Barriers to Internal Rotation in Carbonium Ions: a Non-empirical LCAO–MO–SCF Investigation of 1- and 2-Fluoroethyl Cations

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Summary The barriers to rotation in 1- and 2-fluoroethyl cations have been investigated and it is shown that for both ions the most stable conformer has hydrogen eclipsing fluorine.

NON-EMPIRICAL SCF–LCAO–MO calculations can provide invaluable information on conformational processes.[1,2] In contrast to the large number of studies of barriers to internal rotation in neutral molecules, there have been few studies of charged species and in particular carbonium ions. The barrier to internal rotation in the ethyl cation has been the most extensively studied[3] and is indistinguishable from zero. This corresponds to the picture normally assumed by organic chemists, that in simple alkyl carbonium ions there is free rotation. It is of considerable interest therefore to investigate the effect of substituents on barriers to internal rotation of ethyl cations. We present here preliminary results obtained for the 1- and 2-fluoroethyl cations.

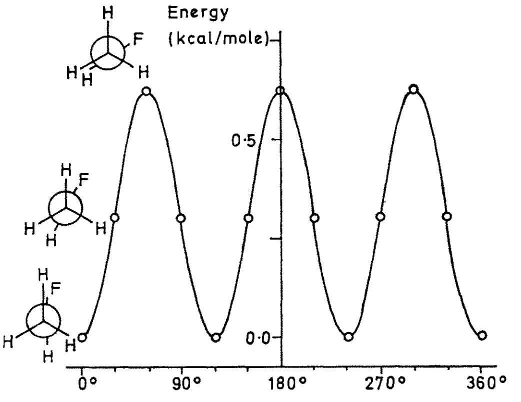

FIGURE 1

The calculations have been carried out using the IBMOL IV computer program.[4] The basis set of 60 Gaussian functions consisted of a seven *s*, three *p* atomic set[5] for the C and F atoms and three atomic set[4] for the H atoms. The 60 Gaussian functions were then reduced to 22 contracted Gaussians. The geometries were derived from that previously optimized for the ethyl cation,[6] with a hydrogen atom at C-1 or C-2 being replaced by fluorine, the C–F bond length being taken as 1·33 Å.[7]

For both ions, calculations were carried out on distinct staggered and eclipsed conformations. A total of three calculations on 1-fluoroethyl cation and four on 2-fluoroethyl cation allows the construction of energy diagrams corresponding to intervals of 30° in the angle of rotation about the C–C bonds.

The results for the 1-fluoroethyl cation are shown in Figure 1. There are two features of interest. Firstly, the very low barrier to rotation (0·62 kcal./mole) and secondly, the most stable conformation is with hydrogen eclipsing fluorine. It is of interest to compare this situation with that in the isoelectronic acetaldehyde molecule. The barrier to rotation in this case is 1·16 kcal./mole and the most stable conformer has hydrogen eclipsing oxygen.[8] The results for the 2-fluoroethyl cation are shown in Figure 2. The most stable conformer has hydrogen eclipsing fluorine, and the least stable conformation is staggered.

On simple grounds the reverse might have been expected. In contrast to ethyl and 1-fluoroethyl cations, there is a substantial (10·53 kcal./mole) barrier to rotation and this has important ramifications as far as any discussions of the reactions of the carbonium ion are concerned. This is particularly striking when compared with the situation in ethane and ethyl fluoride, where calculations using a comparable basis set give values of 2·72 and 2·60 kcal./mole respectively for the barriers to rotation. Preliminary analysis of the component energy terms shows that for both of the carbonium ions the barriers are of the attractive type as in acetaldehyde, whereas the barriers in ethane and ethyl fluoride are of the repulsive type. Pictorially the stability of the eclipsed conformations of the 1- and 2-fluoroethyl cations could perhaps be attributed to favourable interactions between the eclipsed H and F atoms. However, a population analysis shows little evidence of this, and the bond overlap populations between the eclipsing atoms for both ions is small and negative.

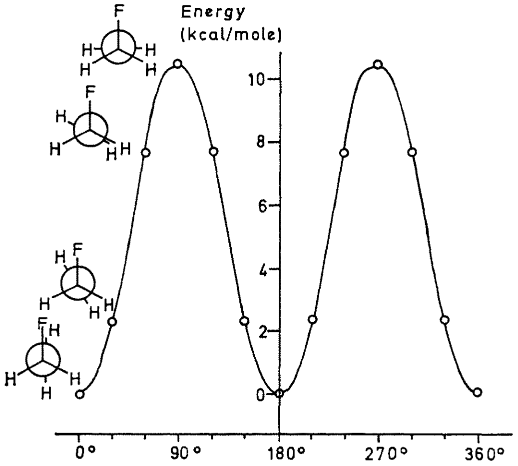

FIGURE 2

It is of interest to compare the total energies of the 1- and 2-fluoroethyl cations and the effect of introducing fluorine into the ethyl cation. The 1-fluoroethyl cation is calculated to be 39·36 kcal./mole lower in energy than the 2-fluoroethyl cation (total energies −176·528818 and −176·52545 a.u. respectively), and this can be attributed to the substantial $+M$ effect of fluorine attached to an electron-deficient centre. This is clearly shown by a population analysis, the gross atomic population on fluorine in ethyl fluoride, 1-fluoroethyl cation, and 2-fluoroethyl cation, being 9·28, 9·10, and 9·22 respectively. Some measure of the electronic effect of fluorine can also be obtained by comparing the relative energies for the process RH → R^+ + H^-. Taking this reaction with ethane as standard, the relative energies for production of CH_3CH^+F is −29·5 kcal./mole and for $CH_2F–CH_2^+$ + 9·9 kcal./mole. The stabilizing and destabilizing influence of substituting F for H at the 1- and 2-positions respectively in ethyl cation, is clearly shown. From mass spectrometric appearance potentials, Martin and Taft[9] have estimated that for the methyl cation, replacement of H by F stabilizes the resulting ion by 27 ± 3 kcal./mole. This agrees favourably with that calculated here for the 1-fluoroethyl cation.

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