Molecular Orbital Theory of the Electronic Structure of Organic Compounds. XIX. Geometries and Energies of $C_3H_5^+$ Cations. Energy Relationships among Allyl, Vinyl, and Cyclopropyl Cations[1a]

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Abstract: The geometries and energies of various $C_3H_5^+$ carbocations have been determined by standardized *ab initio* molecular orbital methods. Geometries were optimized using the minimal STO-3G basis set. The extended 4-31G and especially the 6-31G* basis sets were employed to obtain more accurate energies. The latter basis, with d-type polarization functions on carbon, is known to give superior results when small rings are involved. The planar allyl cation (I) is the most stable $C_3H_5^+$ isomer; its perpendicular form II, corresponding to the transition state for methylene rotation, lies 35 kcal mol^{-1} (6-31G*) higher in energy. This value, or the stabilization of I relative to the ethyl cation (26 kcal mol^{-1}; 6-31G*), affords alternative estimates of the resonance energy in the allyl cation. The cyclopropyl cation (III), 39 kcal mol^{-1} less stable than I, is also found not to be an energy minimum. Disrotatory opening to the allyl cation (I) is favored; during this process the methine hydrogen moves out of the carbon plane and then returns. The conrotatory opening of III to I is complex, there being *two* local potential minima for some values of the methylene twist angle. The conrotatory process is at least 23 kcal mol^{-1} less favorable than disrotatory opening. The 2-propenyl cation (IV) is the only other stable minimum found on the $C_3H_5^+$ energy surface. IV is 17 kcal mol^{-1} less stable than the allyl cation (I), but an additional 17 kcal mol^{-1} barrier separates the two species (6-31G*). The 1-propenyl cation (VI) is 16 kcal mol^{-1} less stable than IV and should rearrange to the latter with little or no activation. Protonation of allene gives the 2-propenyl cation (IV) preferentially since it is much more stable than the perpendicular allyl cation (II). Barriers to 1,2 shifts are substantially higher in vinyl than in corresponding aliphatic systems (Table XIV). Due to the higher relative energy of the C≡C over the C=C bond, the protonation energies of acetylenes are only slightly higher than those of olefins. The ground states of vinyl chlorides and bromides are not stabilized; the solvolytic inertness of these halides is due to the fact that vinyl cations are generally 10–15 kcal mol^{-1} less stable than comparably substituted aliphatic cations (the inavailability of the SN2 mechanism to vinyl systems also plays a major role). The monovalent propylidyne (X) and propan-1-yl-3-ylidene (XII) cations also were examined. Unfortunately, these are indicated to be unstable, high-energy species incapable of experimental preparation. It is also predicted that the stereomutation of the 2-methylallyl cation (XXII) should proceed through the 1-methylcyclopropyl cation (XXV) rather than by nonconcerted rotation of one methylene as in the parent allyl system. Estimates of the heats of formation (otherwise unavailable) are provided for the cyclopropyl (257 kcal mol^{-1}), 2-propenyl (233 kcal mol^{-1}), and 1-propenyl (249 kcal mol^{-1}) cations. The estimated $\Delta H_f°$ of the allyl cation, 218 kcal mol^{-1}, is 8 kcal mol^{-1} lower than the experimental value. Otherwise agreement between experimental and theoretical energy differences is good (summarized in Tables XII and XIII).

The structures and stabilities of $C_3H_5^+$ cations are of considerable interest as these systems exhibit electronic features characteristic of many larger carbocations. Some aspects of their electronic structure have been examined in previous molecular orbital treatments,[2-4] but there has been no full study involving extensive geometry optimization at the *ab initio* level.

In this laboratory we have been engaged in a systematic investigation of the geometries and energies of small hydrocarbons and their cations using a uniform level of molecular orbital theory.[5-7] We report here the results of such a study of the $C_3H_5^+$ cations, which closely parallel those of recent work on $C_3H_7^+$.[6] Fully optimized geometries and relative energies have been determined for several well-defined $C_3H_5^+$ structures using a minimal basis set. These include various conformations of the allyl (I), 2-propenyl (IV, V), 1-propenyl (VI, VII), cyclopropyl (III), propylidyne (X, XI), and propan-1-yl-3-ylidene (XII) cations and corner protonated cyclopropene. In addition, calculations have been carried out on several structures representing intermediates or transition states for the interconversion of some of these cations.

Method

Standard self-consistent field molecular orbital theory

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(1) (a) Presented in part at the XXIII International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971; (b) Carnegie-Mellon University; (c) Princeton University.

(2) D. T. Clark and D. R. Armstrong, *Theor. Chim. Acta*, 13, 365 (1969). Also see ref 51a.

(3) S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **51**, 2528 (1969).

(4) (a) M. J. S. Dewar and S. Kirschner, *J. Amer. Chem. Soc.*, **93**, 4290, 4291, and 4292 (1971); (b) M. J. S. Dewar, XXIII International Congress of Pure and Applied Chemistry, Boston, Mass., Vol. 1, Butterworths, London, 1971, p 1; we are indebted to Professor Dewar for a preprint of this manuscript; (c) N. C. Baird, *Tetrahedron*, **28**, 2355 (1972); (d) M. Shanshal, *J. Chem. Soc., Perkin Trans. 2*, 335 (1972).

(5) (a) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971); see also (b) W. A. Lathan, W. J. Hehre, L. A. Curtiss, and J. A. Pople, *ibid.*, **93**, 6377 (1971); and (c) W. A. Lathan, L. A. Curtiss, W. J. Hehre, J. B. Lisle, and J. A. Pople, *Progr. Phys. Org. Chem.*, submitted for publication; (d) L. Radom, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 5339 (1971).

(6) (a) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 1813 (1971); (b) L. Radom, J. A. Pople, V. Buss, and P. v. R. Schleyer, *ibid.*, **94**, 311 (1972); (c) P. C. Hariharan, L. Radom, J. A. Pople, and P. v. R. Schleyer, *ibid.*, submitted for publication.

(7) (a) P. C. Hariharan, W. A. Lathan, and J. A. Pople, *Chem. Phys. Lett.*, **14**, 385 (1972); (b) P. C. Hariharan and J. A. Pople, *ibid.*, **16**, 217 (1972).

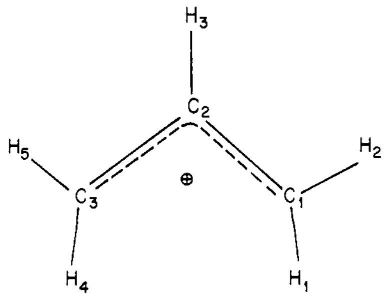


Figure 1. Allyl cation (I).

is used. The molecular orbitals (ψ_i) are written as linear combinations of basis functions (ϕ_μ).

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

Solution of the Roothaan[8] equations then yields the coefficients $c_{\mu i}$ and energy for each nuclear configuration considered.

We use three different basis sets in this work. The first is the minimal STO-3G basis with standard molecular exponents.[9] This has previously produced molecular geometries in close agreement with experiment for a large number of neutral cyclic and acyclic molecules.[5,10] We therefore use this basis set to determine optimized geometries for the $C_3H_5^+$ cations. The second, extended basis (4-31G)[11] is computationally more expensive than STO-3G but is more successful in predicting relative energies.[5,11-13] We have therefore used the 4-31G basis for single computations at the STO-3G optimized geometries to estimate the relative energies. One of the shortcomings of the 4-31G basis set has been that the energies of cyclic molecules are too high relative to their acyclic isomers. Recent calculations[7] have shown that there is considerable improvement if polarization functions are included in the basis set. In particular, results obtained with the 6-31G* basis for the neutral C_3 hydrocarbons are in close agreement with experimental data.[7b] This basis set is similar to the 4-31G basis except that for carbon, six Gaussian functions (instead of four) are used to represent the 1s orbital and, in addition, a set of d-type functions, each represented by a single Gaussian, is included. The 6-31G* basis unfortunately represents a substantial additional increase in computation time but is used here in a limited number of cases to obtain more reliable estimates of the relative energies.

The optimized geometry for each particular structure is obtained by specifying a symmetry (and possibly other restrictions) and then minimizing the energy with respect to all remaining geometric parameters. The optimized geometries determined in this manner are local minima for the specified symmetries. The STO-3G geometrical parameters so derived are listed in Tables I–X and the corresponding total energies in Table XI.

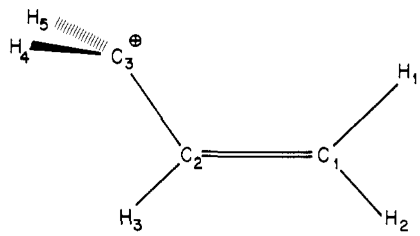


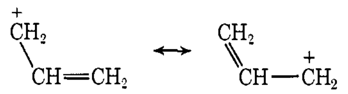
Figure 2. Perpendicular allyl cation (II).

Results and Discussion

Equilibrium Geometries.[14] **Allyl Cation (I).** The optimized geometry for the allyl cation (I, Figure 1) with C_{2v} symmetry is given is Table I. The C–C bond length (1.385) lies between the values for normal single (1.538 for ethane) and double (1.306 for ethylene) bonds and is close to that for benzene (1.39).[10] This result is expected because of the contributions from the valence structures

Table I. Geometry of Allyl Cation (I)

C_1–C_2	1.385	$C_1C_2C_3$	118.9°
C_1–H_1	1.100	$C_2C_1H_1$	122.0°
C_1–H_2	1.101	$C_2C_1H_2$	121.4°
C_2–H_3	1.084		
(C_1–C_3)	2.385		



The CCC angle (118.9°) is slightly less than the trigonal value. Previous *ab initio* calculations by Clark and Armstrong[2] yielded a C–C bond length of 1.37 when trigonal bond angles and C–H bond lengths of 1.08 were assumed. Peyerimhoff and Buenker[3] find CCC = 123°, assuming the values of all the remaining parameters. Movement of H_3 perpendicular to the CCC plane leads to an increase in calculated energy.

Perpendicular Allyl Cation (II). The optimized geometry of the perpendicular allyl cation (II, Figure 2) with C_s symmetry is given in Table II. This structure may be contrasted with the conformation of the planar allyl cation (I). In I, the methylene groups at C_1 and C_3 are coplanar and both C–C bonds are equivalent

Table II. Geometry of Perpendicular Allyl Cation (II)

C_1–C_2	1.313	$C_1C_2C_3$	126.4°
C_2–C_3	1.489	$C_2C_1H_1$	123.5°
C_1–H_1	1.088	$C_2C_1H_2$	119.7°
C_1–H_2	1.088	$C_1C_2H_3$	124.4°
C_2–H_3	1.095	$C_2C_3H_{45}$	176.5°
C_3–H_4	1.119	$H_4C_3H_5$	115.8°
(C_1–C_3)	2.502		

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(8) C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

(9) W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

(10) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, **52**, 4064 (1970).

