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SEMIEMPIRICAL MO CALCULATIONS IN THE $C_3H_7^+$-SERIES

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The $C_3H_7^+$ system is currently under active investigation, both experimentally and theoretically. The present state of affairs has been well surveyed in a paper by Lee and Kruger (1). There seems to be strong evidence for protonated cyclopropane as an intermediate for which structures I to III have been discussed. Calculations by Hoffman (2) using extended Hückel theory (EHT) and an ab initio calculation by Petke and Whitten (3) favor edge-protonated (I) over face-protonated (III) cyclopropane. However, a disadvantage of both these calculations is that the results depend on assumptions made for the geometry of these species for which no experimental data are available. We have recently shown (4) that the INDO method (5) can be used to predict geometries of organic molecules with reasonable accuracy. Using the INDO method and a modified CNDO method (to be described below) we were able to characterize all the transition states and intermediates in the $C_3H_7^+$ series with respect to their geometry and their energy. This was accomplished by a complete minimization of the total energy as a function of the nuclear coordinates. The C-C and C-H bondlengths thus obtained with modified CNDO deviate in general less than 2% from experimental values.

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*) This work was initiated while the authors were at Carnegie-Mellon University Pittsburgh, Pa.

The results of our calculations may be summarized as follows:

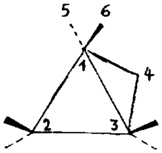
1) The most stable $C_3H_7^+$ species is an edge-protonated cyclopropane (I) where two C-C bonds have the same length as in cyclopropane while the third is considerably longer. The distance of the "proton" from the two equivalent carbon atoms is 1.29 Å. The stretching force constant calculated for each of the nonclassical bonds of the proton at the edge is 4.2 (6.7 in INDO) mdyne/Å as against 8.6 (11.9 in INDO) mdyne/Å for the other C-H bonds. The energy gained on protonation of cyclopropane (V) amounts to 235 (321 in INDO) kcal/mole compared with 155 kcal/mole calculated by Petke and Whitten without complete minimization of the energy.

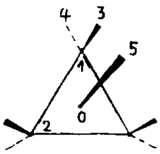
2) The methyl-bridged ethylene ion (III) which our calculations indicate to correspond to a local energy minimum is 10 kcal/mole higher in energy than edge-protonated cyclopropane (I) (22 kcal/mole in INDO). The "ethylene bond" in III has a length of 1.44 Å and the distance between the pseudo-methyl group and the carbon atoms of the "ethylene unit" is 1.63 Å. The C-H bondlengths in the pseudo-methyl group are not all equal. The stretching force constant for the nonclassical C-C bonds is 4.9 (11.0 in INDO) mdyne/Å and for the "ethylene bond" 10.2 (17.5 in INDO) mdyne/Å compared with a C-C stretching force constant of 8.4 (15.2 in INDO) mdyne/Å calculated for cyclopropane. The stabilization energy of III with respect to CH_3^+ and ethylene amounts to 108 (416 in INDO) kcal/mole. The EHT method predicts (2) III to be unstable with respect to CH_3^+ and ethylene.

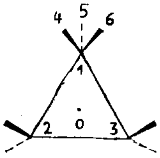
3) C-protonated cyclopropane (IV) in which one carbon atom has a configuration similar to a trigonal bipyramid is a transition state between two edge-protonated species if the proton is forced to remain in the plane of the ring. The energy of IV is 43 kcal/mole higher than that of I (90 kcal/mole in INDO).

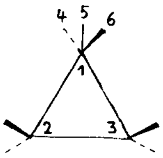
4) Face-protonated cyclopropane (II) does not correspond to an energy minimum in the $C_3H_7^+$ system. The lowest energy found for a species having C_{3v} symmetry was 76 (120 in INDO) kcal/mole relative to the energy of I. Klopman (6) calculated 50 kcal/mole for this energy difference.

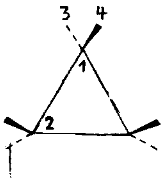
5) No energy minimum was found for n-propyl cation which (in the gas phase)











I	mod. CNDO	INDO
E_{rel} *)	0	
$\overline{12}$	1.52	1.48
$\overline{13}$	1.67	1.59
$\overline{14}$	1.29	1.28
∢516	111	111

II	mod. CNDO	INDO
E_{rel}	76	120
$\overline{12}$	1.55	1.50
$\overline{13}$	1.12	1.13
$\overline{05}$	1.04	1.06
∢013	134	132
∢014	119	122

III	mod. CNDO	INDO
E_{rel}	10	22
$\overline{12}$	1.63	1.56
$\overline{23}$	1.44	1.41
$\overline{14}$	1.13	1.13
$\overline{15}$	1.12	1.12
∢4103	34	35
∢510	118	119
∢410	111	108

IV	mod. CNDO	INDO
E_{rel}	43	90
$\overline{12}$	1.54	1.48
$\overline{23}$	1.50	1.48
$\overline{14}$	1.16	1.16
$\overline{15}$	1.20	1.20
∢415	60	62

V	mod. CNDO	INDO
E_{rel}	235	321
$\overline{12}$	1.51	1.48
$\overline{13}$	1.11	1.12
∢314	110	109

should collapse to the edge-protonated form I without activation energy. This may not necessarily be true in solution since it is to be expected that solvent molecules will stabilize an open chain n-propyl cation (1). The isopropyl cation will be discussed in a forthcoming paper.

6) The barrier between III and I was found to be lower than 1 kcal/mole. This difference is obviously too small to be of chemical significance. In view of the high energies of structures II and IV the interconversion of two (identical) edge-protonated species must pass through III and this process can be thought of as a rotation of the pseudo-methyl group in I through an angle of 60^{o} with a barrier of 10 kcal/mole. The description as a rotation is of course an oversimplification since there are considerable C-C and C-H bondlength changes involved in the rotation. Our calculations thus support the mechanism suggested by Lee and Gruber (7) for the solvolysis of cyclopropane.

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*) E_{rel} = total energy in kcal/mole relative to I; distances $\overline{AB}$ in Å; angles in degrees.

The modified CNDO method we propose was found to give better energies and bond lengths as will be shown elsewhere (8). It is identical with the original CNDO method (9) except for a different evaluation of the core matrix elements $H_{\mu\nu}$ for which we write:

$$H_{\mu\mu} = I_{\mu} - (Z_A - 1)\cdot \gamma_{AA} - \sum_{B \neq A} V_{AB} \qquad \mu \in A$$

$$\mu \neq \nu : \quad H_{\mu\nu} = \frac{1}{2}\cdot(\beta_A \cdot I_{\mu} + \beta_B \cdot I_{\nu})\cdot S_{\mu\nu} \qquad \nu \in B$$

$$V_{AB} = Z_B \cdot \left[0.78\cdot\gamma_{AB} + 0.22\cdot\mu_A \,/\, \left(\sqrt{1 + (\mu_A R_{AB})^2}\right)\right]$$

The following empirical parameters were found to give the best fit for hydrocarbons: $I_{2s}(C) = -20.00$, $I_{2p}(C) = -10.00$, $I_{1s}(H) = -13.605$ eV; $\beta_C = 0.987$, $\beta_H = 0.594$; $\mu_H = Z_H' = 1.16$, $\mu_C = Z_C'/2 = 1.625$. Thus V_{AB} is assigned a value somewhere in between the values proposed in CNDO/1 (9) and CNDO/2 (10) respectively. In addition, the invariance of the theory with respect to hybridization is given up.

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