On the Structure of $C_4H_7^+$

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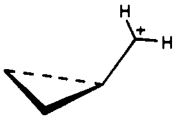
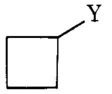
Abstract: The potential surface of $C_4H_7^+$ in the vicinity of the bisected cyclopropylcarbinyl cation has been investigated by ab initio molecular orbital theory using the 4-31G split-valence basis set. In addition to the bisected cyclopropylcarbinyl cation, a second potential minimum, 0.5 kcal mol^{-1} higher in energy at the 6-31G*//4-31G level, has been uncovered, the structure for which is best represented in terms of approximately equal contribution to the two classical valence forms A and B.

$C_4H_7^+$ has been the focus of a number of experimental and theoretical studies directed at rationalizing the facile interconversion of cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl derivatives under solvolytic conditions, and at explaining the observed proton and carbon magnetic resonance spectra of stable cationic species derived from such precursors in superacid media.[1,2] It is presently believed that the solvolysis transition state(s) and the intermediate(s) observed under "stable ion" conditions may not be represented by any static structure. It is also likely that the bisected cyclopropylcarbinyl cation (I) plays some role in the overall scheme. It is not obvious, however, whether any dynamic scheme involving the bisected (classical) cyclopropylcarbinyl cation alone (Scheme I) is capable of satisfactorily explaining the experimental observations. In particular, the observed carbon chemical shifts of $C_4H_7^+$ under stable ion conditions do not appear to be consistent with such a model. Therefore, it was earlier proposed that the equilibrium involved a set of equivalent σ-delocalized "bicyclobutonium" structures (Scheme II).[2e,i] More recent NMR evidence has suggested that the dynamic equilibrium must involve at least two different species of very similar stability, the bicyclobutonium ion (II) and the bisected cyclopropylcarbinyl cation (I), separated by a small energy barrier.[2a]

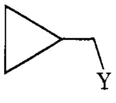


I

Additional experimental evidence[3] points to (a) stable cyclic structure(s) for tritiated $C_4H_7^+$ in the gas phase. β-Decay by $C_4H_{7-n}T_{n+1}$ yields $C_4H_{7-n}T_n^+$ cations which, upon being intercepted by bases Y = NH_3 or H_2O, yield significant quantities of tritiated products, i and ii.

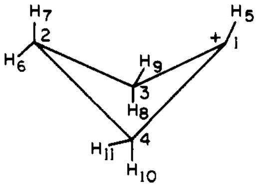


i

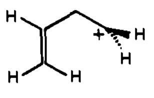


ii

Theoretical investigations to date have determined that the bisected cyclopropylcarbinyl cation is a local minimum on the STO-3G[4] potential surface, and that structures such as the puckered cyclobutyl cation (III) and homoallyl cation (IV) collapse without barrier to such a form.[2g,h] No evidence for other stable $C_4H_7^+$ forms was discovered at this level. Based on this data, it was earlier proposed that $C_4H_7^+$ exists as a rapidly equilibrating set of classical structures (Scheme I), the transition state for interconversion being a puckered cyclobutyl cation (III).

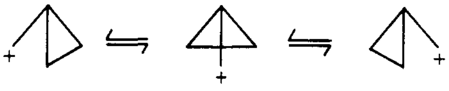


III



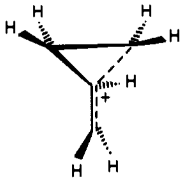
IV

Scheme I



I

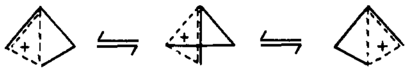
We report here that reinvestigation of the $C_4H_7^+$ potential surface using the more flexible split-valence 4-31G basis set[5] has yielded a second minimum energy form (V), similar in energy and structure to the bisected cyclopropylcarbinyl cation, yet lacking the plane of symmetry possessed by this ion. The calculated 4-31G geometry for V as well as for the bisected cyclopropylcarbinyl (I) cation and puckered cyclobutyl cation (III) are presented in Table I. While the bisected cyclopropylcarbinyl cation corresponds to an energy minimum on the 4-31G potential surface, the puckered cyclobutyl cation represents an energy maximum, and therefore may not be considered a stable form of $C_4H_7^+$.[6,7]



