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A CNDO INVESTIGATION OF THE STRUCTURES AND ENERGIES OF $C_4H_7^+$ ISOMERS

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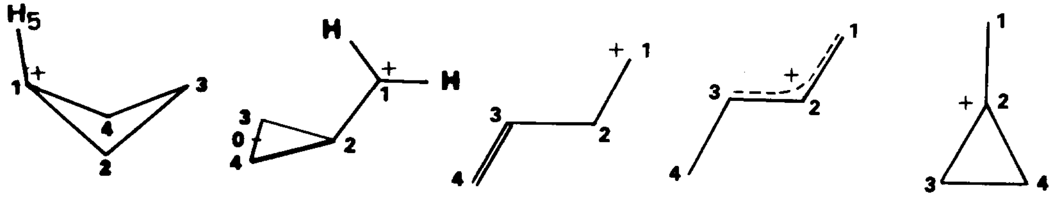
Extensive research has been done on the reactions of the cations of the C_4H_7 series (1). Solvolysis of $C_4H_7^+$ derivatives under S_N1 conditions usually yields a mixture of cyclopropylcarbinyl, cyclobutyl and homoallyl compounds. It has been demonstrated that such reactions involve partial positional degeneracy of the carbon atoms, which led Mazur, et al. (2) to suggest that nonclassical bicyclobutonium ions might play an important part as intermediates or transition states. Theoretical calculations (3) using extended Hückel theory suggested that such ions could be stable, but the method used is subject to some question as to its accuracy. More recently, Wiberg (4) studied the rearrangements of C_4H_7 cations with the CNDO/2 method (5), and Trindle (6), in a novel approach to the description of rearrangements, used CNDO/2 localized orbitals to examine several possible reaction paths between $C_4H_7^+$ systems. However, neither CNDO study included complete minimization of the geometries of the cations studied. Thus there is a degree of arbitrariness in the results. In particular, it is not possible to identify energy minima without such a treatment.

Our calculations were performed with a modified CNDO method (7) which has proven to be successful in predicting energetic relationships and geometries for hydrocarbons and carbonium ions (8). Through minimization of the total energies with respect to the geometrical parameters (with exception of the reaction coordinates in some cases) we have obtained good estimates of the energetic relationships in the $C_4H_7^+$ series.

The relative energies and the main features of the geometries of several important species are summarized in table 1. The homoallyl ion III is calculated to be unstable with respect to both the bicyclobutonium ion I and the methylallyl ion IV. The most stable of the ions which play a part in the solvolysis reactions mentioned earlier is the symmetrical bicyclobutonium cation I. The most favored conformation of the four-membered ring is the puckered form, but the planar form is also more stable than the next species, the "bisected" cyclopropylcarbinyl cation II. The transition of II to I requires an activation energy of at most 4 kcal/mol (all transitions were examined by calculating energies for several points along possible reaction paths and minimizing the energy of any transition states encountered). An interesting result of our calculations is the surprising stability of the methylcyclopropyl cation V. The hydrogen shift from II to V is hindered only by the rotational barrier of the methylene group in II (9 kcal/mol).

Table 1: Relative Energies and Geometries of C_4H_7 Cations*)



I	II	III	IV	V
$E_{rel} = 0$	$E_{rel} = 20$	$E_{rel} = 60$	$E_{rel} = 32$	$E_{rel} = 1$
$\overline{12} = 1.46$	$\overline{12} = 1.41$	$\overline{12} = 1.47$	$\overline{12} = 1.39$	$\overline{12} = 1.47$
$\overline{13} = 1.63$	$\overline{23} = 1.58$	$\overline{23} = 1.53$	$\overline{23} = 1.43$	$\overline{23} = 1.50$
$\overline{23} = 1.60$	$\overline{34} = 1.46$	$\overline{34} = 1.36$	$\overline{34} = 1.50$	$\overline{34} = 1.52$
$\overline{24} = 2.35$	$\overline{13} = 2.61$	$\sphericalangle 123 = 116^\circ$	$\sphericalangle 123 = 123^\circ$	
$\sphericalangle 513 = 123^\circ$	$\sphericalangle 120 = 126^\circ$	$\sphericalangle 234 = 125^\circ$	$\sphericalangle 234 = 126^\circ$	

*) Energies in kcal/mol; distances in Å. Detailed geometries will be furnished upon request.

The non-classical nature of I and II is best demonstrated by the results of an energy partitioning analysis (9) in table 2. In I, C-3 is approximately equidistant from the other carbon atoms. Two of the bonds can be described as weak single bonds, while the transannular interaction (E^R_{13}=-0.359) is typical of non-classical bonds (8b). The two other bonds to C-1 are somewhat shorter than normal single bonds to cationic centers, but the strengths of the bonds are normal. The most striking feature of the energy partitioning analysis for II is the unusually strong bond from the cationic carbon to the ring. This bond is comparable in strength to that of the allyl cation (8b), and localized orbitals constructed with the method proposed by Edmiston and Ruedenberg (10) show that the pertinent bond orbital involves all four carbon centers in a π system quite similar to that in the allyl cation (the orbitals involved are C-1:p_y; C-2:p_y; C-3,4:s,p_x,p_z when the plane of symmetry is the xz plane). The analogy to the allyl system is strengthened by the similarity of the energy partitioning terms, the bond lengths and the rotational barriers in the two systems (E^R_{12}=-0.909 a.u.; r_{12}=1.408 Å; E_{rot}=11kcal/mol, respectively, for the allyl cation).

Table 2: Energy Partitioning Analysis of I and II*)

AB	I		II	
	$-E^R_{AB}$	$-E_{AB}$	$-E^R_{AB}$	$-E_{AB}$
12	.728	.719	.922	.907
13	.359	.304	-.006	-.005
24	-.008	-.026	.486	.516
34	.514	.506	.725	.734

*) E_{AB} defined by: total energy $E=\sum_{A} E_A + \sum_{A<B}\sum E_{AB}$; resonance energy $E^R_{AB}=2\sum_{\mu\in A}\sum_{\nu\in B} P_{\mu\nu}\beta_{\mu\nu}S_{\mu\nu}$; all values in atomic units (=27.21 eV).

These findings seem to be in good agreement with experimental results. Olah recently found strong evidence for a non-classical structure for the stable cation which is formed from cyclobutanol or cyclopropylcarbinol in SbF_5-SO_2ClF at -80° (11). Our calculations indicate that the first product formed in S_N1 solvolysis of cyclobutyl and cyclopropylcarbinyl compounds should be the bicyclobutonium ion. The scrambling of the carbon atoms occurs during the equilibration of this ion with the bisected cyclopropylmethyl cation (activation energy 24 kcal/mol). Furthermore, the ring opening of I to the homoallylic system should be irreversible, and probably occurs only after nucleophilic attack at the four-membered ring. The fact that 1-methylallyl derivatives are not generally produced in such reactions would tend to support this conclusion, because the homoallyl cation would be expected to rearrange to this system to a great extent (deamination of allylcarbinyl amine was reported to yield 28% methylallyl product (12)).

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