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

(12) (a) R. Ditchfield, W. J. Hehre, J. A. Pople, and L. Radom, *Chem. Phys. Lett.*, **5**, 13 (1970); (b) W. J. Hehre, R. Ditchfield, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4796 (1970).

(13) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 289 (1971).

(14) In the discussion that follows, for consistency, comparisons of given parameters are made between calculated values rather than between calculated and experimental values even when the latter are available. All bond lengths in this paper are in ångströms.

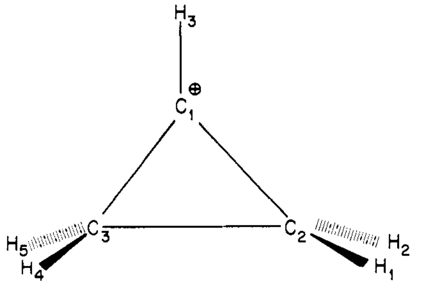

Figure 3. Cyclopropyl cation (III).

and intermediate between normal single and double bonds. In the perpendicular allyl cation (II) on the other hand, the bonds may be recognized distinctly as single (C_2—C_3) and double (C_1=C_2). The lengths of these bonds (1.489 and 1.313) are similar to those for normal C—C^+ (1.484 in $CH_3C^+H_2$) and C=C (1.305 for ethylene) bonds, respectively. The bonds at the carbonium center are not coplanar, the C^+H_2 group being slightly bent (3.5°) toward the C_2–H_3 bond leading to a staggered arrangement. The CCC angle (126.4°) is quite large, but is similar to that in propene (125.1°).[5d] Peyerimhoff and Buenker[3] find 132° with assumed values for the other parameters. Movement of H_3 out of the CCC plane again leads to an increase in calculated energy.

The perpendicular allyl cation (II) is considerably less stable than the planar form (I). The calculated energy difference (34.8 kcal mol^{-1} by 6-31G*) corresponds to the barrier to nonconcerted rotation of one of the CH_2 groups and is reasonably close to an indirect estimate from experimental data (38–43 kcal mol^{-1}).[15] A barrier of 42 kcal mol^{-1} has been obtained from a previous *ab initio* calculation.[3] Recent semiempirical estimates of this barrier are 38 and 29 kcal mol^{-1}, using two different methods.[4c] A MINDO/2 estimate of 14.1 kcal mol^{-1} appears to be unrealistically low.[4d]

Cyclopropyl Cation (III). The cyclopropyl cation (III, Figure 3) with imposed C_{2v} symmetry has the geometric parameters shown in Table III. The resulting structure is not very different from that of cyclopropane. The C_2–C_3 bond (1.518) is slightly longer and the C_2–C_1^+ bond (1.485) slightly shorter than the C–C bonds (1.502) in cyclopropane,[5d] as would be expected. The C_1–H_3 bond again prefers to lie in the CCC plane. Peyerimhoff and Buenker[3] calculate a $C_3C_1C_2$ angle of 80°, higher than our value (61.5°) but probably overestimated because of the assumption of the same C–C bond lengths as in the allyl cation.

Table III. Geometry of Cyclopropyl Cation (III)

C_1–C_2	1.485	($C_2C_1C_3$)	61.5°
C_2–C_3	1.518	$C_3C_2H_{12}$	156.9°
C_2–H_1	1.094	$H_1C_2H_2$	114.2°
C_1–H_3	1.110		

2-Propenyl Cation (IV, V). Two conformations of the 2-propenyl cation have been considered: first, the eclipsed form (IV, Figure 4a), in which $H_1C_1H_2$ lies in the $C_2C_3H_3$ plane, and, second, the *perpendicular* form (V, Figure 4b), in which $H_1C_1H_2$ is bisected by the $C_2C_3H_3$ plane. All geometric parameters in these structures (both of C_s symmetry) have been optimized with the results shown in Table IV.

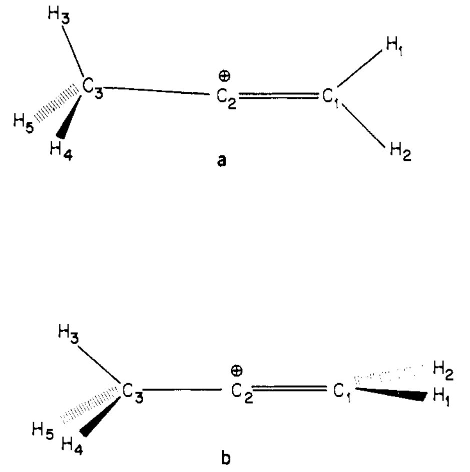

Figure 4. (a) 2-Propenyl cation, eclipsed conformation (IV). (b) 2-Propenyl cation, perpendicular conformation (V).

Table IV. Geometry of 2-Propenyl Cation (Cis Form IV and Perpendicular Form V)

IV	C_1–C_2	1.282	$C_1C_2C_3$	179.0°
	C_2–C_3	1.480	$C_2C_1H_1$	121.1°
	C_1–H_1	1.099	$C_2C_1H_2$	120.3°
	C_1–H_2	1.100	$C_2C_3H_3$	105.0°
	C_3–H_3	1.102	$C_2C_3H_{45}$	129.0°
	C_3–H_4	1.094	$H_4C_3H_5$	112.3°
V	C_1–C_2	1.282	$C_1C_2C_3$	180.0°
	C_2–C_3	1.481	$C_2C_1H_{12}$	180.0°
	C_1–H_1	1.100	$H_1C_1H_2$	118.6°
	C_3–H_3	1.092	$C_2C_3H_3$	111.7°
	C_3–H_4	1.098	$C_2C_3H_{45}$	120.5°
			$H_4C_3H_5$	107.7°

The –C^+=CH_2 fragment geometry in both conformations is very similar to that of the vinyl cation.[16] Thus the C=C bond length, somewhat shorter than double bonds in neutral hydrocarbons, is 1.282 in IV and V (compared with 1.281 in the vinyl cation), the C_1–H lengths are 1.099 and 1.100 (compared with 1.106), and the HC_1H angle is 118.6° (compared with 118.6°). The C–C^+ bond lengths (1.480 in IV and 1.481 in V) are close to the value in the ethyl cation (1.484) as well as the C(sp^3)–C(sp) single bond length in propyne (1.484).[5d] The bonds at the carbonium center in the vinyl cation are calculated to be collinear.[5a,17] Substitution of hydrogen by methyl in the vinyl cation reduces the symmetry (from C_{2v} to C_s) and is expected to lead to some deviation from linearity. This is apparently too small to be detected by our calculations for V, but for IV a small deviation of 1.0° from linearity is found. There is a significant difference between the $C_2C_3H_3$ angles in IV and V. In IV, the axis of the formally vacant 2p orbital at the positive carbon (which we shall call the 2p(C^+) orbital) is coplanar with C_3–H_3 and H_3 may move toward a bridging position.

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(15) V. Buss, R. Gleiter, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **93**, 3927 (1971).

(16) Comparisons are made throughout this paper with similar calculations on the vinyl cation reported in ref 5a.

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

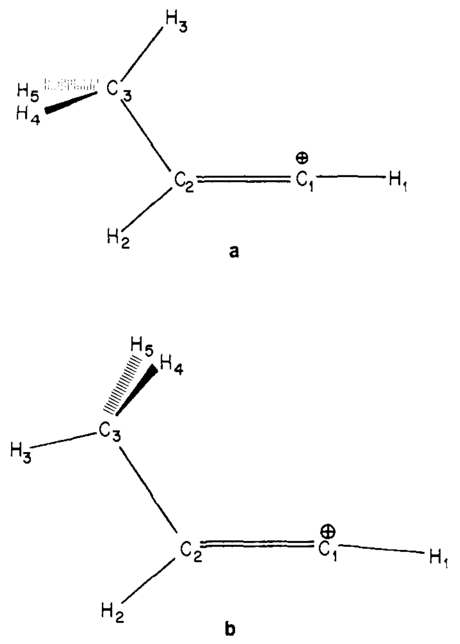

Figure 5. 1-Propenyl cation (a) CCCH cis (VI) and (b) CCCH trans (VII).

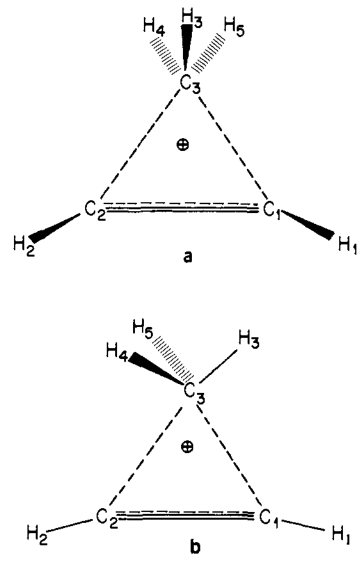

Figure 6. Corner-protonated cyclopropene (a) VIII and (b) IX.

Table V. Geometry of 1-Propenyl Cation (CCCH Cis VI and CCCH Trans VII)

VI	C_1–C_2	1.283	$C_1C_2C_3$	125.4°
	C_2–C_3	1.550	$C_2C_1H_1$	180.0°
	C_1–H_1	1.101	$C_1C_2H_2$	116.3°
	C_2–H_2	1.106	$C_2C_3H_3$	111.1°
	C_3–H_3	1.088	$C_2C_3H_{45}$	121.2°
	C_3–H_4	1.091	$H_4C_3H_5$	109.8°
	(C_1–C_3)	2.520		
VII	C_1–C_2	1.283	$C_1C_2C_3$	126.8°
	C_2–C_3	1.553	$C_2C_1H_1$	178.9°
	C_1–H_1	1.101	$C_1C_2H_2$	114.2°
	C_2–H_2	1.108	$C_2C_3H_3$	108.3°
	C_3–H_3	1.088	$C_2C_3H_{45}$	124.5°
	C_3–H_4	1.091	$H_4C_2H_5$	110.2°
	(C_1–C_3)	2.539		

This is reflected in a small $C_2C_3H_3$ angle (105.0°). On the other hand, the 2p(C^+) orbital in V is perpendicular to C_3–H_3 and therefore does not facilitate the bridging of H_3. Accordingly, the $C_2C_3H_3$ angle is somewhat widened (111.7°).

The most stable conformation of the 2-propenyl cation is IV. The energy difference between IV and V (0.08 kcal mol^{-1} by STO-3G, 0.09 kcal mol^{-1} by 4-31G) is very small and corresponds to the sixfold rotational barrier of the methyl group. Such sixfold barriers are almost invariably found[18] and calculated (as, for example, in toluene,[19] the ethyl cation,[5a,20] CH_5^+,[5b,21] and corner-protonated cyclopropane[6]) to be small.