V

The theoretical geometry for V (two views of which are given in Figure 1) closely resembles that of the bisected cyclopropylcarbinyl cation (I), Figure 2. The (formal) cationic center in cyclopropylcarbinyl has been twisted slightly, and the $C_4C_1C_2$ bond angle decreased such that the (formally) empty p orbital is now directed toward the C_1C_2 bond. As a result, electron density has been drained from the σ bond connecting C_1 and C_2 and the linkage lengthened. Also of note is the shortening of the C_1C_3 bond distance, reflecting the decreased overlap between the p orbital and the C_1C_3 σ bond. Little changed from cyclopropylcarbinyl is the C_1C_4 bond length (1.357 Å), nearly equal to that of a normal CC double bond (e.g., 1.318 Å for propene at the 4-31G level[9]). The near planarity of the three-carbon "propene" skeleton of V is apparent

Scheme II



II

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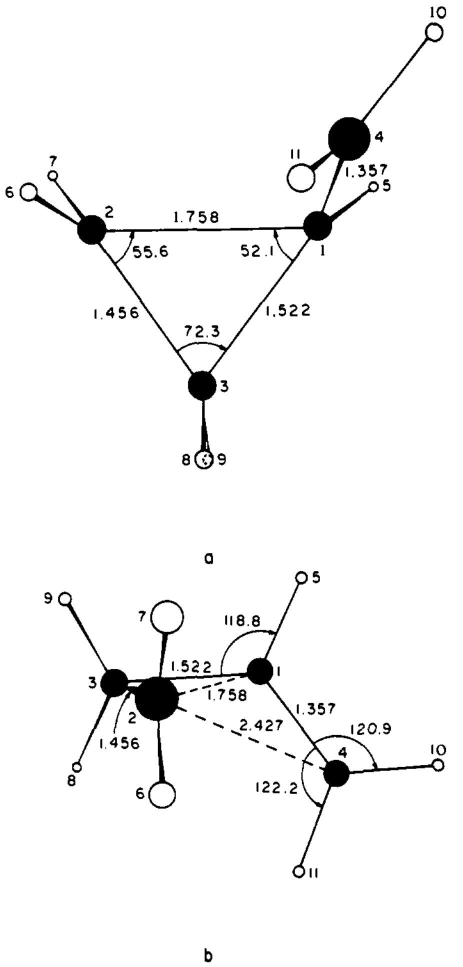


Figure 1. V, 4-31G optimized geometry. Geometrical parameters are summarized in Table I. View (a): the three carbons of the propane ring are in the plane of the paper. View (b): the plane of the (formal) cationic center is in the plane of the paper.

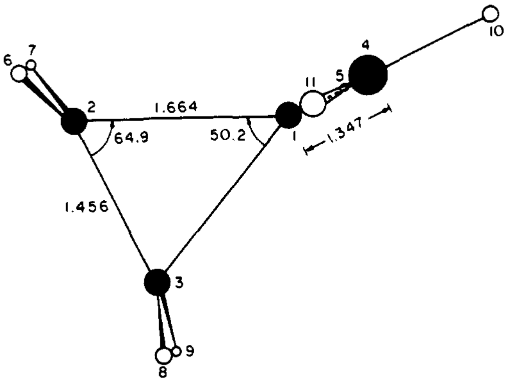


Figure 2. Bisected cyclopropylcarbinyl cation. 4-31G optimized geometry. Geometrical parameters are summarized in Table I.

from Figure 1b. In this view, the structure closely resembles that of a perpendicular form of cis homoallyl cation (IV).

Examination of the coefficients of the lowest unoccupied molecular orbital of V indicates that the electron vacancy is shared to a nearly equal extent by carbons 2 and 4. This result, in addition to the calculated equilibrium geometry, suggests that the ion is best represented by the pair of resonance forms A and B, or alternatively in terms of a single delocalized structure V. The latter representation coincides approximately with earlier formulations for the bicyclobutonium ion,[2a,b,e] although the apparent lack of significant bonding interactions between carbons 2 and 4 makes us reluctant to use such a name to describe V.

