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HINDERED ROTATION IN 1,2-DINEOPENTYLTETRAMETHYLBENZENE

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1,2-Dineopentyltetramethylbenzene, I, is an extremely crowded molecule[1]. We have found that the rate of rotation about the C_{Ar}-CH_2 bonds is sufficiently slow to be measured by the methods of n.m.r. spectroscopy[2,3]. This is the first example of hindered rotation of alkyl groups attached to a single benzene ring.

The chemical shifts of the hydrogens obtained from a 5% solution in CCl_4 of I are as follows: $C(CH_3)_3$, 9.16; $C_{Ar}CH_3$, 7.785, and 7.744;[4] CH_2 centered at 7.083, tau units respectively. The magnitudes of these shifts are unexceptional. However, by -30° the methylene hydrogens become magnetically nonequivalent. Their absorption then consists of a typical AB quartet where $\delta_{AB} = 0.240$ ppm and $J_{AB} = 14.2$ cps, see Figure 1a.

With increasing temperature the AB quartet which remains centered at 7.083 tau collapses progressively to a single line by 80°, Figure 1a-f.

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[1] M. S. Newman, J. R. LeBlanc, H. A. Karnes and G. Axelrod, J. Am. Chem. Soc., 86, 868 (1964).

[2] S. Alexander, J. Chem. Phys., 37, 966 (1962).

[3] M. Saunders and F. Yamada, J. Am. Chem. Soc., 85, 1882 (1964).

[4] It is not possible to assign the ring methyl groups.

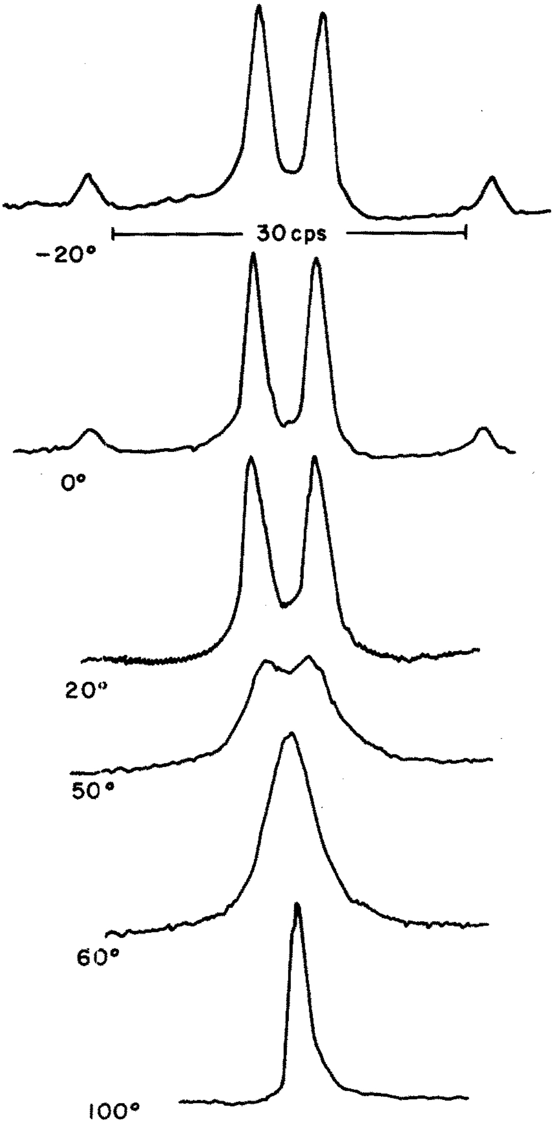

Fig. 1

n.m.r absorption, 60 Mc, for the methylene hydrogens in 1,2-dineopentyltetramethylbenzene, 5% in CCl_4.

From the appearance of these curves it is evident that their shapes are determined by the rate at which H_A and H_B exchange places[2].

The line-shapes for the above AB system undergoing different rates of $H_A \rightleftarrows H_B$ exchange have been calculated with a computor program[5]. Comparison of the observed line-shapes with the calculated ones gave the mean-life-times, τ, between $H_A \rightleftarrows H_B$ exchange in the methylene groups of 1,2-dineopentyltetramethylbenzene. The Arrhenius plot for these data shown in Figure 2 yields an activation energy of 11.5 ± 0.6 K cal for the exchange process.

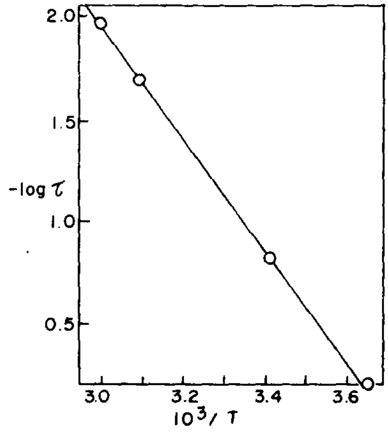

FIG. 2

Arrhenius plot for the rate of rotation about C_{Ar}-CH_2 in 1,2-dineopentyltetramethylbenzene.

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[5] Kindly donated by Professor Martin Saunders, Yale University.

That the average shift of H_A and H_B remains at 7.083 tau strongly implies that the same species predominates throughout all these measurements.

The slow $H_A \rightleftarrows H_B$ exchange observed here is most likely due to hindered rotation about the C_{Ar}-CH_2 bonds. Inspection of models reveals that the stable state of I has the two neopentyl groups on opposite sides of the ring. The methylene hydrogens are (in two environments) labeled A and B in Figure 3.

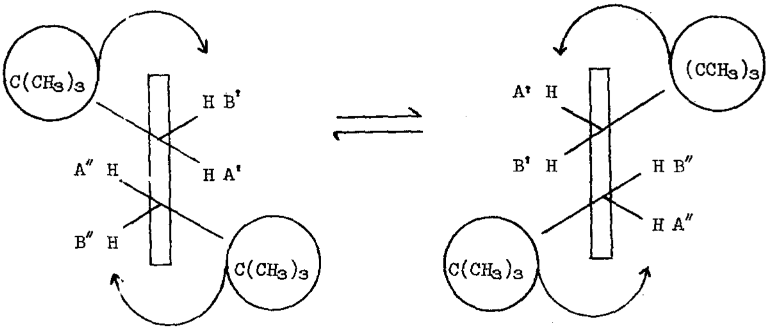

FIG. 3

End on view of 1,2-dineopentyltetramethylbenzene showing neopentyl groups and plane of ring. Arrows indicate direction of rotation of groups.

The exchange of the methylene hydrogens between the A and B environments is envisaged to take place by concerted rotations of the neopentyl groups about the C_{Ar}-CH_2 bonds, one conrotatory with respect to the other, Figure 3. In this way the methylene hydrogens pass each other and the *t*-butyl groups are always as far apart as possible.

Similar experiments were performed with isomeric dineopentyltetramethylbenzenes (1,4-dineopentyl- and 1,3-dineopentyl-)[1]. Neither of these compounds exhibited the behavior found for compound I.

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