1-Propenyl Cation (VI, VII). The 1-propenyl cation has also been considered in two conformations, the CCCH cis form (VI, Figure 5a) and the CCCH trans form (VII, Figure 5b). Optimized geometries for both these structures of C_s symmetry are listed in Table V. The geometries of the $>C{=}C^+{-}H$ portion of VI and VII are again similar to that of the vinyl cation. Thus, the $C{=}C^+$ bond length is 1.283 (*vs.* 1.281) and C^+H = 1.101 (*vs.* 1.106). The bonds at the positive carbon are indistinguishably close to linearity in VI (although strictly not allowed to be so by symmetry) but are bent by 1.1° in VII. In both conformations, the $C_1C_2C_3$ angle is large (125.4° in VI and 126.8° in VII) suggesting that there is little tendency toward forming a methyl-bridged structure. The C_2–C_3 bond (1.550 in VI, 1.553 in VII *vs.* 1.520 for the C(sp^3)–C(sp^2) single bond length in propene[5d]) is surprisingly long and indicates C–C hyperconjugation. An analogy is afforded by the lengthening of the C_2–C_3 bond in the conformation of the methyl-staggered 1-propyl cation which permits hyperconjugation.[6]

The most stable conformation of the 1-propenyl cation (VI) has CCCH cis, analogous to the most stable form of propene. The calculated threefold rotational barriers are 1.20 (STO-3G) and 1.24 (4-31G) kcal mol^{-1}, slightly lower than the corresponding calculated barrier in propene[22] (1.55 kcal mol^{-1}, STO-3G).

Corner-Protonated Cyclopropene (VIII, IX). Corner-protonated cyclopropene is taken by definition to have the bridging carbon equidistant from the other two carbon atoms. The geometries of the two conformations considered (VIII, Figure 6a, and IX, Figure 6b) are given in Table VI. Both have C_s symmetry. The C_1–C_2 bond length (1.219) is similar to the value (1.227) in protonated acetylene and lies between normal double (1.306) and triple (1.168) bond lengths. The bridging C–C distances (1.834, 1.833) are close to those calculated for other systems.[6] The C_1–H_1 and C_2–H_2 bonds are bent (average bending 8.7°) from the C_1–C_2 line more than in protonated acetylene (2.5°). Finally, the methyl group geometries in VIII and IX are similar to geometries of the bridging methyl groups in the corresponding conformations of CH_5^+ [5a,b] and corner-protonated cyclopropane.[6]

The difference in energy (0.02 kcal mol^{-1}) between

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(18) J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

(19) W. J. Hehre, L. Radom, and J. A. Pople, *J. Amer. Chem. Soc.*, **94**, 1496 (1972).

(20) 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).

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

(22) L. Radom and J. A. Pople, *J. Amer. Chem. Soc.*, **92**, 4786 (1970).

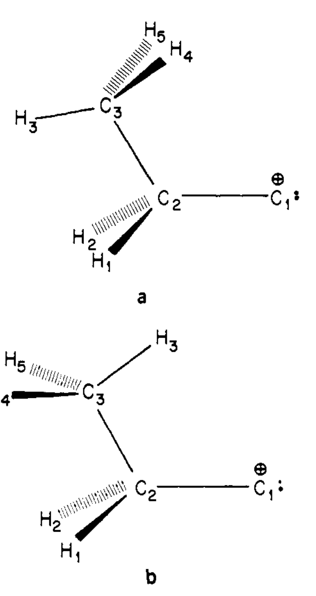


Figure 7. Propylidyne cation: (a) staggered (X), (b) eclipsed (XI).

Table VI. Geometries of Corner Protonated Cyclopropenes (VIII, IX)[a]

VIII	C_1-C_2	1.219	$(C_1C_2C_3)$	70.6°
	C_1-C_3	1.834	C_2C_1Q	171.3°
	C_1-H_1	1.088	H_1C_1Q	0.7°
	C_3-H_3	1.090	$O\ C_3H_3$	108.7°
	C_3-H_4	1.095	$O\ C_3H_{45}$	120.0°
			$H_4C_3H_5$	107.6°
IX	C_1-C_2	1.219	$(C_1C_2C_3)$	70.6°
	C_1-C_3	1.833	$C_2C_1H_1$	170.2°
	C_1-H_1	1.087	$C_1C_2H_2$	172.4°
	C_2-H_2	1.089	$O\ C_3H_3$	106.6°
	C_3-H_3	1.097	$O\ C_3H_{45}$	125.5°
	C_3-H_4	1.092	$H_4C_3H_5$	114.6°

[a] O is at the midpoint of the C_1-C_2 bond. Q is on the projection of the C_1-H_1 bond in the CCC plane.

VIII and IX corresponds to the expected small sixfold rotational barrier of the methyl group. The most stable conformation predicted by STO-3G is IX and by 4-31G is VIII. However, because of the very small energy differences involved, this discrepancy is not significant.

Propylidyne Cation (X, XI). This monocoordinate cation was considered in staggered (X, Figure 7a) and eclipsed (XI, Figure 7b) conformations, both with C_s symmetry. Calculations were carried out for the singlet state only and the optimized geometries are given in Table VII. These may be compared with the $CH_3C{:}^+$ structure.[5c] The C_2–H bond lengths are the same (1.104) and the HC_2H angles very similar for the two cations. However, there is a slight decrease in the C–C^+ bond lengths (1.453, 1.451 *vs.* 1.463) analogous to the difference in C–C^+ lengths observed[6] for the ethyl and 1-propyl cations (when the latter is in a conformation which permits C–C hyperconjugation). This suggests increasing hyperconjugation and hence increasing double bond character in the C–C^+ bond when a C–H bond is replaced by C–CH_3. This effect is also reflected in the C_2–C_3 bonds which are long in both X (1.584) and XI (1.591) and similar to the C_2–C_3 bond length in the 1-propyl cation (1.592). In contrast to the 1-propyl cation, there is no noticeable tendency toward a methyl-bridged structure. Thus the CCC angles are "normal" (109.7 and 107.9°). The staggered conformation (X) of the propylidyne cation is favored over the eclipsed (XI) by 1.66 (STO-3G) and 1.42 (4-31G) kcal mol^{-1}.

Table VII. Geometry of Propylidyne Cation (Staggered, X, and Eclipsed, XI)

X	C_1-C_2	1.453	$C_1C_2C_3$	109.7°
	C_2-C_3	1.584	$C_1C_2H_{12}$	120.4°
	C_2-H_1	1.104	$C_2C_3H_3$	106.3°
	C_3-H_3	1.089	$C_2C_3H_{45}$	127.6°
	C_3-H_4	1.088		
	(C_1-C_3)	2.485		
XI	C_1-C_2	1.451	$C_1C_2C_3$	107.9°
	C_2-C_3	1.591	$C_1C_2H_{12}$	120.8°
	C_2-H_1	1.104	$C_2C_3H_3$	112.2°
	C_3-C_3	1.090	$C_2C_3H_{45}$	122.6°
	C_3-H_4	1.088		
	(C_1-C_3)	2.461		

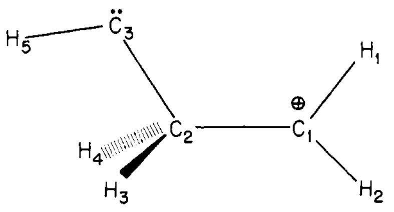


Figure 8. Propan-1-yl-3-ylidene cation (XII).

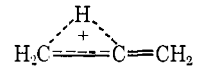
Propan-1-yl-3-ylidene Cation (XII). The geometry of the propan-1-yl-3-ylidene cation (XII, Figure 8) of C_s symmetry is given in Table VIII. The structure is somewhat similar to that of the CCCH cis form of the methyl-staggered 1-propyl cation.[6] The C–C^+ (1.508) and C_2–C_3 (1.553) bonds in XII are both slightly larger than the corresponding bonds in this form of the 1-propyl cation (1.492 and 1.541, respectively) and the CCC angle somewhat smaller (112.3 *vs.* 115.7°).

Table VIII. Geometry of Propan-1-yl-3-ylidene Cation (XII)

C_1-C_2	1.508	$C_1C_2C_3$	112.3
C_2-C_3	1.553	$C_2C_1H_1$	120.7
C_1-H_1	1.117	$C_2C_1H_2$	121.9
C_1-H_2	1.116	$C_1C_2H_{34}$	117.0
C_2-H_3	1.103	$C_2C_3H_5$	102.9
C_3-H_5	1.120		
(C_1-C_3)	2.543		

Calculations were also carried out on the conformation of the propan-1-yl-3-ylidene cation in which the CCC plane bisects the $H_1C_1H_2$ angle. However, upon energy minimization this structure was found to collapse directly to the cyclopropyl cation (III).

Bridged Protonated Allene (XIII). In order to provide an estimate for the energy of the transition state for the interconversion of the 2-propenyl cation (IV) to the allyl cation (I), we examined structures of the type



$$\overset{H}{\overbrace{H_2C\overset{+}{=\!=\!=}C}}{=}CH_2$$

To simplify the calculations, we assumed the bridging hydrogen to be equidistant from the two carbon atoms but *all* remaining geometric parameters in this structure (no symmetry assumed) were varied. The relative energy of this structure then provides a *minimum* value

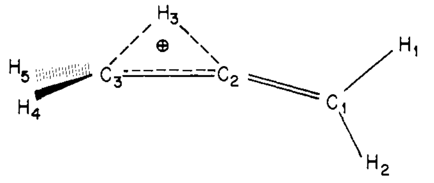


Figure 9. Bridged protonated allene (XIII).

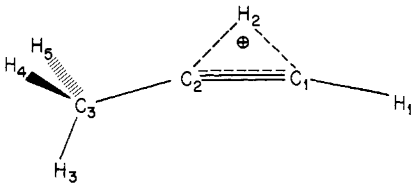


Figure 10. H-Bridged propenyl cation (XIV).

of the activation energy required for the 2-propenyl–allyl cation transformation. The lowest energy was found for XIII (Figure 9) which has C_s symmetry. Geometric parameters are summarized in Table IX and are closer to those of the 2-propenyl cation than the allyl cation. The main differences (from the 2-propenyl cation) are in the bridging C---H bonds whose lengths (1.346) are similar to the approximately one-electron C---H bond lengths found inrelated molecules,[5,6] and in the shortened C=C bond (1.378). The deviation from linearity (3.0°) of the carbon skeleton and the deviation from planarity (3.6°) of the bonds at C_3 are quite small.

Table IX. Geometry of Bridged Protonated Allene (XIV)

C_1–C_2	1.295	$C_1C_2C_3$	177.0°
C_2–C_3	1.378	$C_2C_1H_1$	123.0°
C_1–H_1	1.093	$C_2C_1H_2$	118.6°
C_1–H_2	1.095	$C_2C_3H_{45}$	176.4°
C_3–H_3	1.346	$H_4C_3H_5$	119.1°
C_3–H_4	1.100		

H-Bridged Propenyl Cation (Bridged Protonated Propyne, XIV). In a similar way, we have calculated the energy of the H-bridged propenyl cation. The bridging hydrogen was assumed to be equidistant from C_1 and C_2 and the conformation of the methyl group was taken to be the same as that favored for the 1-propenyl cation (VI), *i.e.*, C–H eclipsing C≡C. All remaining parameters in this structure (XIV, Figure 10) of C_s symmetry were optimized. The relative energy of this structure provides a *minimum* value of the activation energy required for the 1-propenyl–2-propenyl cation interconversion. The geometric parameters for this cation are shown in Table X and are similar to those for bridged protonated acetylene.[5c] In particular, the long bridging C---H bond length (1.328), and the C≡C bond length (1.230), which is intermediate between that of double and triple bonds, should be noted.

