Can. J. Chem.*, **48**, 1025 (1970); (b) C. C. Lee and D. J. Woodcock, *J. Amer. Chem. Soc.*, **92**, 5992 (1970); (c) G. J. Karabatsos, C. Zioudrou, and S. Meyerson, *ibid.*, **92**, 5996 (1970).

(49) R. L. Baird and A. A. Aboderin, *ibid.*, **86**, 252 (1964).

(50) C. C. Lee and L. Gruber, *ibid.*, **90**, 3775 (1968).

(51) C. C. Lee, W. K.-Y. Chwang, and K. M. Wan, *ibid.*, **90**, 3778 (1968).

(52) N. C. Deno, D. LaVietes, J. Mockus, and P. C. Scholl, *ibid.*, **90**, 6457 (1968).

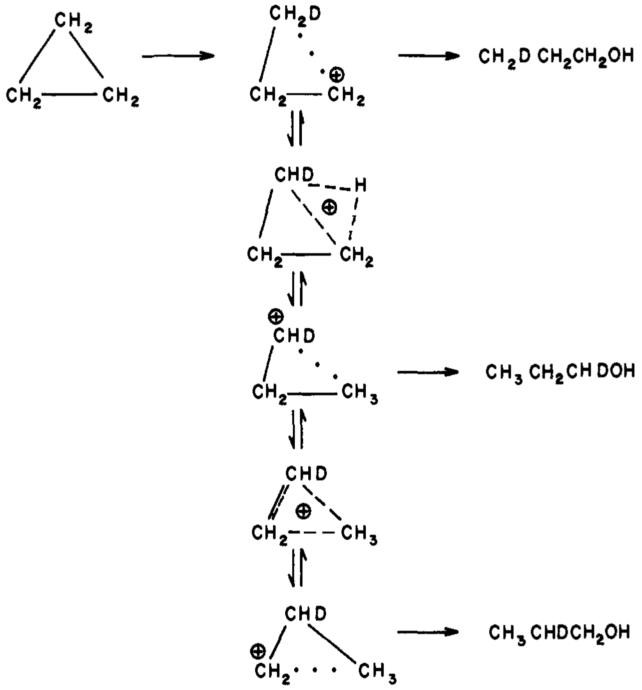
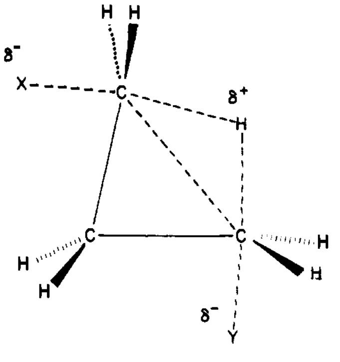


Figure 13. Scheme for solvolysis of cyclopropane in D_2SO_4 involving postulated distorted corner-protonated cyclopropanes (III).

to III is too high for this reaction in solution. A *symmetric* corner-protonated cyclopropane predicts that (in the absence of isotope effects) $[CH_3CH_2CHDOH] = [CH_3CHDCH_2OH]$.

A second example is the product distribution in reactions (solvolyses or amine deaminations) of 1-propyl derivatives labeled at C_1. The reaction scheme written in terms of III is shown in Figure 14. This scheme would predict that $[CH_3CH_2{}^*CH_2Y] > [CH_3{}^*CH_2CH_2Y] > [{}^*CH_3CH_2CH_2Y]$. Thus more label should be found at C_2 than at C_3 because a 1,2-methyl shift is calculated to occur more easily than a 1,3-hydride shift.

In general, however, label incorporation at C_2 and at C_3 is found to be approximately equal.[2,48a] There are a number of possible reasons for this discrepancy. (1) The energy for the 1,3-hydride shift may be overestimated by the theory (see discussion above). However, after making allowance for this effect, it is unlikely that the energy required for a 1,3-hydride shift (in the gas phase) is less than 4 kcal mol^{-1}. (2) A second possibility is that the 1,3-hydride shift is solvent assisted, *e.g.*, if it involves an intermediate of the type



(3) A third possibility is that the bridging hydrogen may be preferentially solvated (hydrogen bonded) by solvent.

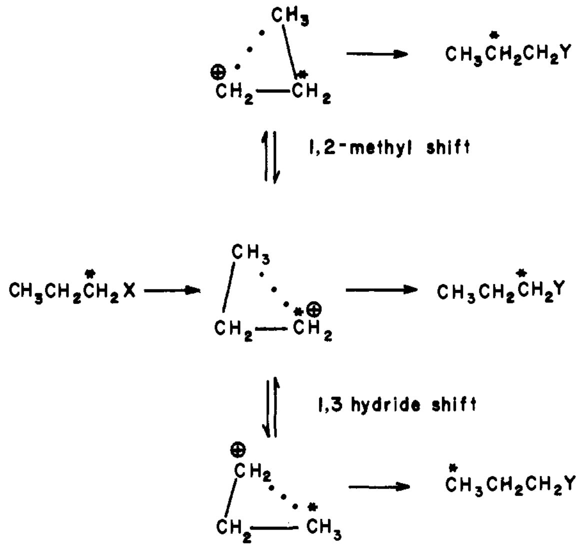
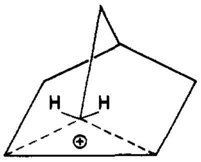


Figure 14. Scheme for reactions of 1-propyl derivatives labeled at C_1 involving postulated distorted corner-protonated cyclopropanes (III).

