Nuclear Magnetic Resonance. Slow Rotation of a Methyl Group

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Summary The n.m.r. spectrum of the CH_3 and CD_2H groups in (**3**) and (**4**) respectively is temperature-dependent, indicating that the barrier to rotation of the methyl group is 7·2 kcal mol^{-1} at $-131°$.

IT is fundamental to proton magnetic resonance spectroscopy that the three hydrogen atoms of a methyl group have the same chemical shift. Although so far this has been observed to be true, it should be so only if rotation of the methyl group is fast on the n.m.r. time-scale, in practice when the barrier to rotation is 4—6 kcal mol^{-1}. Since the highest recorded barrier[1] to methyl group rotation is 5·8 kcal mol^{-1} in 1,1,1-trichloroethane,[2] it is not surprising that there is no record of hydrogens in a methyl group being non-equivalent in the n.m.r.

From work on the effect of substituents on barriers to rotation in substituted ethanes,[3] one might hope to devise a molecule CH_3-C(X,Y,Z), (**1**) in which rotation of the methyl group is slow on the n.m.r. time scale. We have noted several studies[4,5] which suggest that the barrier in (**1**) should be higher if X, Y, and Z are linked together in a bridged molecule.

For a suitable molecule (**1**) the low-temperature spectrum of the methyl group should be complex (either an A_2B spectrum if $X = Y \neq Z$, or an ABC if $X \neq Y \neq Z \neq X$), and for this reason we chose to look for a compound of the type CD_2H–C(X,Y,Z), (**2**). While the CD_2H-signal might be broadened or appear as a quintet at ambient temperatures owing to hydrogen–deuterium coupling, rapid deuterium quadrupolar relaxation at low temperatures should result in decoupling of the deuterium, and the spectra in the two cases above should then be a 2:1 doublet or a 1:1:1 triplet respectively.[6]† We already know how to extract kinetic data from such spectra.[3b]

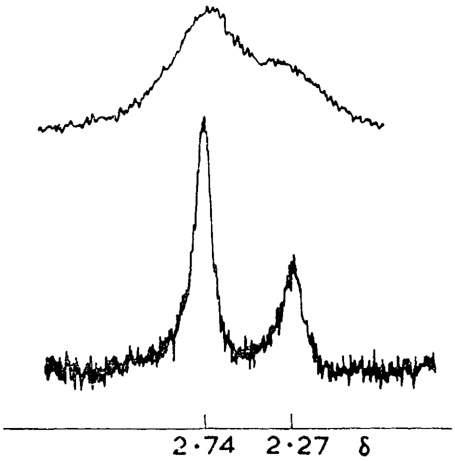
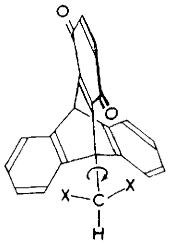


FIGURE. ^{1}H N.m.r. spectra at *ca.* −141°, in dichlorofluoromethane–vinyl chloride solutions (3:1). (a) CH_3 region for (**3**); (b) CD_2H region for (**4**). The linewidth of the stronger signal in (b) is 10·7 Hz, while that of Me_4Si is 3·3 Hz in the same solution at 100 MHz operating frequency.

On the basis of previous results,[5] we examined the n.m.r. spectra of (**3**) and (**4**). At ambient temperatures (**3**) shows a singlet for the methyl group while the CD_2H-group of (**4**) appears as a broadened singlet of linewidth 6·8 Hz, both at δ 2·5. These signals appear as 2:1 doublets at *ca.* −141°, (Figure). There are two staggered positions for a hydrogen of a methyl group in (**3**) and (**4**) either between a phenyl ring and a quinone ring or between two phenyl rings. The former is twice as likely, explaining the appearance of these doublets.



(3) X = H
(4) X = D

From a comparison of calculated and experimental spectra,[3b] the CD_2H group in (**4**) is rotating about 30 times per second at −131°, whence the barrier to rotation is 7·2 ± 0·3 kcal mol^{-1} at that temperature. It is to be expected that the barrier will be similar in (**3**), and that it is particularly high owing to the three *peri*-interactions in an eclipsed transition state.

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† As the temperature is lowered the correlation time for molecular tumbling increases and relaxation of the deuterium nuclei becomes more rapid. Eventually decoupling of the hydrogen and deuterium spins takes place.[6] In contrast slow tumbling of (**1**) should lead to *broader* signals owing to more ready dipole–dipole relaxation of the hydrogen atoms.

[1] A recent list of such values is given in J. P. Lowe, *Progr. Phys. Org. Chem.*, 1968, **6**, 1.

[2] J. J. Rush, *J. Chem. Phys.*, 1967, **46**, 2285. This is the highest liquid-phase barrier we know of. A solid-state barrier of 6·08 kcal mol^{-1} has been reported for 1,1,1-tribromoethane: J. R. Durig, S. M. Craven, C. W. Hawley, and J. Bragin, *J. Chem. Phys.*, 1972, **57**, 131.

[3] (a) B. L. Hawkins, W. Bremser, S. Borcic, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1971, **93**, 4472; (b) J. E. Anderson and H. Pearson, *J.C.S. Perkin II*, 1973, 960, and work cited therein; (c) C. H. Bushweller and W. G. Anderson, *Tetrahedron Letters*, 1972, 1811.

[4] J. P. N. Brewer, H. Heaney, and B. A. Marples, *Chem. Comm.*, 1967, 27.

[5] H. Nakanishi, O. Yamamoto, M. Nakamura, and M. Oki, *Tetrahedron Letters*, 1973, 727, and work cited therein; H. Iwamura, *J.C.S. Chem. Comm.*, 1973, 232; Y. K. Grishin, N. M. Sergeyev, O. A. Subbotin, and Y. A. Ustynyuk, *Mol. Phys.*, 1973, **25**, 297, and work cited therein.

[6] C. Brevard, J. P. Kintzinger, and J. M. Lehn, *Tetrahedron*, 1972, **28**, 2447 and work cited therein.