Table X. Geometry of H-Bridged Propenyl Cation (XIV)

C_1–C_2	1.230	$C_1C_2C_3$	178.8°
C_2–C_3	1.506	$C_2C_1H_1$	177.2°
C_1–H_1	1.092	$C_2C_3H_3$	106.5°
C_2–H_2	1.328	$C_2C_3H_{45}$	109.7°
C_3–H_3	1.093	$H_4C_3H_5$	110.1°
C_3–H_4	1.092		

Energy Comparison and Discussion

Calculated total and relative energies for the $C_3H_5^+$ cations are summarized in Table XI. Although results with all three basis sets are included in this table and in the following discussion, we should emphasize that the 6-31G* values are the most reliable and, when available, are the values quoted in text. Examination of Table XI shows that for the $C_3H_5^+$ cations, the relative energies obtained with the three basis sets are generally quite similar except when cyclic and acyclic structures are compared. Recent calculations[7] have shown that in several instances, relative energies of isomeric hydrocarbons are substantially modified when polarization functions (d-type functions on C, p-type functions on H) are included in the basis set. A major effect is that cyclic structures become relatively more stable when the more complete basis set is used. The relative energies of the cyclic structures listed in Table XI demonstrate this same effect.

One method of deriving better relative energies from the total energies calculated with the smaller basis sets is to take advantage of the fact that heats of certain types of isodesmic reactions (*i.e.*, reactions in which the number of bonds of each type is conserved) are often given well by relatively simple basis sets. In such reactions, there are good prospects of cancellation of errors due to the approximations (limited basis set, single determinant) inherent in the method used. The calculated heats of these reactions may be used in conjunction with known energy data (either experimental or from more accurate calculations) to provide information (*e.g.*, calculated heat of formation) for molecules of interest. Examples of this approach are provided in Table XII which presents the energies of some of the $C_3H_5^+$ isomers relative to the classical ethyl cation as standard. Values for the methyl, vinyl, and the two classical propyl cations are included for comparison. In addition to determining the relative energies of the various $C_3H_5^+$ structures, it is also important to establish which of these represent local minima in the potential surface. This has been attempted for some of the lower energy forms.

Allyl Cation (I). The planar allyl cation (I) is the absolute minimum (and therefore, *a fortiori*, a local minimum) in the STO-3G potential surface for $C_3H_5^+$. This structure also gives the lowest energy with the 4-31G and 6-31G* basis sets and has the lowest calculated heat of formation.

It is of interest to obtain estimates of the stabilization of the allyl cation, commonly attributed to delocalization of the positive charge, $C^+H_2CH{=}CH_2 \leftrightarrow CH_2{=}CHC^+H_2$. The magnitude of this stabilization (resonance energy), although of considerable interest, cannot be derived unambiguously. The problem lies in the arbitrary nature of the choice of reference molecules.

Wheland defines *resonance energy* "as the quantity obtained by subtracting the actual energy of the molecule from that of the most stable contributing structure."[23] Ordinarily, the energy of the hypothetical

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(23) G. W. Wheland, "Resonance in Organic Chemistry," Wiley, New York, N. Y., 1955, p 75.

Table XI. Calculated Energies for $C_3H_5^+$ Cations

Cation		STO-3G Total, hartrees	STO-3G Relative, kcal mol^{-1}	4-31G Total, hartrees	4-31G Relative, kcal mol^{-1}	6-31G* Total, hartrees	6-31G* Relative, kcal mol^{-1}
Allyl	I	−114.80953	0	−116.02511	0	−116.19106	0
2-Propenyl	IV	−114.79296	10.4	−116.00048	15.5	−116.16451	16.7
2-Propenyl	V	−114.79283	10.5	−116.00033	15.6		
H-Bridged propenyl	XIV	−114.75238	35.9	−115.95875	41.6	−116.13981	32.2
1-Propenyl	VI	−114.76859	25.7	−115.97503	31.4	−116.13925	32.5
1-Propenyl	VII	−114.76668	26.9	−115.97306	32.7		
Bridged protonated allene	XIII	−114.74340	41.5	−115.96211	39.5	−116.13687	34.0
Perpendicular allyl	II	−114.75464	34.4	−115.96939	35.0	−116.13561	34.8
Cyclopropyl	III	−114.76523	27.8	−115.95095	46.5	−116.12865	39.2
Corner-protonated cyclopropene	VIII	−114.74243	42.1	−115.94583	49.8	−116.12319	42.6
Corner-protonated cyclopropene	IX	−114.74247	42.1	−115.94580	49.8		
Propylidyne	X	−114.71272	60.7	−115.89515	81.5		
Propylidyne	XI	−114.71007	62.4	−115.89288	83.0		
Propan-1-yl-3-ylidene	XII	−114.65286	98.3	−115.85610	106.1		

Table XII. Ethyl Stabilization Energies (Energy Changes (kcal mol^{-1}) for the Reactions $R^+ + C_2H_6 \rightarrow RH + C_2H_5^+$ (classical))

Cation, R^+	Calcd[a] STO-3G	Calcd[a] 4-31G[b]	Calcd[a] 6-31G*	Exptl[26]
Methyl	−30.9	−29.9	−27.3	−40
Vinyl (classical)	−6.6	−14.7	−15.0	−14
Allyl (I)	29.7	26.0	25.7	18
Perpendicular allyl (II)	−4.7	−9.0	−9.1	
Cyclopropyl (III)	−1.8	−7.2	−6.8	(−7)[c]
1-Propenyl (IV)	4.0	−5.4	−6.8	(−5)[c]
2-Propenyl (VI)	19.3	10.5	9.0	(11)[c]
1-Propyl	5.0	5.1		6
2-Propyl	24.7	22.5		22

[a] Data from this paper and ref 5-7. [b] Energies for geometries optimized with the STO-3G basis. [c] Calculated using our derived heats of formation for the cyclopropyl (259 kcal mol^{-1}), 1-propenyl (249 kcal mol^{-1}), and 2-propenyl (233 kcal mol^{-1}) cations.

"most stable contributing structure" can be estimated by the use of group increments[24] or equivalent procedures. Unfortunately, unlike neutral molecules and free radicals,[24] the energies of carbonium ions are highly dependent upon structure and no general set of group increments can be derived simply. Thus, other methods have to be used to estimate the resonance energy of the allyl cation.

The rotational barrier in the allyl cation, 34.8 kcal mol^{-1} (6-31G*), appears to afford a reasonable estimate of this value. However, the perpendicular allyl cation (II) is not without objection as a model for a hypothetical "nonresonating" allyl cation. This is because the double bond in II has a strong destabilizing effect as revealed by the negative ethyl stabilization energy of −9.1 kcal mol^{-1} (6-31G*; Table XII). The planar allyl cation (I), on the other hand, shows a marked stabilization relative to ethyl of 25.7 kcal mol^{-1} (6-31G*; Table XII). On this basis, the barrier to rotation in the allyl cation (35 kcal mol^{-1}) can be attributed to a combination of a stabilization of 26 kcal mol^{-1} in the planar form (I) and a destabilization of 9 kcal mol^{-1} of the perpendicular form (II). Experimental evidence in rigid systems with such perpendicular conformations supports this postulated destabilization.[15,25]

The magnitude of the stabilization in the allyl cation can be estimated in a number of alternative ways. The methyl cation or the 1-propyl cation might be chosen in place of the ethyl cation as reference standard. Since the methyl, ethyl, and 1-propyl cations differ significantly in stability (see Table XII), so will these various estimates of the resonance energy of I. Estimates based on methyl and 1-propyl in hydride transfer reactions (a) and (b) are summarized in Table XIII. Finally, the energy of the isodesmic bond separation reaction (eq 1) can be employed.

$$(\mathrm{CH_2}\overset{\cdots}{-}\mathrm{CH}\overset{\cdots}{-}\mathrm{CH_2})^+ + \mathrm{CH_4} \longrightarrow \mathrm{CH_2{=}CH_2} + \mathrm{CH_3{-}C^+H_2} \quad (1)$$

The experimental value[26] of the heat of this reaction is +23 kcal mol^{-1} compared with the theoretical +29.6 kcal mol^{-1} (6-31G*). These values and the ethyl stabilization energy (Table XII) are probably the most appropriate estimates of the resonance energy in the allyl cation. For both estimates, the theoretical values are approximately 7 kcal mol^{-1} larger than experiment.

Because the absolute values of total energies obtained using single determinant molecular orbital theory are not good, it is necessary to derive heats of formation from calculated heats of reaction such as those in Tables XII and XIII. The $\Delta H_f°$ values so determined using both the STO-3G and 4-31G basis sets have been found to be in very reasonable agreement with experimental results for a number of neutral molecules[13,31] and cations.[32] The $\Delta H_f°$ for the allyl cation derived from its 6-31G* ethyl stabilization energy (Table XII) and the experimental heats of formation[26] for ethane, propene, and the ethyl cation is +218 kcal mol^{-1} compared with the experimental value of +226 kcal mol^{-1}.[28,33]

(24) (a) S. W. Benson, "Thermochemical Kinetics," Wiley, New York, N. Y., 1968; (b) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969); (c) S. W. Benson, *et al.*, *ibid.*, **69**, 279 (1969).

(25) B. Ree and J. C. Martin, *J. Amer. Chem. Soc.*, **92**, 1660 (1970).

(26) In calculating the experimental heats of reaction we use $\Delta H_f°$'s for neutral molecules as summarized in ref 13 and for cations as follows (in kcal mol^{-1}): CH_3^+ (+261),[27] $C_2H_5^+$ (+219),[27] vinyl (+266),[28] allyl (+226),[28] 1-propyl (+208),[27] 2-propyl (+192).[27] All values are at 298° without correction for vibrations. See ref 27–30 for further discussion.

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

(28) F. P. Lossing, *Can. J. Chem.*, **49**, 357 (1971); **50**, 3973 (1972).

(29) D. M. Golden, N. A. Gac, and S. W. Benson, *J. Amer. Chem. Soc.*, **91**, 2136 (1969).

(30) R. J. Field and P. I. Abell, *J. Amer. Chem. Soc.*, **91**, 7226 (1969).

(31) L. Radom, W. J. Hehre, and J. A. Pople, *J. Chem. Soc. A*, 2299 (1971).

(32) L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 5935 (1972).