Generally, the so-called protonated cyclopropane intermediate has been found to give almost entirely 1-propyl product and cyclopropane.[2] This behavior contrasts with the large amount of 2-propyl product and propene formed from 1-propyl derivatives in a process *not* involving the protonated cyclopropane. We would suggest that the 1-propyl cation formed initially (which may be the methyl-staggered 1-propyl cation (I) or a highly solvated SN2 type species) can, with little or no activation energy, (1) react further with solvent to form a 1-propyl product, (2) undergo a 1,2-hydride shift giving 2-propyl product and propene, or (3) form a distorted corner-protonated cyclopropane (III). The reactions of III are different from those of I. Scrambling of carbons and protons in III occurring *via* 1,2-methyl and 1,3-hydride shifts, proton elimination to give cyclopropane, and reaction with solvent to give 1-propyl product apparently compete successfully with 1,2-hydride shifts in III so that little 2-propyl product or propene is formed.

Comparison with the 2-Norbornyl Cation

Analogy may be drawn between protonated cyclopropane and the nonclassical 2-norbornyl cation. Recent nmr and laser Raman studies by Olah and coworkers[53] have shown that the 2-norbornyl cation is a corner-protonated species.



This structure is analogous to the symmetrical corner-protonated cyclopropane IV, which has only a slightly higher energy (0.4 kcal mol^{-1}) than the distorted corner-protonated species III.

Additional evidence for a symmetric corner-protonated norbornyl cation structure comes from a compar-

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[53] G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Liu, *J. Amer. Chem. Soc.*, **92**, 4627 (1970).

ison between calculated and experimental carbon 1s orbital energies. The X-ray photoelectron spectrum of the 2-norbornyl cation has recently been measured[54] and shows a higher energy shoulder corresponding to two carbon atoms separated by about 1 eV from the lower energy signal of the remaining five carbons. Our calculations on $C_3H_7^+$ (Figure 12 and above) suggest that this result is more likely to arise from structures similar to our corner- (IV) or edge- (VI) protonated forms than from structures analogous to I, II, VII, or even III. Since the possibility of an edge-protonated structure for the norbornyl cation has been eliminated on the basis of other spectroscopic measurements,[53] the X-ray photoelectron results provide further support for the preferred symmetric corner-protonated 2-norbornyl cation form.

Another important result from the recent nmr study of the 2-norbornyl cation[53] is the value 5.9 kcal mol^{-1} determined for the activation energy for the 6,1,2-hydride shift. Our $C_3H_7^+$ calculations suggest that an edge-protonated norbornyl cation (protonated nortricyclene) may be the transition state in this hydride shift; if so, the energies of edge and symmetrical corner-protonated norbornyl cations should differ by 5.9 kcal mol^{-1}. This is somewhat lower than our energy difference (10 kcal mol^{-1}) for the corresponding protonated cyclopropanes, IV and VI, but, of course, these values in different systems are not directly comparable.

Finally, it is interesting to consider reasons for the preferred bridged structure for the 2-norbornyl cation. Experimental evidence[53,55] indicates that classical structures are generally preferred by simple secondary carbocations. Why is the 2-norbornyl cation an exception?

Although the 2-norbornyl cation system is too large for *ab initio* calculation with a full geometry search,[56] it is likely the bond lengths we have found for the $C_3H_7^+$ species will pertain reasonably well to other nonclassical cations. We call particular attention to the long (1.803-Å) one-electron C···C bonds in IV and V. Such long bonds in the symmetrically bridged 2-norbornyl cation would have important consequences energetically. Norbornane, with its distorted five-membered rings, is quite strained. Much of the estimated 17.55 kcal mol^{-1} strain energy[57] can be attributed to distortions from the normal bond angles. The *classical* 2-norbornyl cation suffers from the same problems. However, in the bridged structure with long 1.8-Å bonds, much relief of angle strain would be expected through flattening of the five-membered rings. This relief of strain may be the chief factor responsible for the favored bridged structure of the 2-norbornyl cation in contrast to the behavior of simple secondary cations where such strain-relief opportunities are not present.[58,59]

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(54) G. A. Olah and G. D. Mateescu, unpublished results.

(55) *E.g.*, G. A. Olah and J. Lukas, *J. Amer. Chem. Soc.*, **90**, 933 (1968); M. Saunders, E. L. Hagen, and J. Rosenfeld, *ibid.*, **90**, 6882 (1968).

(56) Even semiempirical calculations on the norbornyl system were carried out using only assumed geometries: G. Klopman, *ibid.*, **91**, 89 (1969).

(57) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *ibid.*, **92**, 2377 (1970).

(58) P. v. R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965).

(59) R. Howe, E. C. Friedrichs, and S. Winstein, *ibid.*, **87**, 379 (1965).