Table II gives the relative energies for the $C_4H_7^+$ isomers considered in the present study, both at the 4-31G level and as obtained from single point calculations (assuming optimum 4-31G geometries) using the 6-31G* polarization basis set.[10]

Table I. 4-31G Optimized Geometries[a]

geometrical parameter	V[b]	bisected cyclopropyl-carbinyl (I)[c]	puckered cyclobutyl (III)[d]
C_1C_2	1.758	1.664	1.778
C_1C_3	1.522	1.664	1.435
C_2C_3	1.456	1.412	1.650
C_4C_1	1.357	1.347	1.435
H_5C_1	1.069	1.067	1.074
H_6C_2	1.069	1.070	1.073
H_7C_2	1.071	1.071	1.070
H_8C_3	1.072	1.070	1.073
H_9C_3	1.072	1.071	1.071
$H_{10}C_4$	1.073	1.073	1.073
$H_{11}C_4$	1.073	1.074	1.071
$\angle C_3C_1C_2$	52.1	50.2	60.7
$\angle C_1C_2C_3$	55.6	64.9	49.3
$\angle C_1C_3C_2$	72.3	64.9	70.0
$\angle C_4C_1C_3$	121.0	117.7	108.8
$\angle C_4C_1C_2$	101.7	117.7	60.7
$\angle H_5C_1C_2$	115.5	115.2	116.4
$\angle H_5C_1C_3$	118.8	115.2	120.0
$\angle H_6C_2C_1$	117.4	113.6	137.9
$\angle H_6C_2C_3$	121.2	120.6	107.5
$\angle H_7C_2C_1$	106.6	108.1	107.8
$\angle H_7C_2C_3$	120.9	120.5	117.4
$\angle H_8C_3C_1$	116.3	113.6	119.4
$\angle H_8C_3C_2$	117.3	120.6	107.2
$\angle H_9C_3C_1$	113.0	108.1	117.9
$\angle H_9C_3C_2$	117.7	120.5	119.9
$\angle H_{10}C_4C_1$	120.9	121.4	119.4
$\angle H_{11}C_4C_1$	122.2	122.2	117.9
$\angle H_{10}C_4C_1C_3$	179.7	154.9	60.6
$\angle H_{11}C_4C_1C_3$	1.1	25.1	152.4
$\angle H_5C_4C_1C_3$	178.3	154.9	143.7

[a] Bond lengths in ångstroms, bond angles in degrees. [b] C_1 symmetry. [c] C_s symmetry. [d] C_s symmetry; puckering angle $C_1C_{3,4}C_2$ = 124.4° (where $C_{3,4}$ is the midpoint between C_3 and C_4).

Table II. Relative Energies of $C_4H_7^+$ Isomers[a] (kcal mol^{-1})

	4-31G//4-31G	6-31G*//4-31G
bisected cyclopropylcarbinyl (I)	0[b]	0[b]
V	1.5 (2.0)[c]	0.5 (1.0)[c]
puckered cyclobutyl (III)	10.9 (10.9)[c]	3.7 (3.7)[c]

[a] The nomenclature A//B indicates a calculation performed with basis set A using a geometry optimized with basis set B; e.g., 6-31G*//4-31G indicates a 6-31G* calculation using a geometry optimized at the 4-31G level. [b] 4-31G energy for cyclopropylcarbinyl cation = −154.998 06 au; 6-31G* energy = −155.227 50 au. [c] Corrected for zero-point vibrational energy via calculation of complete harmonic force field at the 4-31G level. Calculated zero-point energy for the bisected cyclopropylcarbinyl cation is 65.5 kcal mol^{-1}.

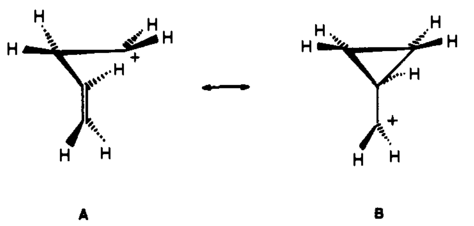
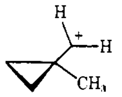
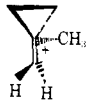
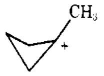


Table III. Relative Energies of 1-Methyl Derivatives of $C_4H_7^+$ Cations[a] (kcal mol^{-1})

cation	4-31G
	0^b
	0.8
	2.4

[a] Optimum 4-31G structures for $C_4H_7^+$ ions summarized in Table 11 were substituted in appropriate positions by methyl groups with standard model geometries (∠HCH = 109.4712°; CH = 1.09 Å; CC = 1.52 Å). [b] 4-31G energy for 1-methylcyclopropylcarbinyl cation is −193.980 18 au.