(33) This value is higher than that (+216 kcal mol^{-1}) recommended in a recent compilation.[34] An even higher value (+232 ± 3 kcal mol^{-1}) has received other recent support.[35]

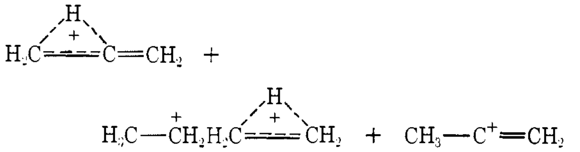
(34) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron,

Table XIII. Energy Changes (kcal mol^{-1}) for Hydride Transfer and Isomerization Reactions

Reaction	Calcd[a] STO-3G	Calcd[a] 4-31G[b]	Calcd[a] 6-31G*	Exptl[26]
(a) $[CH_2{\cdots}CH{\cdots}CH_2]^+$ (I) + $CH_4 \rightarrow CH_3CH{=}CH_2 + CH_3^+$	60.6	55.9	53.0	58
(b) $[CH_2{\cdots}CH{\cdots}CH_2]^+$ (I) + $C_3H_8 \rightarrow CH_3CH{=}CH_2 + CH_3CH_2CH_2^+$	24.7	25.9		12
(c) $CH_3CH{=}CH^+ + CH_2{=}CH_2 \rightarrow CH_3CH{=}CH_2 + CH_2{=}CH^+$	10.6	9.3	9.3	(9)[c]
(d) $CH_3C^+{=}CH_2 + CH_2{=}CH_2 \rightarrow CH_3CH{=}CH_2 + CH_2CH^+$	25.9	25.3	24.0	(25)[c]
(e) $CH_3CH_2CH_2^+ \rightarrow CH_3CH^+CH_3$	−19.7	−17.4	−17.0	−16
(f) $CH_3CH{=}CH^+ \rightarrow CH_3C^+{=}CH_2$	−15.3	−15.9	−15.8	(−16)[c]
(g) $CH_3C^+{=}CH_2 + CH_3CH_2CH_3 \rightarrow CH_3CH{=}CH_2 + CH_3CH^+CH_3$	−5.4	−12.0		(−11)[c]
(h) $CH_3CH{=}CH^+ + CH_3CH_2CH_3 \rightarrow CH_3CH{=}CH_2 + CH_3CH_2CH_2^+$	−1.0	−10.4		(−11)[c]

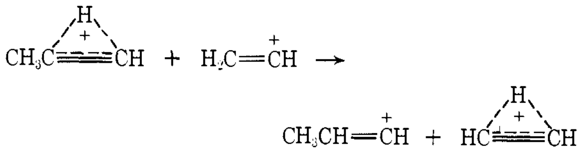
[a] Data from this paper and refs 5–7. [b] Energies for geometries optimized with the STO-3G basis. [c] Calculated using our derived heats of formation for the 1-propenyl (249 kcal mol^{-1}) and 2-propenyl (233 kcal mol^{-1}) cations.

2-Propenyl Cation (IV). In order to determine whether this cation (IV) is a local minimum in the $C_3H_5^+$ surface, it is necessary to see whether activation energy is required for the transformation (by means of a hydride shift) to the lower energy species, the allyl cation (I). We have approached this problem by optimizing the geometry of a structure in which the hydrogen atom involved in the hydride shift is equidistant from the two carbon atoms XIII (*vide supra*). The energy difference between XIII and IV represents a lower limit to the energy required for the 2-propenyl–allyl cation transformation. The calculated value for this difference is 17.3 kcal mol^{-1} (6-31G*). Larger differences are found within the other basis sets since we are comparing cyclic and acyclic species. Another estimate can be made by examining the energy change (ΔH) in the reaction


(2)

Using the 4-31G value for ΔH (−17.3 kcal mol^{-1}), and the energy difference between the bridged and open forms of $C_2H_5^+$ derived from the best previous calculations (−0.9 kcal mol^{-1}[1,7a] leads to the result that XIII has an energy 18.2 kcal mol^{-1} higher than the 2-propenyl cation. This is reasonably close to the 6-31G* value obtained above directly from the difference in total energies. We conclude that the 2-propenyl cation is a stable local minimum on the $C_3H_5^+$ potential surface.

1-Propenyl Cation (VI). The 1-propenyl cation (VI) may be transformed to the isopropenyl cation (IV) by means of a 1,2-hydride shift. From the energy of the H-bridged propenyl cation (XIV), an approximate value of the energy required for this 1,2-hydride shift (VI → XIV → IV) may be obtained. It should be noted that because of the assumed position of the bridging hydrogen, the value obtained will be less than the full activation energy for the process. Estimates derived from direct energy differences (XIV–VI) are 10.2 (both STO-3G and 4-31G) and −0.3 kcal mol^{-1} (6-31G*). Again there is a large difference between the 6-31G* and the other results. Better estimates with the smaller basis sets may be obtained using the calculated energy change in the reaction


(3)

together with a value of the energy difference between the bridged and open forms of the vinyl cation derived from previous 6-31G* calculations.[7a] The activation energy values for the 1,2-hydride shift obtained in this manner are −2.2 (STO-3G) and −3.2 (4-31G) kcal mol^{-1} in much closer agreement with the directly calculated 6-31G* value (−0.3 kcal mol^{-1}). As noted above, these are lower limits. Nevertheless, it seems that little or no activation energy is required to convert the 1-propenyl cation to the 2-propenyl cation by means of a 1,2-hydride shift. The corresponding activation energy in the vinyl cation[7a] is +7.4 kcal mol^{-1} (using 6-31G*) so it is clear that the methyl substituent has facilitated the transformation. A similar effect was noted for the corresponding propyl cations.[6]

An additional transformation that may take place for the 1-propenyl cation is a 1,2-methyl shift *via* a corner-protonated cyclopropene (VII) transition state. The best estimate of the activation energy required for this process obtained as a direct energy difference is 10.1 kcal mol^{-1} (6-31G*).

The barriers to 1,2 shifts are summarized in Table XIV. To facilitate comparison, corresponding aliphatic and vinylic processes are grouped together. This emphasizes the higher barriers predicted for vinylic rearrangements. This can be understood in simple strain terms, if one takes cyclopropane to be a model for the bridged aliphatic cations and cyclopropene as a model for bridged vinyl cations. As the strain in cyclopropene is nearly twice that in cyclopropane,[36] it is not surprising that the tendency toward neighboring group participation is very much diminished in vinyl systems.[37]

Heats of Formation for the 2-Propenyl and 1-Propenyl Cations. The energies of the hydride transfer reactions (c) and (d), Table XIII, are measures of the stabilization of the vinyl cation by β- (9.3 kcal mol^{-1}) and α-methyl (24.0 kcal mol^{-1}; 6-31G*) substitution (relative to the

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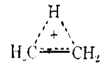
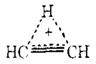
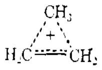
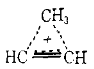
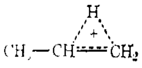
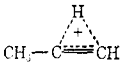
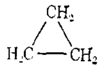
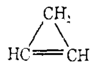
and K. Draxl, "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS-26, National Bureau of Standards, Washington, D. C., 1969.

(35) G. G. Meisels, J. Y. Park, and G. B. Giessner, *J. Amer. Chem. Soc.*, 92, 254 (1970).

(36) P. v. R. Schleyer, J. E. Williams, and K. R. Blanchard, *J. Amer. Chem. Soc.*, 92, 2377 (1970).

(37) Reviews on vinyl cations: (a) H. G. Richey and J. M. Richey, "Carbonium Ions," Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N. Y., 1970, p 899; (b) M. Hanack, *Accounts Chem. Res.*, 3, 209 (1970); (c) G. Modena and U. Tonellato, *Advan. Phys. Org. Chem.*, 9, 185 (1970); (d) P. J. Stang, *Progr. Phys. Org. Chem.*, 10, 205 (1973).

Table XIV. Open *vs.* Cyclic Structures (Barriers to 1,2-Shifts)

Reaction		Energy change, kcal mol^{-1}		
	STO-3G	4-31G	6-31G*	Exptl
$CH_3CH_2^+$ → 	11.4[a]	7.3[a]	0.4[b]	
$CH_2{=}CH^+$ → 		19.2[b]	7.4[b]	
$CH_3CH_2CH_2^+$ → 	3.2[c]	0.5[c]	−4.0[c]	
$CH_3CH{=}CH^+$ → 	16.4[d]	17.1[d]	10.1[d]	
$CH_3CH_2CH_2^+$ → 	4.2[c]	1.3[c]		
$CH_3CH{=}CH^+$ → 	10.2[d]	10.2[d]	−0.3[d]	
$CH_3CH{=}CH_2$ → 	−3.7[e]	13.2[e]	7.8[f]	7.4
$CH_3C{\equiv}CH$ → 	30.0[e]	36.4[e]	25.3[f]	22.3

[a] Reference 5a. [b] Reference 7a. [c] Reference 6. [d] This work. [e] Reference 5d. [f] Reference 7b.

corresponding stabilization of ethylene). The corresponding stabilizing effects of β-methyl (5.1 kcal mol^{-1}) and α-methyl (22.5 kcal mol^{-1}, 4-31G) substitution in the ethyl cation are somewhat smaller (Table XII). However, the energy differences between the 1 and 2 cations are comparable in the propyl and propenyl cases (eq (e) and (f), Table XIII).

The 6-31G* data of Table XIII together with experimental heats of formation for ethylene, propene, and the vinyl cation[26] may be used to obtain estimated $\Delta H_f{}^\circ$ values for the 2-propenyl and 1-propenyl cations. These are summarized in Chart I along with similarly

Chart I

Cation	Estimated $\Delta H_f{}^\circ$, kcal mol^{-1}
Allyl (I)	+218
Cyclopropyl (III)	+257
2-Propenyl (IV)	+233
1-Propenyl (VI)	+249

calculated values for the allyl and cyclopropyl cations; the exact equations used are discussed separately. We should note, however, that our calculations indicate that only the allyl and 2-propenyl cations represent stable structures (minima) on the $C_3H_5^+$ energy surface.

Thermodynamics of Vinyl Cation Formation. There are two principal methods of generating vinyl cations: (1) heterolytic cleavage of vinyl-X bonds, and (2) additions of electrophiles to acetylenes or to allenes. It is found that vinyl halides and vinyl tosylates are relatively inert toward ionization.[37] In contrast, protonic additions to acetylenes proceed at rates comparable with similar additions to olefins.[37,38] These results are apparently inconsistent if it is assumed that the reaction rates depend primarily on the energies of the vinyl cation intermediates. In fact, the rates depend, in addition, on the stabilities of the un-ionized reactant molecules. Thus, for example, the relative inertness of vinyl halides and vinyl tosylates toward ionization has been ascribed not only to transition state destabilization due to the instability of vinyl relative to aliphatic cations but also to lowered ground state energies of the un-ionized vinyl derivatives. Previous analyses of this problem[37-39] have been limited to the parent vinyl cation due to the lack of thermochemical data on the more representative substituted species.

