Conformational Energy Differences and Barriers to Rotation in Fluoroethanes

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Summary Molecular mechanics calculations when combined with a non-tetrahedral but standardised geometry are shown to give a quantitative explanation of the observed barrier heights and rotamer energies of all the fluoroethanes; in particular the 'attraction' of the two fluorines in 1,2-difluoroethane can be explained on this basis without the necessity for any additional mechanisms.

THERE have been a number of attempts to calculate the conformational behaviour exhibited by highly electronegative atoms such as fluorine and oxygen.[1–3] In the case of 1,2-difluoroethane, however, the conformation with the two fluorine atoms in a *gauche* orientation is considerably more stable than all such calculations have predicted.

This phenomenon has been 'rationalised' in terms of 'the maximum number of *gauche* interactions between the polar substituents,'[1,4] by delocalisation effects,[5] and by substituent electronegativity effects,[6] but none of these rationalisations provides any general quantitative explanation. Quantum mechanical calculations (extended Huckel,[7] CNDO/2,[8] STO-3G[9]) have also so far failed to reproduce the observed data.

We report that molecular mechanics calculations based on the conventional formalism[3] but allied to a real standardised non-tetrahedral geometry provide a complete quantitative explanation of all the conformational data yet observed in fluoroethanes. The calculations compute all the non-bonded interactions in any molecule using equation (1), where θ is the dihedral angle, V_0 the torsional

$$E/\text{kcal mol}^{-1} = V_0(1 + \cos 3\theta)/2 + \sum_{ij}\{\epsilon_{ij}[(\sigma_{ij}/r_{ij})^{12} - (\sigma_{ij}/r_{ij})^{6}] + 332{\cdot}0\, e_i e_j/r_{ij}\} \quad (1)$$

potential, ϵ_{ij} and σ_{ij} steric interaction parameters characteristic of atoms i and j, e_i the electronic charge on atom i, and r_{ij} the interatomic distance in Å. The steric interaction potentials for carbon and hydrogen were chosen to agree with those used by Hendrickson[10] but the fluorine potential used has been derived from the polarisability and the ionic radius of the fluorine atom. (Similar considerations were used for all the other halogens.)

TABLE

Observed and calculated barriers to rotation and conformational energy differences (in kcal mol^{-1}) for the fluoroethanes

Compound	Calculated $E^{\ddagger}$ or ΔE ($E_g - E_t$)	Observed[3,14]
CH_3CH_2F[a]	3·3	3·3
CH_3CHF_2[a]	3·1	3·2
CH_3CF_3[a]	3·1	3·1
CF_3CH_2F[a]	3·8	3·7, 4·2
CF_3CHF_2[a]	4·4	3·7, 4·4
CF_3CF_3[a]	3·6	3·9
CH_2FCH_2F[b]	0·6	±0·2
CHF_2CH_2F[b]	0·8	1·2
CHF_2CHF_2[b]	1·0	1·2

[a] Barrier to rotation ($E^{\ddagger}$). [b] $E_g - E_t$.

The charge on an individual atom was calculated using a simple additivity scheme in which the parameters were chosen to resemble the excess electron densities obtained using the programme CNDO/2.[11]

A fundamental difference between this and previous studies lies in the choice of the molecular geometries. In the present case all the bond angles were taken as being tetrahedral, with the exception of the FCF angles. There is a substantial amount of evidence[12,13] that when two fluorine atoms are bonded to the same carbon, the magnitude of the FCF angle is considerably less than the tetrahedral value. The value of 103·42° was adopted for the FCF angle in both

CHF_2-, and CF_3-groups, this being the value obtained in a recent X-ray study on a compound containing a CF_3 group.[13]

The model has been applied to the calculation of the barriers to rotation, and rotamer energy differences ($E_{\text{gauche}} - E_{\text{trans}}$) of the nine possible fluoroethanes.

The results obtained (Table) show a reasonable correlation between the observed and calculated values and demonstrate that it is possible to explain the conformational behaviour of the fluoroethanes using the same basic interactions as for other molecules. Consequently the necessity of introducing additional interactions in the case of fluorine-containing compounds has merely reflected the uncertainties in the steric and polar terms for fluorine and the geometry of the molecule as a whole, rather than signifying some unique interaction which is present only in the case of fluorine and presumably the other highly electronegative atoms.

The discrepancies that remain between the calculated and observed energy differences and barriers may reflect the limitations of the model used and its rigidly defined geometry. In addition the experimentally observed values are themselves subject to some uncertainty. However, bearing in mind the limitations of the approach the agreement between the observed and calculated values is very pleasing and indicates the feasability of a classical approach of this kind when applied to fluorine-containing compounds.

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