THE EFFECT OF HALOGEN ATOMS ON BARRIERS TO ROTATION IN SUBSTITUTED ETHANES

J.E.Anderson and H.Pearson[1]

Chemistry Department, University College, Gower Street, London WC1E 6BT.

There have been reports recently on the effect of alkyl groups on barriers to rotation in highly substituted ethanes[2a-d]; we here report the effect of halogen atoms. The Table shows rate constants and barriers to rotation in the series 1a-1e, and the augmentation of the barrier compared with 1a (the P-value[2c]) in each case. These barriers have been determined by the nmr method.[2b,2c]
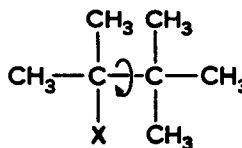
1   a)   X = H
    b)   X = F
    c)   X = Cl
    d)   X = Br
    e)   X = I

The barrier increases along the series although the increase is small beyond the chloro-compound. It is interesting to compare the series with barriers to rotation in the ethyl halides[3] and with axial-equatorial free-energy differences in the cyclohexyl halides (A-values[4]), which form the last two lines of the Table. Again there is an increase in the free-energy term as each series progresses to chlorine, but thereafter the progression stops or even reverses slightly. Further in both these cases, the relative differences in free-energy terms are smaller, reflecting the fact that in the series 1, interacting groups come much closer together.

TABLE

Compound and	1a X = H	1b X = F	1c X = Cl	1d X = Br	1e X = I
Temperature ($^{\circ}$K)	143.4	149.8	208.0	214.2	212.3
Rate Constant for Rotation (sec^{-1})	72	6.0	48	50	14.9
Rotational Barrier$^{\neq}$ (kcal/mol)	6.97	8.04	10.43	10.73	11.14
P-value^{2c} (kcal/mol)	0	1.1	3.5	3.8	4.2
Rotational Barrier^{3} for CH_3-CH_2X (kcal/mol)	2.88	3.33	3.68	3.68	3.22 ($\pm$ 0.5)
A-value^{4} (kcal/mol)	0	0.28	0.53	0.48	0.47

$\neq$ $\pm$0.1 kcal/mol. Value for 1a measured from a sample of $(CD_3)_2CD$—$C(CH_3)_3$

In the three series there is a wide variation in the geometry of the interactions involving the halogen atom, so the consistent tailing off along the series may reflect a general steric characteristic of these atoms. The interactions involved should be considered in terms of the interatomic distances, of van der Waals radii, and of the anisotropy of the van der Waals surface of a bound halogen atom, some measure of which is given by the polarisability of the carbon-halogen bond. We shall expound this approach elsewhere, noting that it has been useful already in the cyclohexyl series.[4]

References

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(2) a)B.L.Hawkins, W. Bremser, S. Borcic, and J.D. Roberts, J.Amer.Chem.Soc., 93 4472, (1971); b)J.E. Anderson and H. Pearson, J.Chem.Soc.B, 1209,(1971); c)J.E. Anderson and H. Pearson, Chem.Commun., 871,(1971); d)C.H.Bushweller and W.G.Anderson, Tetrahedron Letters, 1811,(1972).

(3) Values are taken from J.P. Lowe, Progr.Phys.Org.Chem., 6,1,(1968) where original references are cited.

(4) a)F.R. Jensen, C.H. Bushweller, and B.H. Beck, J.Amer.Chem.Soc., 91,344,(1969). b)F.R. Jensen and C.H. Bushweller, Adv. Alicyclic Chem.,3, 139 , (1971)