

Six-fold Rotational Potentials in Substituted Ethanes; a Dynamic N.M.R. Study of Tri-t-alkylmethanols

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Contrary to conventional thinking about carbon-carbon single bonds, there are *six different* locations for a methyl group and *six equivalent* conformations during 360° rotation of a t-butyl group in adamantyldi-t-butylmethanol; there is a high barrier to passage through an eclipsed conformation (rotation), and an almost as high barrier to passage through perfectly staggered transition states (libration); similar results obtained for other methanols R¹R²R³COH (R = adamantyl or t-butyl).

While the barrier to rotation in ethane is three-fold [Figure 1(A)], relatively simple substitution introduces six-fold character.¹ In hexamethylethane for example, the potential profile is calculated^{2,3} to be as in Figure 1(B), with three sets of two minima each, located about 14° on either side of the staggered 60°, 180°, and 300° orientations.⁴ The double minimum arises because skewing away from perfect staggering either in a clockwise or in an anticlockwise direction reduces the parallel 1,3-interactions between hydrogen atoms and methyl groups, some of which are indicated in (1), without an equal increase in torsional interactions. Rotation in the same sense about all seven carbon-carbon bonds is involved.

This skewing becomes more important in more highly substituted ethanes; Mislow and Wroczynski⁵ have reported changes in the ¹³C n.m.r. spectrum of tri-t-butylmethane and calculations which indicate that, in addition to a rotational barrier between skewed conformations (2) ⇌ (3), there is an almost as large barrier to passage through the staggered conformation (2) ⇌ (4), which they call libration. From the information they report these barriers are about 8 and 6 kcal mol⁻¹† respectively. There is thus a six-fold rotational potential for t-butyl group rotation in that molecule, with six sites of three different kinds for a methyl group as indicated qualitatively in (5).

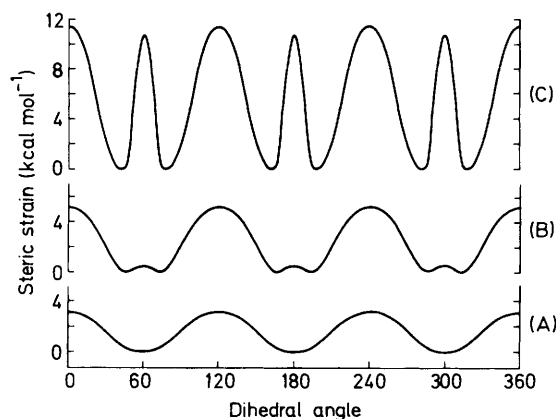
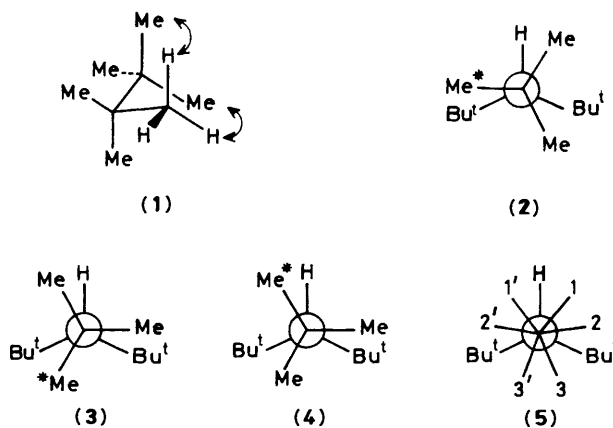


Figure 1. Experimental rotational potentials for (A) ethane and (C) adamantyldi-t-butyl methanol (8); (B) calculated potential for hexamethylethane.

The syntheses of compounds (6)–(9) have been reported elsewhere.⁶ Their n.m.r. spectra at various temperatures indicate a six-fold potential for t-butyl and adamantyl group rotation and in particular six *different* locations for each methyl group in a t-butyl group in (8) [as shown in (10)], and for the adamantyl carbon atoms in (7). Increasing complexity in the ¹³C n.m.r. spectra of all these compounds as the temperature is lowered indicates that two different processes are becoming slow on the n.m.r. timescale. The changes for (8) are illustrative of what happens for all four compounds and so will be described in some detail (see Figure 2). At 110°C there are sharp singlets in the ¹³C n.m.r. spectrum for each group [labelled 1 to 7 in (11)].

As the temperature is lowered from 110°C, the t-butyl methyl signal broadens, followed about 20°C lower by the adamantyl signals, then these signals split so that the C-1 signal appears as a 1:1:1 triplet and those of C-5, C-6, and C-7 as 2:1 doublets. Other signals remain unchanged as singlets. On cooling further there is renewed broadening of t-butyl and adamantyl signals, this time over the same temperature range. Eventually there is further splitting so that the t-butyl C-1 signal appears as six lines of equal intensity at -90°C, and those of C-5, C-6, and C-7 appear as 1:1:1 triplets. Strikingly, the C-2 signal appears as a 1:1 doublet, since the two t-butyl groups are non-equivalent [as structure (12) indicates]. These changes can be followed in Figure 2, although the two sets of changes interfere with each other in the middle temperature range.

We have written a computer program (SIXFOLD) using a McConnell-type modification⁷ of the Bloch equations, to



† 1 cal = 4.184 J.