Both sets of theoretical results show the bisected cyclopropylcarbinyl cation to be the most stable form, although the energy of V is only 0.5 kcal mol^{-1} higher at the 6-31G* level. Listed in parentheses in Table II are relative energies corrected for zero-point vibrational energies obtained from the 4-31G calculations. Such corrections do very little to change the qualitative shape of the potential surface. It is not evident to these authors how further improvements in basis set (beyond the 6-31G* level) or inclusion of partial account of electron correlation will alter the calculated energy difference between the bisected cyclopropylcarbinyl cation (I) and the new form (V). The geometrical structures of the two ions are, qualitatively speaking, very similar (differing mainly by a slight twist of the formal carbocation center, and by distortion of the three-membered ring) and one might hope that whatever corrections higher level calculations might introduce would be small. The energy of the puckered cyclobutyl cation (III) is 3.7 kcal mol^{-1} above that of the cyclopropylcarbinyl cation and 3.2 kcal mol^{-1} higher than that of V) at the 6-31G* level. It represents a maximum on the potential energy surface, although it is unlikely that it plays a significant role in the interconversion of I and equivalent forms of V. Our theoretical results seem to be consistent with recent NMR spectral data of Olah and Roberts,[2a] their interpretation of which requires the participation of at least two different $C_4H_7^+$ isomers. They are not inconsistent with the gas-phase investigations of Cacace and Speranza,[3] although the second cyclic form of $C_4H_7^+$ uncovered theoretically more closely resembles cyclopropylcarbinyl than it does the puckered cyclobutyl cation. Species such as I or V, in which there is little positive charge on C_1, would seem unlikely to undergo facile interconversion of the methylene and methine positions as is required to explain the observed ^{13}C scrambling.[2b] The puckered cyclobutyl cation (III) is a more likely candidate, although our calculations indicate that it is not a minimum energy form.

4-31G calculations have been performed on the 1-methyl derivatives of I, III, and V. Geometries for these systems have been constructed by replacing the appropriate hydrogen on the corresponding parent ion by a "standard model" methyl group (tetrahedral, r_{CH} = 1.09 Å) using a connecting CC bond length of 1.52 Å. The relative energies of the methyl derivatives (Table III) mimic those of the parent systems. Assuming that the first two structures represent energy minima and the third a maximum (the complete force fields which are required to substantiate such assumptions have not as yet been obtained), our results on these systems are again consistent with the recent low-temperature NMR studies which also suggest the presence of at least two stable forms.

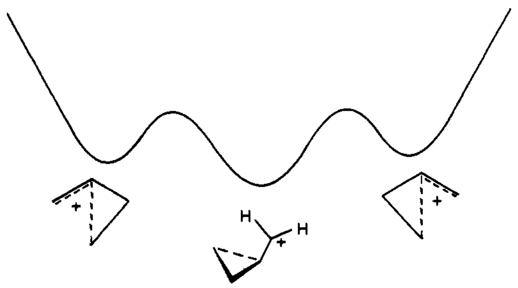


Figure 3. Potential energy surface for $C_4H_7^+$ in the region of the bisected cyclopropylcarbinyl cation.

We conclude that the potential surface for $C_4H_7^+$ contains a pair of equivalent asymmetrical minimum energy forms (V) in the region of the bisected cyclopropylcarbinyl cation (I) (Figure 3). These forms are presumably separated from the more stable cyclopropylcarbinyl cation by a very low energy barrier in view of the similarity of their structures. We further demonstrate that another isomeric form of $C_4H_7^+$, the symmetrical puckered cyclobutyl cation (III), is a maximum on the potential energy surface. These findings appear to be consistent with the model put forth by Olah and Roberts and their coworkers[2a,b] that averaging of the methylene carbons occurs via a rapid equilibrium involving two different forms of $C_4H_7^+$.

References and Notes

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(6) A structure corresponds to an energy minimum if the eigenvalues of the matrix of force constants are all positive. Transition structures are defined as those forms in which a single eigenvalue is negative. For all equilibrium and transition-state structures discussed herein, a full force field analysis was carried out employing the 4-31G basis set and assuming quadratic potentials.

(7) An algorithm to compute analytical first derivatives (gradient) has been incorporated into the GAUSSIAN 77 program.[8] This is used for geometry optimizations and for the calculation of quadratic force constants.

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