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ON THE INTERACTION OF GEMINAL FLUORINES AND GEMINAL CYANO GROUPS. 'ANOMALOUS' ORDERING OF ROTATIONAL BARRIERS IN FLUOROETHANES

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In the course of a study of an additivity scheme for conformational energies of substituted ethanes, [2,3] we were intrigued by the *lack* of additivity displayed by the haloethanes.[4] Thus, whereas monofluoro-substitution in ethane leads to an increase in experimentally observed barrier from 2.93 to 3.33 kcal mol^{-1}, additional geminal fluorine substituents decrease the barrier to 3.18 kcal mol^{-1} (1,1-difluoroethane) and 3.25 (±0.2) kcal mol^{-1} (1,1,1-trifluoroethane), respectively.[5] Geminal chloro substituents in ethane show a similar trend with observed barriers of 3.68 kcal mol^{-1} (chloroethane), 3.49 (±0.2) kcal mol^{-1} (1,1-dichloroethane) and 2.91 (±0.2) kcal mol^{-1} (1,1,1-trichloroethane).

Because of the large uncertainties associated with some of the experimental barrier values, previous workers[6] have questioned whether the anomalous barrier ordering is a real effect. For this reason, we have carried out ab initio molecular orbital calculations on 1,1-di- and 1,1,1-tri-fluoroethane to supplement calculations on ethane and fluorethane already available[7]. The calculations were performed with the Gaussian 70 series of programs[8] and the extended 4-31G basis set[9]. Minimal basis sets have previously been found unsatisfactory in describing the conformational behaviour of fluoroethanes[10,11]. Standard[12] bond lengths and bond angles have been used except where noted; the effect of relaxing this constraint is under investigation.

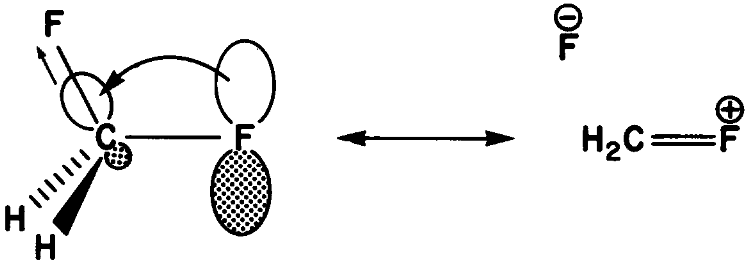
The theoretical barriers follow the ordering

ethane (3.26 kcal mol^{-1}) < fluoroethane (3.63 kcal mol^{-1}) > 1,1-difluoroethane (3.39 kcal mol^{-1}) ≈ 1,1,1-trifluoroethane (3.40 kcal mol^{-1})

thus reproducing the experimental results, in contrast to classical methanical[6], CNDO/2[13] and minimal basis set STO-3G[11] calculations on the same molecules. The effect of geminal fluoro substituents on the rotational barrier in ethane is clearly not additive. Given that the first fluoro substituent leads to an *increase* in rotational barrier[10], the question we seek to answer is why does subsequent fluoro substitution lead to a *decrease* in barrier height?

Our explanation stems from noting the following:

(i) Geminal fluoro-substitution on a saturated carbon leads to double bond character in the C-F bonds (I);[14] and

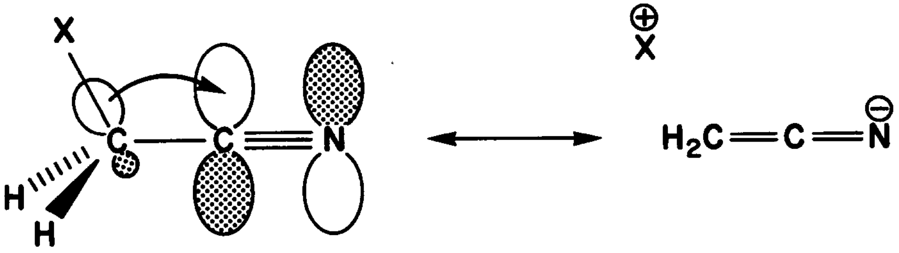


I

(ii) the preferred orientation of a methyl group adjacent to a double bond (as, for example, in propene, acetaldehyde, etc.) is well established experimentally and theoretically to have a C-H eclipsing the double bond[15].

