

Effect of Alkyl Groups on the Barrier to Rotation in Substituted Ethanes†

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Summary The effect of alkyl substituents R on the barrier to rotation about the central bond in the substituted ethane (I) is reported and discussed.

THE origin of the barrier to rotation about the carbon-carbon bond in ethane is a matter of dispute.¹ The barrier increases when hydrogen atoms are replaced by larger

substituents, such as halogen atoms.¹ Whatever the origin for ethane itself, the barrier for more highly substituted ethanes arises principally from steric interactions.‡ We report in Table I the barriers to rotation about the C-1-C-2 bond of compounds (Ia—g) as measured by the n.m.r. method.

TABLE I

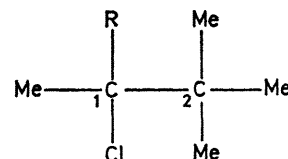
Barriers to rotation about the C-1-C-2 bond in substituted ethanes

Compound	T/K^a	$k_{\text{rotation}}/s^{-1}$	$\Delta G_T/kcal\ mol^{-1}$
(Ia) R=H	157.2	9	8.32 ± 0.2
(Ib) R=Me	208.0	48	10.43 ± 0.1
(Ic) R=Et	203.4	10	10.82 ± 0.2
(Id) ^b R=Pr ^t			
(Ie) PhCH ₂	209.1	19.7	10.85 ± 0.1
(If) Bu ^t	213.0	8.3	11.43 ± 0.1
(Ig) Ph	210.5	115	10.19 ± 0.1

^a The temperature of the sample ($\pm 1^\circ$) in the region of the RF-coil. ^b After repeated attempts we have been unable to prepare this compound free of elimination products which complicate the spectrum.

† For previous paper in series Rotation about Single Bonds see: J. E. Anderson and H. Pearson, *J. Chem. Soc. (B)*, 1971, 1209.

‡ This picture excludes ethanes containing more than one highly polar substituent. Barriers to rotation in several such molecules have been measured by the n.m.r. method,³ but there is no reliable means of separating electrostatic and steric interactions. We hope that by restricting our studies to ethanes with one polar substituent, or occasionally two polar substituents on the same carbon atom, the steric interactions will overwhelm electrostatic ones.



(I) a; R = H
 b; R = Me
 c; R = Et
 d; R = Pr^t
 e; R = PhCH₂
 f; R = Bu^t
 g; R = Ph

The barrier to rotation increases with the size of the group R, for no matter how poorly defined size is in this context, there is no doubt that a hydrogen atom is smaller than a methyl group which is in turn smaller than a t-butyl

group. The barrier in the phenyl compound (Ig) is relatively low. There is no simple explanation of this as the conformation about the phenyl-C-1 bond may change as rotation about the C-1-C-2 bond takes place.

The best-known free energy measure of the size of alkyl groups is the *A*-value, that for the axial-equatorial difference in substituted cyclohexanes.³ Table 2 lists such

TABLE 2

Conformational energies (kcal mol⁻¹)

	H	Me	Et	Pr ^t CH	PhCH ₃	But ^t	Ph
<i>A</i> -value ^a	0	1.70	1.75	2.15	b	4.2 ^d	3.0
<i>P</i> -value ^a	0	2.1	2.5	c	2.5	3.1	1.9

^a Barrier relative to (Ia) taken from Table 1. ^b Not known. ^c See footnote b of Table 1. ^d This is the most likely lower limit.³

values and a second set of values (for convenience, *P*-values) based on the results of Table 1.

These values are differences between energy terms, and therefore are not measures of absolute size. *A*-values are

the difference between the sums of all interactions of a group in an axial and in an equatorial position, *i.e.* they reflect principally 1,3-interactions. *P*-values reflect principally the difference in 1,2-interactions of an eclipsed and a staggered group. There may be no simple relation between the two series but each gives an estimate of size in a particularly common situation. The wide application of *A*-values in conformational analysis suggests that *P*-values reflecting the size of a group in the conformational environment of a carbon-carbon single bond might be useful.

The difference in the barriers to rotation of propane and ethane is 0.5 kcal mol⁻¹, which contrasts strikingly with the *P*-value of the methyl group, 2.1 kcal mol⁻¹. This discrepancy may mean that *P*-values have no general applicability, but it is more likely to reflect the fact that barriers to rotation in monosubstituted ethanes cannot be explained on simple steric grounds.

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¹ J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, 6, 1, which also lists barriers for substituted ethanes.

² F. J. Weigert, M. B. Winstead, J. I. Garrels, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1970, 92, 7359, and references therein.

³ J. A. Hirsch, *Topics in Stereochemistry*, 1967, 1, 199.