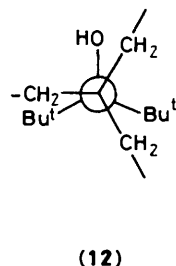
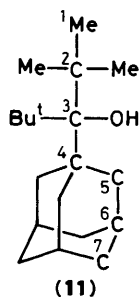
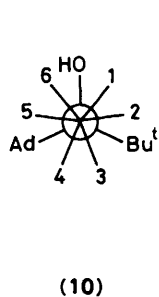
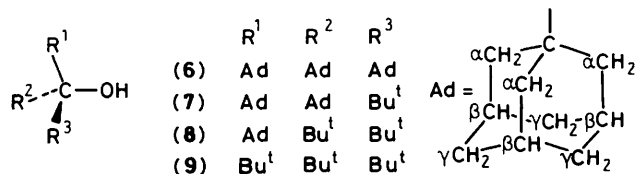


Table 1. Rotational and librational barriers (ΔG) for trialkylmethanols at specified temperatures [kcal mol^{-1} ($^\circ\text{C}$)].

Compound and substituents	t-Butyl rotational barrier	Adamantyl rotational barrier	Concerted librational barrier
(6) (Ad) ₃		15.4 (+50)	14.0 (-10)
(7) (Ad) ₂ , Bu ^t	14.4 (+115)	13.0 (-17)	11.6 (-42)
(8) Ad, (Bu ^t) ₂	11.7 (-45)	10.8 (-50)	10.3 (-60)
(9) (Bu ^t) ₃	10.0 (-60)		9.2 (-80)

model the changes to be expected in the spectrum with various values of the rate constants for passage through 0° and 60° conformations (k_0 and k_{60} , respectively). By matching calculated and experimental spectra, we have determined barriers of 11.7 and 10.8 kcal mol^{-1} to rotation of the t-butyl and adamantyl groups, respectively, and a barrier to concerted libration of 10.3 kcal mol^{-1} . The two processes can be distinguished by the need for the two groups to produce the same barrier to concerted libration.

Similar treatment of spectra for (6), (7), and (9) leads to the set of barriers shown in Table 1. Libration is assigned the lower barrier in (6) and (9) by analogy with what demonstrably obtains in (7) and (8).

The rotational barriers increase with the number of adamantyl groups, confirming earlier experience with simpler adamantyl and t-butyl compounds,^{8,9} but in contrast to simpler compounds,⁸ adamantyl group barriers are greater than those for t-butyl groups in the same situation. The range of rotational barriers (10.0–15.4 kcal mol^{-1}) belies the superficial similarity of the tri-t-alkylmethanol structures. Since t-butyl barriers may well be increased by loss of entropy during rotation in a way not possible for adamantyl groups,⁸ it may be that enthalpies of activation for rotation range even more widely.

The barriers on the whole are uncommonly large. If rotation of tertiary alkyl groups attached to a saturated quaternary hydrocarbon fragment is taken as a model,¹⁰ the highest known barrier^{2a} is 11.7 kcal mol^{-1} . The hydroxy group is not known to act as a substituent which greatly raises rotational barriers.¹¹ Barriers are high probably because rotation away from perfect staggering can be particularly well concerted in

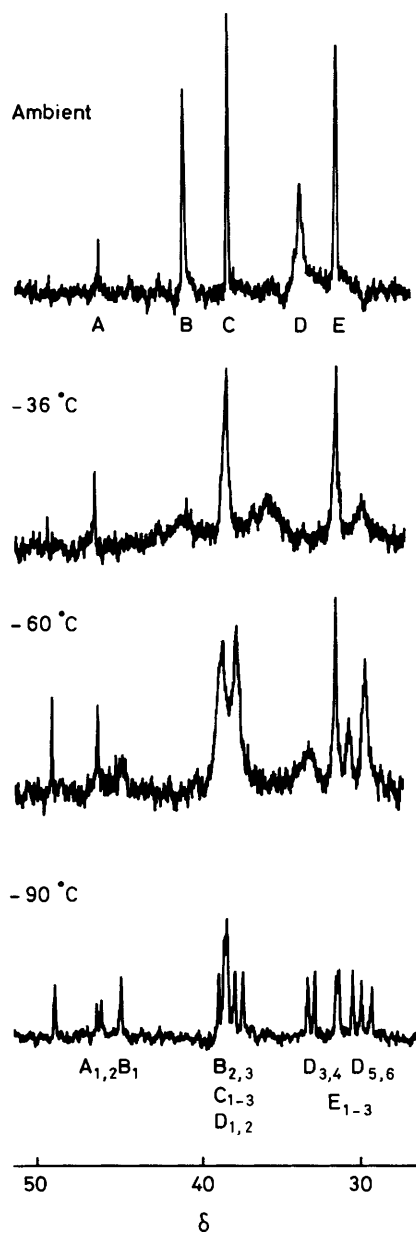


Figure 2. Upfield region of 50 MHz ^{13}C n.m.r. spectrum of (8) (1:1 $\text{CHF}_2\text{Cl}-\text{CHFCl}_2$ solution) at various temperatures. The peaks A–E are assigned to C_2 , C_5 , C_6 , C_1 and C_7 , respectively, see (11). At -90°C , these have split to doublets, triplets, and sextuplets as indicated.

these molecules. That the perfectly staggered conformations are between 9.2 and 14.0 kcal mol^{-1} less stable than the ground state is good evidence for this.

A potential energy diagram for t-butyl rotation in (8) can therefore be drawn in which the dihedral angle represented is an average of those which can be defined.^{6c} This diagram can be taken to represent a six-fold potential or as a superposition of two out-of-phase three-fold potentials. Certainly, during a 360° rotation cycle, there are six chemically different sites which a methyl group may occupy, six deep equivalent minima, and six by no means small barriers, see Figure 1(C).

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