The proton transfer reaction

$$CH_3{-}CH_2^+ + HC{\equiv}CH \longrightarrow CH_2{=}CH_2 + CH_2{=}C^+H \quad (4)$$

endothermic as written, shows in effect that it is more difficult to protonate acetylene than ethylene. The energy differences are 4.4 (6-31G*) and 5 (exptl)[26] kcal mol^{-1}. However, the analogous proton transfer reaction (reaction 5) in the C_3 series is more nearly thermo-

$$CH_3C^+HCH_3 + CH_3C{\equiv}CH \longrightarrow CH_3CH{=}CH_2 + CH_3C^+{=}CH_2 \quad (5)$$

neutral (energy differences of 2.0 (4-31G) and 2 (exptl)[26] kcal mol^{-1}) due to the greater methyl stabilization of vinyl than of aliphatic cations. One can expect this trend to continue; it should actually be slightly more favorable thermodynamically to protonate 2-butyne than 2-butene, at least in the gas phase. In general, additions of protons to double and to triple bonds should be and are comparably easy. This is because acetylenes are more highly "strained" than are olefins (C≡C bond energies are less than $^3/_2$ C=C bond energies), and this compensates for the higher "strain" (instability) of vinyl cations relative to alkyl cations.

Vinyl cations are indeed less stable than their aliphatic counterparts.[40] Table XII shows the vinyl cation to be less stable than the ethyl cation by 14–15 kcal mol^{-1}.

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(38) K. Yates, G. H. Schmid, T. W. Regulski, D. G. Garratt, H.-W. Leung, and R. McDonald, *J. Amer. Chem. Soc.*, **95**, 160 (1973).

(39) L. L. Miller and D. A. Kaufman, *J. Amer. Chem. Soc.*, **90**, 7282 (1968).

(40) The stabilities of the cations are compared relative to the corresponding neutral species; *i.e.*, we compare the cation stabilities with respect to hydride ion addition.

This magnitude is only slightly reduced when the stabilities of comparably substituted propenyl and propyl cations are compared (eq (g) and (h), Table XIII). While the 2-propenyl cation is 9–11 kcal mol^{-1} more stable than the ethyl cation (Table XII), this is a consequence of the different degrees of substitution of the two species.

Are the ground states of vinyl derivatives stabilized? Available experimental and theoretical thermodynamic data[41,42] allow this question to be answered *via* evaluation of the energy of reaction 6.

$$CH_3—CH_2X + CH_2{=}CH_2 \longrightarrow CH_3—CH_3 + CH_2{=}CHX \quad (6)$$

Experimental data[41] for X = Br and Cl show that this reaction is slightly *endothermic* by 0.8 and 1.1 kcal mol^{-1}, respectively. This means that halogen attachment to ethyl is actually *more* favorable than to vinyl, contrary to the usual assumption. However, when X = OC_2H_5 (the best model for X = OSO_2R for which thermodynamic data are available), the heat of reaction is -5.9 kcal mol^{-1} indicating substantial vinyl ground state stabilization relative to ethyl. Theoretical results are available[42] for X = OH and F (6-31G*). The calculated energy changes in reaction 6 are -3.9 (X = OH) and $+0.5$ (X = F) kcal mol^{-1} in reasonable agreement with the experimental trends.

The ground state factor is incorporated into eq 7 and

$$CH_2{=}CHX + CH_3C^+H_2 \longrightarrow CH_2{=}C^+H + CH_3CH_2X \quad (7)$$

8. Using experimental data,[41] the heats of reaction

$$CH_3CX{=}CH_2 + CH_3C^+HCH_3 \longrightarrow CH_3C^+{=}CH_2 + CH_3CHXCH_3 \quad (8)$$

are: (7), X = H (14), X = Br or Cl (13), X = OC_2H_5 (20 kcal mol^{-1}); for (8), X = H (11), X = OCH_3 (16 kcal mol^{-1}). Theoretical values[42] for (7) are $+15.6$ (X = F, 6-31G*) and 20.0 kcal mol^{-1} (X = OH, 6-31G*). These results are consistent with solvolysis rate data on alkyl and vinyl systems[37–39] which indicate activation free energy differences of the order of 8–11 kcal mol^{-1}.

Mechanistic factors contribute substantially to the relative inertness of vinyl derivatives toward solvolysis. Accumulating evidence shows that simple primary and secondary aliphatic solvolyses generally proceed through SN2 or ion pair SN2 pathways rather than *via* energetically unfavorable free carbonium ions (SN1).[44] Vinyl substrates appear not to undergo SN2 reactions and are forced to react *via* unstable cationoid intermediates.[45] If both vinyl and alkyl derivatives were to react by the same SN1 mechanism, the reactivity differences would be reduced somewhat although they would still remain large.

Vinyl cations can also be formed by electrophilic additions to allene and its 1-alkyl and 1,3-dialkyl but not 1,1-dialkyl derivatives.[37] The π-electron systems in allene are orthogonal and proton addition would tend to give the perpendicular allyl cation (II) rather than the 35 kcal mol^{-1} more stable allyl cation (I). One can infer from the uniformity of the experimental results (allene itself always adds electrophiles to C_1 or C_3 but not to C_2)[37] that significant twisting of II toward I does not occur in the addition transition state. Thus, formation of the 2-propenyl cation (V), only 16 kcal mol^{-1} less stable than I, is the favored process. A single alkyl substituent at either end of the allene system is generally insufficient to favor the formation of allyl over vinyl products.[37] Although secondary alkyl cations are more stable than secondary vinyl cations, proton attachment to C_2 of 1,2-butadiene would tend to yield the *perpendicular* 1-methylallyl cation; as we have seen such perpendicular allyl cations suffer substantial destabilization due to the presence of the unconjugated vinyl substituent. Thus, electrophiles attack 1,2-butadiene at C_1 rather than at C_2.

Propylidyne Cation. The stabilization of the ethylidyne cation $CH_3C{:}^+$ by methyl substitution to give X as measured by the energy change in the reaction

$$CH_3CH_2C{:}^+ + CH_3CH_3 \longrightarrow CH_3CH_2CH_3 + CH_3C{:}^+ \quad (9)$$

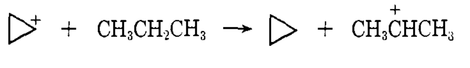
is also of interest. Values are 6.5 (STO-3G) and 7.6 kcal mol^{-1} (4-31G) indicating slightly greater stabilization than corresponding substitution in the ethyl cation (Table XII) but considerably less stabilization than methyl substitution in the methylidyne cation ($HC{:}^+$).

$$CH_3C{:}^+ + CH_4 \longrightarrow CH_3CH_3 + HC{:}^+ \quad (10)$$

Calculated heats of reaction[5c] for (10) are $+54.2$ (STO-3G) and $+57.9$ kcal mol^{-1} (4-31G). The values for (9) and (10) give a comparison of the effects of β- and α-methyl substitution in the general monocoordinate cation $RC{:}^+$.

Cyclopropyl Cation. The best estimate of the cyclopropyl–allyl cation energy difference from Table XI is 39 kcal mol^{-1} obtained with the 6-31G* basis. The STO-3G value (28 kcal mol^{-1}) is considerably lower, a result which is consistent with the fact that STO-3G underestimates the energy difference for the related neutral molecules cyclopropane and propene[5d] by 11 kcal mol^{-1}. Likewise, the high 4-31G value (46 kcal mol^{-1}) is consistent with the overestimation of the cyclopropane–propene energy difference by 6 kcal mol^{-1} with this basis.[5d] With the 6-31G* basis,[7b] the error in the relative energies of cyclopropane and propene is only 0.4 kcal mol^{-1}.

Alternative estimates of the cyclopropyl–allyl cation energy difference with the STO-3G and 4-31G basis sets come from examining the reaction



(11)

Theoretical values for the energy change in (11) are -26.5 (STO-3G) and -29.9 kcal mol^{-1} (4-31G) and illustrate the extent to which the cyclopropyl cation is destabilized due to angle strain.[46] Using the 4-31G

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[41] Experimental heats of formation taken from ref 24c; also see D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, N. Y., 1969; and J. D. Cox and G. Pilcher, "Thermochemistry of Organic and Organometallic Compounds," Academic Press, New York, N. Y., 1970.

[42] 4-31G and 6-31G* energies for neutral substituted molecules refer to standard model geometries and are taken from ref 13 and 43, respectively. The theoretical energies for the cations and unsubstituted neutral hydrocarbons refer to STO-3G optimized geometries and are taken from ref 5–7.

[43] P. C. Hariharan and J. A. Pople, submitted for publication.

[44] D. J. Raber and J. M. Harris, *J. Chem. Educ.*, **49**, 60 (1972), review the available evidence with emphasis on recent work at Princeton.

[45] (a) T. C. Clarke, D. R. Kelsey, and R. G. Bergman, *J. Amer. Chem. Soc.*, **94**, 3627 (1972); (b) R. H. Summerville and P. v. R. Schleyer, *ibid.*, **94**, 3629 (1972); in press; and prior literature cited in these papers.

[46] P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *J. Amer. Chem. Soc.*, **94**, 125 (1972), and references cited therein; see also J. J. Gajewski and J. P. Oberdier, *ibid.*, **94**, 6053 (1972).

value and experimental heats of formation for the other molecules, we obtain $\Delta H_f^\circ = +259$ kcal mol^{-1} for the cyclopropyl cation, making it 41 kcal mol^{-1} less stable than the allyl cation. Since there is some balance of errors associated with ring strain in reaction 11, this estimate should be more reliable than the corresponding value obtained from the difference in total energies. The heat of formation for the cyclopropyl cation, calculated from the 6-31G* ΔH_f° for the allyl cation together with the 6-31G* cyclopropyl–allyl cation energy difference, is +257 kcal mol^{-1}. Our calculated cyclopropyl–allyl cation energy differences are smaller than the estimate of Peyerimhoff and Buenker[3] (70–75 kcal mol^{-1}) but comparable with the figure of 35 kcal mol^{-1} due to Clark and Armstrong.[2] It has been pointed out[47] that the previously determined experimental ΔH_f°'s for the cyclopropyl cation are of doubtful reliability and may correspond to energies of excited allyl cations. In any case, it should be emphasized that the estimated heat of formation applies to the molecular geometry which gives a local minimum in the STO-3G surface.

There is some disagreement in the theoretical literature as to whether the cyclopropyl cation is actually a local minimum in the $C_3H_5^+$ surface. Clark and Armstrong[2] used *ab initio* molecular orbital theory to examine both disrotatory and conrotatory openings of the cyclopropyl to the allyl cation with assumed geometries. They found that, in agreement with the Woodward–Hoffmann predictions,[49,50] the disrotatory mode is favored and that no activation energy is required for the ring opening. Extended Hückel calculations by Kutzelnigg[51] also predicted that no activation energy is required for the disrotatory ring opening. More recently, Dewar and Kirschner[4] have reported results of a MINDO/2 study of these processes. In variance with the earlier calculations, they find that a barrier of 7.4 kcal mol^{-1} is required for the disrotatory transformation. However, they point out that this result may be influenced by the fact that MINDO/2 overestimates the stabilities of small cyclic molecules. Indeed, the MINDO/2 calculations predict that the cyclopropyl cation is more stable than the allyl cation so that energy would *have* to be required to convert cyclopropyl to allyl cation. Dewar and Kirschner also suggest that the disagreement with the *ab initio* study may alternatively stem from the use of assumed geometries in the latter work.

