Secondary Steric Effects on Barriers to Rotation in Substituted Ethanes

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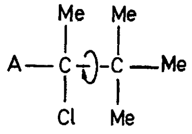
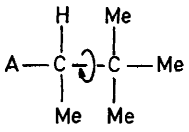
Summary Two secondary steric effects of substituents on barriers to rotation in substituted ethanes are reported, illustrated, and discussed.

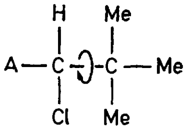
Bulky substituents, alkyl groups[1] or halogen atoms,[2] raise the barrier to rotation about a carbon–carbon single bond, due to increased steric interactions along the bond in an eclipsed transition state. The concept of size of an atom or group is not uniquely defined,[2] implying that more subtle effects might be important, and we now report two of these: (i) that barriers to rotation in molecules with parallel (1,3) interactions[3] in the ground state are unusually low and (ii) that bulky groups in a β-position with respect to the ethane bond may give rise to unusually high barriers to rotation.



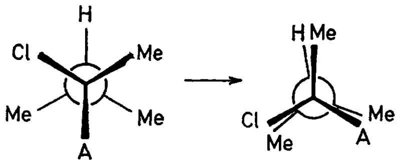
(1) X,$\Delta G^{\ddagger}$ = 10·43 Y,$\Delta G^{\ddagger}$ = 11·1



(2) X,$\Delta G^{\ddagger}$ = 6·97 Y,$\Delta G^{\ddagger}$ = 7·87



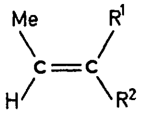
(3) X,$\Delta G^{\ddagger}$ = 7·87 Y,$\Delta G^{\ddagger}$ = 8·87



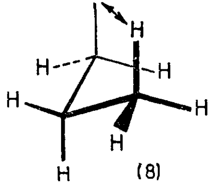
(4) X, $\Delta G^{\ddagger}$ = 7·4 Y, $\Delta G^{\ddagger}$ = 8·4 (5)

For the series of compounds (**1**—**5**) barriers to rotation[†][4] are markedly higher in group Y (A = Cl) than in group X (A = Me). There are many interactions which should be almost the same in the two series and these we shall ignore, concentrating on the two which vary. Firstly the increased barriers in series Y may reflect the fact that chlorine–methyl eclipsed interactions[‡] are greater than methyl–methyl eclipsed interactions.[‡] However we reject this possibility since it disagrees with simple ideas of the relative bulk of methyl groups and chlorine atoms. More specifically[5] compound (**6**) is more stable than compound (**7**) by about 0·8 kcal mol^{-1}. This is presumably a consequence of differing *cis*-interactions[‡] which are geometrically similar to eclipsing interactions.

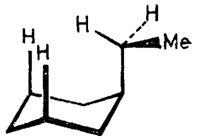
As a second possibility the increased barriers may indicate that in the ground states, methyl–methyl *gauche* interactions[‡] are more destabilising than the corresponding methyl–chlorine ones. Significantly the *gauche* form of n-propyl chloride is more stable than the *trans*-form,[6a] while the *gauche* conformation of butane is less stable than the *trans*[6b] reflecting parallel (1,3) interactions[3] as in (**8**). Thus it seems that the steric interaction present in the ground state of series X leads to barriers to rotation reduced compared with a reference series Y that is free of this interaction.



(6) R^1 = Cl, R^2 = Me
(7) R^1 = Me, R^2 = Cl



(8)



(9)

The axial–equatorial energy difference (*A*-value)[6c,7] for ethylcyclohexane is 1·75 kcal mol^{-1} almost the same as that for methylcyclohexane, 1·7 kcal mol^{-1}.[6c,7] This similarity reflects the fact that the methyl of the ethyl group can be accommodated in a position away from interaction with

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[†] Barriers quoted are representative values of $\Delta G^{\ddagger}$ (kcal mol^{-1}) at varying temperatures, measured by the n.m.r. method.

[‡] These are principally steric but there may be a dipole–dipole-interaction contribution.

the *syn*-axial hydrogen atoms as in (**9**). On a similar rationalisation it might be expected that the barrier to rotation in compounds (**10b**—**d**) should be very similar to that in the parent (**10a**) since the group R can take up a position remote from the substituents at the other end of the ethane bond as in (**11**)§. It is therefore surprising that the barriers to rotation in (**10b**) and (**10c**) are about 0·4 kcal mol^{-1} greater than in (**10a**).

The transition state for rotation in (**10**) is as in (**12**), and it appears that during eclipse and as a consequence of eclipsing interactions, there is compression of the tetrahedra at either end of the ethane bond. The disposition of the group R is now particularly unfavourable since it interacts with chlorine atom and the methyl group, the energy of the transition state is raised, and the barrier is higher. To test this hypothesis, we examined the compound (**10d**), and found the barrier to rotation to be 1·4 kcal mol^{-1} greater than for (**10a**).

Recent results of Bushweller and Anderson[8] for polyalkylethanes show an interplay of these two secondary effects superimposed on the primary steric effect.

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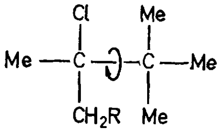
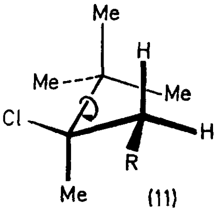


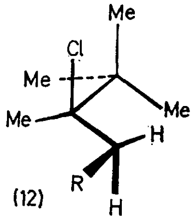
$Me-C(Cl)(CH_2R)-C(Me)_2-Me$

a; R = H $\Delta G^{\ddagger}=10{\cdot}43$
b; R = Me $\Delta G^{\ddagger}=10{\cdot}82$
c; R = Ph $\Delta G^{\ddagger}=10{\cdot}85$
d; R = CMe$_3$ $\Delta G^{\ddagger}=11{\cdot}80$

(**10**)



(**11**)



(**12**)

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§ Further on examining (**11**), the group R will *prefer* the position shown since other positions have parallel (1,3) interactions with methyl groups.

[1] J. E. Anderson and H. Pearson, *Chem. Comm.*, 1971, 871. The value of 8·32 kcal mol^{-1} quoted for $\Delta G^{\ddagger}$ for (**2**)Y, was not obtained by a full line-shape treatment.

[2] J. E. Anderson and H. Pearson, *Tetrahedron Letters*, 1972, 2779.

[3] A. B. Dempster, K. Price, and N. Sheppard, *Spectrochim. Acta*, 1969, **25A**, 1381.

[4] The result for (**1**)Y is from A. Rieker and H. Kessler, *Tetrahedron Letters*, 1969, 1227. The result for (**2**)X was obtained using a sample of $(CD_3)_2CDCMe_3$.

[5] R. P. Neureiter and F. G. Bordwell, *J. Amer. Chem. Soc.*, 1960, **82**, 5354.

[6] (a) E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis", Interscience, New York, 1965, pp. 15—17; (b) *ibid.*, pp. 13—15; (c) *ibid.*, p. 433.

[7] F. R. Jensen and C. H. Bushweller, *Adv. Alicyclic Chem.*, 1971, **3**, 139.

[8] C. H. Bushweller and W. G. Anderson, *Tetrahedron Letters*, 1972, 1811.