The effect of (i) in 1,1-difluoro- and 1,1,1-trifluoroethane is to impart double bond character to the C-F bonds and hence by (ii) to stabilize the eclipsed conformations compared with the staggered forms[16]. The observed barrier trends are thus accounted for.

In order to test this mechanistic proposal further, we have carried out additional calculations on cyano-substituted molecules. In contrast to fluorine which is a Π-donor, the cyano substituent is normally a Π-acceptor and the interaction shown in I is unlikely to occur to a significant extent. Rather, the interaction II is likely to be more important.



II

This effect should be most pronounced for σ-electron donating groups X. It will occur to a slight extent for X = H but much less so for X = CN. For the latter case, the decreased interaction should lead to (a) decreased double bond character and hence a slight *increase* in C-C bond length in $CH_2(CN)_2$ compared with CH_3CN in contrast to the situation for CH_3F and CH_2F_2 where there is a pronounced *decrease* in C-F bond length due to increased double bond character;[17,18] and (b) according to our hypothesis above, slightly increasing barrier increments along the series CH_3CH_3, CH_3CH_2CN, $CH_3CH(CN)_2$,...

Our first step in the process of testing these predictions was to derive optimum 4-31G values of C-C lengths for cyano- and dicyano-methane assuming standard values for the other bond lengths and for the bond angles[19]. Indeed, the bond lengths so obtained, 1.457 Å in CH_3CN (*cf* experimental 1.458 Å) and 1.463 Å in $CH_2(CN)_2$ (*cf* experimental 1.468±0.034 Å) confirm (a) above[20], particularly when compared with lengths obtained in a similar theoretical treatment[18] of CH_3F (1.405 Å) and CH_2F_2 (1.375 Å). On the other hand, electronegativity arguments which provide an alternative rationalization for the decreasing bond lengths in the fluoromethanes would have also predicted decreasing bond lengths in the cyanomethanes.

The next step involved calculations on staggered and eclipsed conformations of cyano- and 1,1-dicyano-ethane. The theoretical rotational barriers increase in the order

ethane (3.26 kcal mol^{-1}) < cyanoethane (3.77 kcal mol^{-1}) < 1,1-dicyanoethane (4.47 kcal mol^{-1})

with increasing barrier increments as anticipated above.

The interactions of geminal cyano groups and of geminal fluorines can be compared in yet another way by examining heats of bond separation reactions[21] (1)

$$CH_2X_2 + CH_4 \rightarrow 2CH_3X \qquad (1)$$

A positive value for the heat of reaction (1) implies a relative stabilising interaction between the geminal C-X bonds. The theoretical values derived using the partially optimised geometries above are +9.8 kcal mol^{-1} (X = F; *cf* experimental value +12.1 kcal mol^{-1}) and -9.9 kcal mol^{-1} (X = CN; no experimental value available). The negative value for $CH_2(CN)_2$ confirms the destabilising interaction of the geminal cyano groups.

In conclusion, we emphasise the following points.

(i) Additivity schemes for conformational energies should be used with caution. Significant deviations from additivity occur for strongly interacting geminal groups.

(ii) In particular, the 'anomalous' ordering of rotational barriers in the geminally substituted fluoroethanes can be rationalised in terms of increasing double bond character in the C-F bonds.

(iii) Interaction of geminal C-CN bonds is destabilising, and leads to lengthening of the C-C bonds, in contrast to the known stabilising interactions of geminal C-F bonds.

(iv) This work provides another example of the importance of the interaction of geminal groups[7,14,22].

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(19) The conclusions are not altered if the C≡N lengths are also optimised. Optimum values in this case are for CH_3CN, 1.457 Å (C-C) and 1.142 Å (C≡N), and for $CH_2(CN)_2$, 1.463 Å (C-C) and 1.140 Å (C≡N).

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