In order to examine these varying conclusions in more detail, we have carried out *ab initio* calculations *with* geometry optimization for several points along the disrotatory and conrotatory paths. Complete geometry optimization (except, of course, for the reaction coordinate) is performed at each point subject only to specified symmetry constraints. The reaction coordinate (ϕ) is taken to be the angle between the planes of the methylene groups and the CCC plane. Structures on the disrotatory path are constrained to have C_s symmetry (XV, Figure 11a) and on the conrotatory path C_2 symmetry (XVI, Figure 11b). In addition to methylene group rotations of 0 (representing the allyl cation, I) and 90° (representing the cyclopropyl cation, III), intermediate rotations of 22.5, 45, and 67.5° were examined. The lowest energies obtained for each angle of rotation are shown in Table XV.

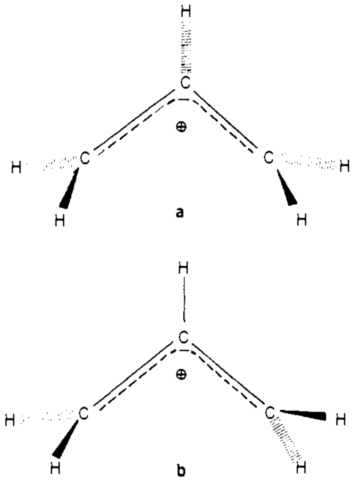

Figure 11. Electrocyclic transformation of the cyclopropyl to the allyl cation. (a) Structure on disrotatory path (XV). (b) Structure on conrotatory path (XVI).

Table XV. Relative Energies (kcal mol^{-1}) for the Disrotatory and Conrotatory Transformations of the Cyclopropyl Cation (III) to the Allyl Cation (I)

	Disrotatory (XV)			Conrotatory (XVI)		
ϕ	STO-3G	4-31G	6-31G*	STO-3G	4-31G	6-31G*
90 (III)	27.8	46.5	39.2	27.8	46.5	39.2
67.5	31.7	37.8	28.8	53.7	69.8	59.8
45	13.6	12.7[a]		35.5	33.1	
22.5	3.3	2.9		9.4	9.1	
0 (I)	0	0	0	0	0	0

[a] When the methine C–H is constrained to remain in the CCC plane, the relative energies are 26.9 (STO-3G) and 23.6 (4-31G) kcal mol^{-1}.

In agreement with previous calculations[2,4,49–51] and experimental results, the disrotatory mode is more favorable than the conrotatory mode of ring opening. Calculations with partially optimized geometries for values of ϕ between 67.5 and 90° show that at the 4-31G level the disrotatory transformation of the cyclopropyl to the allyl cation requires little or no activation energy. At the STO-3G level, a small increase of about 4 kcal mol^{-1} occurs in going from $\phi = 90$ (cyclopropyl cation) to 67.5°. However, these STO-3G results are considerably less reliable than the 4-31G calculations and are probably influenced by the underestimation of the cyclopropyl–allyl cation energy difference with STO-3G (*vide supra*). Our most reliable results (6-31G*) show quite a large drop in energy (10.4 kcal mol^{-1}) in going from $\phi = 90$ to 67.5°. We thus conclude that the isolated cyclopropyl cation is unlikely to exist as a stable species since it may be transformed to the allyl

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(47) While a value of 239 kcal mol^{-1} has been recommended[34] for the heat of formation of the cyclopropyl cation, the original authors[48] of the data cited regarded this value of dubious reliability and suggested that it corresponded not to the cyclopropyl cation but to an excited allyl cation. Higher values in the range 250–252 kcal mol^{-1} have been considered recently as being possibly due to the cyclopropyl cation.[36]

(48) R. F. Pottie, A. G. Harrison, and F. P. Lossing, *J. Amer. Chem. Soc.*, **83**, 3204 (1961).

(49) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).

(50) R. B. Woodward and R. Hoffmann, *J. Amer. Chem. Soc.*, **87**, 395 (1965).

(51) W. Kutzelnigg, *Tetrahedron Lett.*, 4965 (1967).

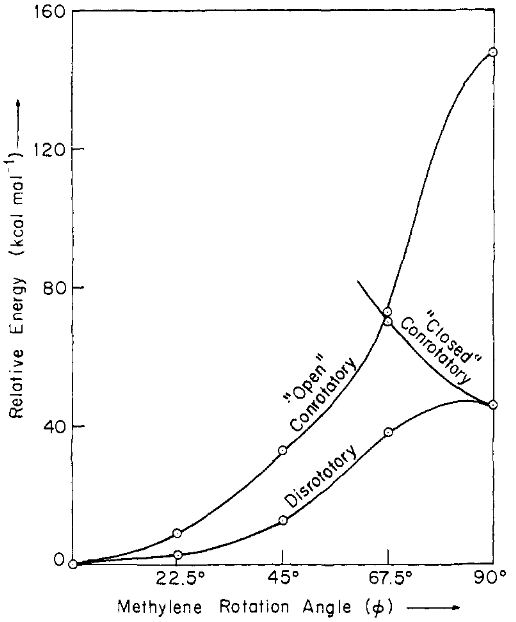

Figure 12. Potential functions for the electrocyclic transformation of the cyclopropyl to the allyl cation.

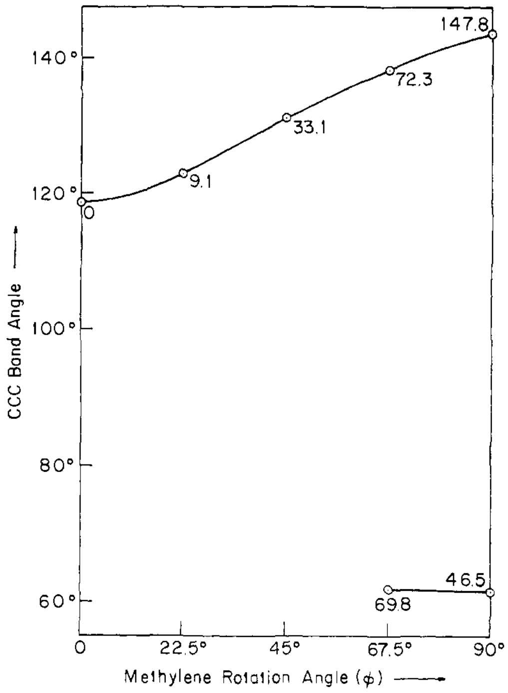

Figure 13. Sections of the conrotatory potential surface for the cyclopropyl–allyl conversion.

cation *via* a disrotatory transformation with little or no activation energy.

There are several interesting structural changes that occur during the rearrangement. Of particular importance is the fact that although the methine hydrogen lies in the plane defined by the three carbon atoms in *both* the cyclopropyl cation and the allyl cation, this hydrogen deviates quite markedly from the plane during the disrotatory opening. This result points out the dangers in using assumed geometries in studies of this type. The angles of deviation from the plane are 16.3 (ϕ = 22.5°), 31.2 (ϕ = 45°), and 38.5° (ϕ = 67.5°), the direction of the displacement being on the opposite side of the hydrogens moving inward as shown in Figure 11a. Such an effect was also indicated in previous theoretical calculations.[2,4a,b] In order to estimate the stabilization associated with such a distortion, we carried out calculations on the 45° disrotatory structure in which the methine C–H bond was constrained to remain in the CCC plane but all remaining parameters were optimized. This structure was considerably higher in energy (by 10.9 kcal mol^{-1} with 4-31G, 13.3 kcal mol^{-1} with STO-3G) than the corresponding form in which the hydrogen is allowed to move out-of-plane. The implications of this result with regard to which of the two possible disrotatory modes of ring opening of cyclopropyl derivatives is likely to occur are discussed later in this paper.

The conrotatory cyclopropyl–allyl cation transformation is considerably more complicated than the disrotatory process. During this transformation, the energies of the highest occupied and lowest vacant molecular orbitals cross. In the crossing region, interaction of configurations is likely to be important and hence a single configuration calculation with real wave functions inadequate.[52] For this reason we have allowed the molecular orbitals to be complex, a procedure which reproduces the major features of a configuration interaction treatment.[53]

The relative energies in Table XIV represent local potential minima of lowest energy for each value of ϕ. However, as in the previously reported MINDO/2 surface,[4a,b] there are *two* local potential minima for some values of ϕ. These correspond to "closed" and "open" structures in which the highest occupied molecular orbital is respectively bonding or antibonding with respect to the C–C σ bond that is being broken.

Figure 12 shows the potential functions for the disrotatory transformation and for the transformations involving the "open" and "closed" conrotatory forms. The conrotatory curves in Figure 12 may easily be misinterpreted. There is a temptation to construct the conrotatory path by joining points which correspond to the lowest values of energy for each ϕ. The activation energy would then be the relative energy of the point of maximum energy on the resultant curve. A further temptation is to say that the activation energy so determined is overestimated in a single configuration treatment.

Inspection of Figure 13 shows that this line of reasoning is likely to be incorrect. This figure gives the conrotatory potential surface as a function of the CCC bond angle and the methylene rotation angle (ϕ). The points plotted correspond to local potential minima (with respect to all other geometric parameters) for each value of ϕ. The conrotatory surface consists of two valleys separated by a barrier in between. The curves in Figure 13 correspond to these two valleys. In order that the conrotatory transformation of the cyclopropyl to the allyl cation take place, the barrier between the two valleys must be traversed and we have no direct information on the energy required for this process. The only conclusion we can make is that the activation

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(51a) Note Added in Proof. An assumed geometry minimal basis set calculation indicates an unrealistically large activation energy: L. Farnell and W. G. Richards, *J. Chem. Soc., Chem. Commun.*, 334 (1973).

(52) For a detailed discussion, see A. R. Gregory and M. N. Paddon-Row, *Chem. Phys. Lett.*, **12**, 552 (1972).

(53) J. A. Pople, *Int. J. Quantum Chem., Symp.*, No. 5, 175 (1971).

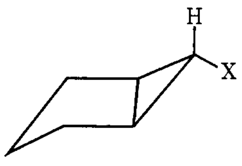
energy required for the conrotatory transformation on the 4-31G surface is *at least* the highest relative energy shown in Table XV (23.3 kcal mol^{-1}) and may be considerably higher.

The calculations with complex wave functions give some idea as to when configuration interaction is likely to be important.[53] The only structure whose wave function we have found to be complex is the "open" cyclopropyl cation. This suggests that the results we have obtained for the conrotatory surface are not likely to be greatly modified by a configuration interaction treatment. It is very likely, however, that points on the barrier separating the two valleys (which we have not studied here) *will* be affected by such a treatment, since this is the region where the orbital energy crossing is likely to take place.

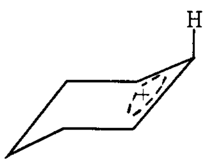
There is considerable experimental information available on this subject. It has now been well established that cyclopropyl solvolyses are generally assisted by concerted, disrotatory ring openings and considerable progression in the transition state toward the eventual allyl cations.[54] During the process of ionization, the substituents at C_2 and C_3 trans to the leaving group move outward disrotatorily. Our calculations are consistent with this process, since they show that the hydrogen at C_1 is bent out of the ring plane and on the same side of the ring as the methylene hydrogens at C_2 and C_3 moving outward.

The properties of a "half-opened" cyclopropyl cation are also interesting to consider, especially since there is evidence that such a species can actually be achieved experimentally.[55] The situation is exemplified by the 6-*exo*-bicyclo[3.1.0]hexyl system XVII.[55a] Because of its fusion to the cyclopentane ring, outward disrotatory opening of the cyclopropane ring during ionization of the leaving group is strongly inhibited. The experimental result is a marked depression of the solvolysis rate and a yield of a substantial amount of *unopened* substitution product with *retention* of configuration. This has been interpreted in terms of a partially opened intermediate, XVIII. The present calculations afford support for XVIII since attack by a nucleophile should be the reverse of the process whereby the leaving group was ejected, *i.e.*, retention of configuration. A second method whereby such a partially opened intermediate might be achieved is by substitution at C_1 by a rather strongly stabilizing carbonium ion substituent, such as C_6H_5S–.[55b] Such a substituent would stabilize a cyclopropyl but not the opened allyl cation. Thus, progression of the cyclopropyl to the allyl cation, normally favored thermodynamically, would be arrested as more and more of the positive charge would be transferred away from the position where it can be stabilized by the substituent. In this instance, the intermediate could well be expected to be only partially opened and the reaction product might well be rich in cyclopropyl substitution product with retention of configuration.[55b]

The Stereomutation of Allyl Cations. In principle, the stereomutation of allyl cations can occur by two

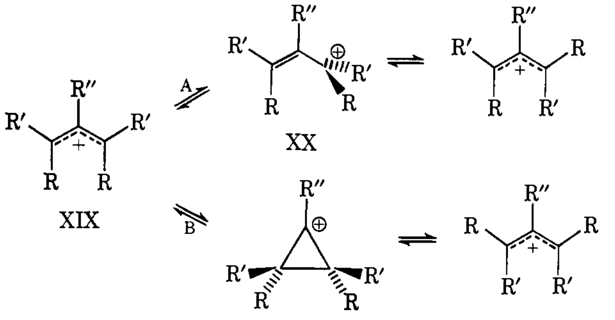


XVII



XVIII

mechanisms involving either simple rotation about one of the C–C bonds at a time (path A) or disrotatory closure to a cyclopropyl cation followed by disrotatory opening in the opposite sense (path B).[56] Path A would



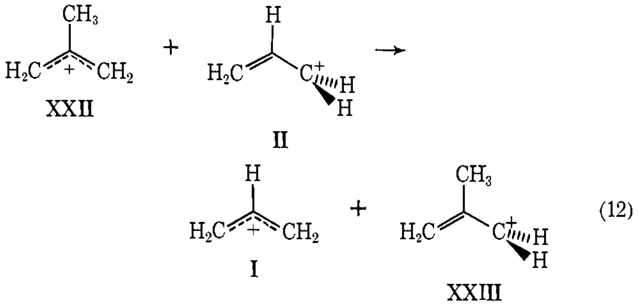
XIX

XX

XXI

be favored by carbonium ion stabilizing substituents R, R′, at C_1 (or C_3), since such groups would lower the energy of XX to a much greater extent than XXI. All allyl cation stereomutations observed to date have involved such substitution patterns and either have been established to proceed *via* path A, or are presumed to have done so.[56,57] Path B should be favored by carbonium ion stabilizing substituents R′′ at C_2 since now XXI and not XX would be stabilized. In the absence of experimental examples of this pathway, it is of interest to establish theoretical expectations.

The parent allyl cation should favor path A over B as the perpendicular allyl cation (II) is more stable than the cyclopropyl cation (III) by 4.4 kcal mol^{-1} (6-31G*). However, STO-3G calculations[58] indicate that the 2-methylallyl cation XXII should stereomutate *via* path B instead. This is best illustrated by the methyl transfer reaction (eq 12 and 13) which should provide reasonably reliable relative energies. 2-Methyl sub-



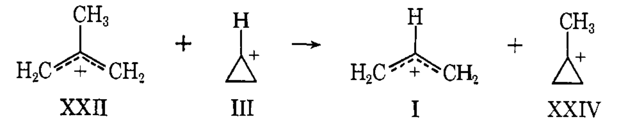
XXII

II

I

XXIII

(12)



XXII

III

I

XXIV

(13)

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[54] See P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, J. Paust, and K. Fellenberger, *J. Amer. Chem. Soc.*, **94**, 125 (1972); W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *ibid.*, **94**, 133 (1972), and references therein.

[55] (a) U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967); (b) U. Schöllkopf, E. Ruban, P. Tonne, and K. Riedel, *ibid.*, 5077 (1970); see also D. Seebach and M. Brown, *Angew. Chem.*, **84**, 60 (1972).

[56] P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

[57] J. M. Bollinger, J. M. Brinich, and G. A. Olah, *J. Amer. Chem. Soc.*, **92**, 4025 (1970); N. C. Deno, R. C. Haddon, and E. N. Nowak, *ibid.*, **92**, 6691 (1970); also see ref 15.

[58] Details of the calculations of XXII–XXIV and related species will be published later: L. Radom, J. A. Pople, and P. v. R. Schleyer, submitted for publication.

stitution in the perpendicular allyl cation XXIII provides a slight stabilization (-1.9 kcal mol^{-1}, eq 12), but 1-methyl substitution produces a much larger effect in going from III to XXIV (-20.4 kcal mol^{-1}, eq 13). Stereomutation of XXII should proceed through the 1-methylcyclopropyl cation (XXIV) since methyl substitution favors path B over path A by 18.5 kcal mol^{-1}.

Electron releasing substituents, R$''$, which stabilize carbonium ions to a greater extent than methyl should favor path B even more. In the extreme such substituents might even render the 1-substituted cyclopropyl cations more stable than their 2-substituted allyl counterparts. From known thermochemical data[59] and theoretical stabilization energies of substituted methyl cations,[60] it would appear that methoxy, hydroxy, and amino groups should be such substituents. Abundant experimental evidence is available already. Many cyclopropane substitutions are known involving 1-RO- and 1-R$_2$N-cyclopropyl cation intermediates; these proceed *without* ring opening.[61] The stable 1-dimethylaminocyclopropyl cation has been observed directly.[62] In addition, reactions involving cyclopropyl cations stabilized by 1-aryl,[63] 1-cyclopropyl,[64] 1-alkenyl,[65] and 1-thiophenoxy[55b] groups are known which proceed with only partial ring opening. However, despite attempts,[66] no cases of closure of 2-substituted allyl cations to 1-stabilized cyclopropyl cations have been discovered yet.[67] The problems appear to be practical rather than thermodynamic.

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(59) R. H. Martin, F. W. Lampe, and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 1353 (1966).

(60) J. A. Pople, submitted for publication.

(61) W. J. M. van Tilborg, S. E. Schaafsma, H. Steinberg, and Th. J. deBoer, *Recl. Trav. Chim. Pays-Bas*, **86**, 417 (1967); J. Szmuskovica, D. J. Duchamp, E. Cerda, and C. G. Chidester, *Tetrahedron Lett.*, 1309 (1969); H. H. Wasserman and M. S. Baird, *ibid.*, 1729 (1970), 3721 (1971); W. J. M. van Tilborg, G. Dooyewaard, H. Steinberg, and Th. J. deBoer, *ibid.*, 1677 (1972); a case which may involve a 1-fluorocyclopropyl cation is also known: P. Weyerstahl, G. Blume, and C. Miller, *ibid.*, 3869 (1971).

(62) E. Jongejan, W. J. M. van Tilborg, Ch. H. V. Dussen, H. Steinberg, and Th. J. deBoer, *Tetrahedron Lett.*, 2359 (1972).

(63) D. B. Ledlie and E. A. Nelson, *Tetrahedron Lett.*, 1175 (1969); D. T. Clark and F. Smale, *Chem. Commun.*, 868 (1969); W. J. M. van Tilborg, J. R. van der Vecht, H. Steinberg, and Th. J. deBoer, *Tetrahedron Lett.*, 1681 (1972).

(64) J. A. Landgrebe and L. W. Becker, *J. Amer. Chem. Soc.*, **89**, 2502 (1967); **90**, 395 (1968); B. A. Howell and J. G. Jewett, *ibid.*, **93**, 798 (1971).

(65) M. L. Poutsma and P. A. Ibaria, *Tetrahedron Lett.*, 4967 (1970).

(66) H. M. R. Hoffmann, private communication, Sept 1971.

(67) For an apparent exception, see D. Cantacuzène and M. Tordeux, *Tetrahedron Lett.*, 4807 (1971); J. C. Blazjewski, D. Cantacuzène, and C. Wakselman, *Tetrahedron*, in press.

Molecular Orbital (CNDO/2 and MINDO) Calculations on Protonated Deoxyribonucleic Acid Bases. The Effects of Base Protonation on Intermolecular Interactions

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Abstract: The electronic reorganization accompanying monoprotonation of DNA bases was examined employing all-valence-electron SCF molecular orbital methods. σ as well as π reorganization upon protonation is evident in all four bases. Stacking and hydrogen-bonding interactions were calculated including monopole–monopole, monopole–induced dipole, and dispersion terms between the various bases in their neutral and monoprotonated states for all possible combinations. The intermolecular interactions are invariably more favorable for half-protonated pairs (*i.e.*, one base protonated) than for neutral pairs. Stacking interactions are always unfavorable in doubly protonated pairs (*i.e.*, both bases protonated).

As part of a continuous program in this laboratory to examine the effect of the state of ionization of nucleic acid components on their electronic structures and intermolecular interactions, recently all-valence-electron CNDO/2 and MINDO SCF calculations were reported on some adenine tautomers and their protonated analogs.[1]

This contribution completes our studies at the level of approximation of base interaction only. Electronic structures of all four protonated bases, adenine (A), guanine (G), thymine (T), and cytosine (C), are described and an attempt is made to predict their interbase interactions both in the vertical (stacking) and horizontal (in-plane) hydrogen-bonding mode.[2]

The theoretical approaches employed are the same as those previously reported, the CNDO/2[3a] and

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(1) F. Jordan and H. D. Sostman, *J. Amer. Chem. Soc.*, **94**, 7898 (1972).

(2) Some other abbreviations used are poly T, poly A, poly G, poly C, and poly U for the homopolymers and ApA, ApG, ApC, etc., for the dinucleoside monophosphates. For example, ApA would have a O-3′ and a O-5′ bound adenosine attached to the phosphate.

(3) (a) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **44**, 3289 (1966); Quantum Chemistry Program Exchange No. 91; (b) N. C. Baird and M. J. S. Dewar, *ibid.*, **50**, 1262 (1969); Quantum Chemistry Program Exchange No. 137.