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Proton Magnetic Resonance at Low Temperatures of Molecular Solids Containing CH_3 Groups

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Summary.

The proton magnetic resonance spectra and spin-lattice relaxation times have been measured between 4° K and their melting points for the five solid hydrocarbons 2.2- and 2.3-dimethylbutane, 1.2.3-, 1.2.4- and 1.3.5-trimethylbenzene. In all five compounds methyl group reorientation causes spectral narrowing, and in the case of the trimethylbenzenes this narrowing persists at the lowest temperature of measurement. Quantum-mechanical tunnelling appears to contribute appreciably to spin-lattice relaxation. Additional forms of molecular reorientation are also reported at higher temperatures in the case of the dimethylbutanes and 1.2.3-trimethylbenzene.

The proton magnetic resonance spectrum and the spin-lattice relaxation time have been measured down to 4° K for 2.2- and 2.3- dimethylbutane and for the three trimethylbenzenes. In all five materials quantum-mechanical tunnelling of the methyl groups plays an important role as might be expected. The two groups of materials provide a contrast in behaviour. In the trimethylbenzenes reorientation by tunnelling causes a narrowing of their resonance spectra even at 4° K, whereas in the dimethylbutanes the tunnelling rate is not sufficiently fast to narrow their spectra at the lowest temperatures.

The Dimethylbutanes. C_6H_{14}.

The absorption spectra of 2.2- and 2.3- dimethylbutane have their expected rigid-lattice second moments below 70° and 80° K respectively. Above these temperatures the second moments fall to values which are quantitatively accounted for by the assumption that the methyl groups are reorienting rapidly about their threefold axes. Both materials exhibit

first-order phase changes (at 127° * and 136° K respectively) which are accompanied by large releases of entropy, much greater than the entropies of fusion. The intermolecular forces above these transitions are therefore much weaker. This is reflected in each compound by a further sharp decrease in second moment to values which indicate a general motion of the molecules about their centres of mass, thus removing the intramolecular contribution to the second moment. The further narrowing of the lines to the very small widths which are recorded between the phase transitions and the melting points (174° and 145° respectively) indicate the onset of molecular diffusion.

The variation of spin-lattice relaxation time T_1 with temperature reflects these molecular motions. Of particular interest is the lower temperature region where the reorientation of the methyl groups controls the relaxation mechanism. The correlation times derived from the relaxation times depart markedly from a simple activation law at low temperatures, and it is necessary to take account of reorientation of the methyl groups by tunnelling. Expected tunnelling rates have been calculated in the way outlined by Das (1956, 1957) and further described by Stejskal and Gutowsky (1958). The methyl groups are considered as rotors restricted from free rotation by a sinusoidal potential barrier which is time-and temperature-independent. The splitting of each torsional energy level is a measure of the rate of reorientation of the groups by tunnelling through the barrier. At high temperatures the theory leads to a classical activation behaviour, while at low temperatures the correlation frequency tends to a constant value given by the splitting of the ground torsional state. The experimentally determined correlation frequencies shown in the figure are in good agreement with the calculated behaviour. For 2.2- dimethylbutane the barrier height indicated is about 4 k cal/mole and the corresponding tunnelling rate at the low temperature limit is about 25 kc/s. This is insufficient to narrow the spectrum, which has a measured width of 75 kc/s. The temperature-dependence of the spectral width indicates the occurrence of effective reorientation around 75° K; at this temperature the theoretical reorientation rate is 150 kc/s, in satisfactory agreement with experiment. The behaviour of the 2.3 isomer is similar and in essential agreement with the tunnelling model with a barrier height of 5 k cal/mole.

* 2.2- dimethylbutane also shows a first-order phase change of minor importance at 141°K

The Trimethylbenzenes. $C_6H_3(CH_3)_3$.

The absorption spectra of all three isomers are appreciably narrower at 4° K than expected for a rigid lattice. To account for the observed width it is necessary to assume that the methyl groups are reorienting with a frequency of several hundred kc/s (Eades, Finch and El Saffar 1959). The mean square widths, which decrease smoothly with increase of temperature, have the following values:

	Theoretical Rigid-lattice Second moment	Experimental Second moment 4.5° K	Experimental Second moment T.pt. or M.pt.
1.3.5-Trimethylbenzene	24.8 G^2	13.6 G^2	8.0 G^2 (M.pt., 222° K)
1.2.4-Trimethylbenzene	25.8 G^2	16.3 G^2	7.7 G^2 (M.pt., 229° K)
1.2.3-Trimethylbenzene	26.8 G^2	14.4 G^2	7.7 G^2 (T.pt., 219° K)

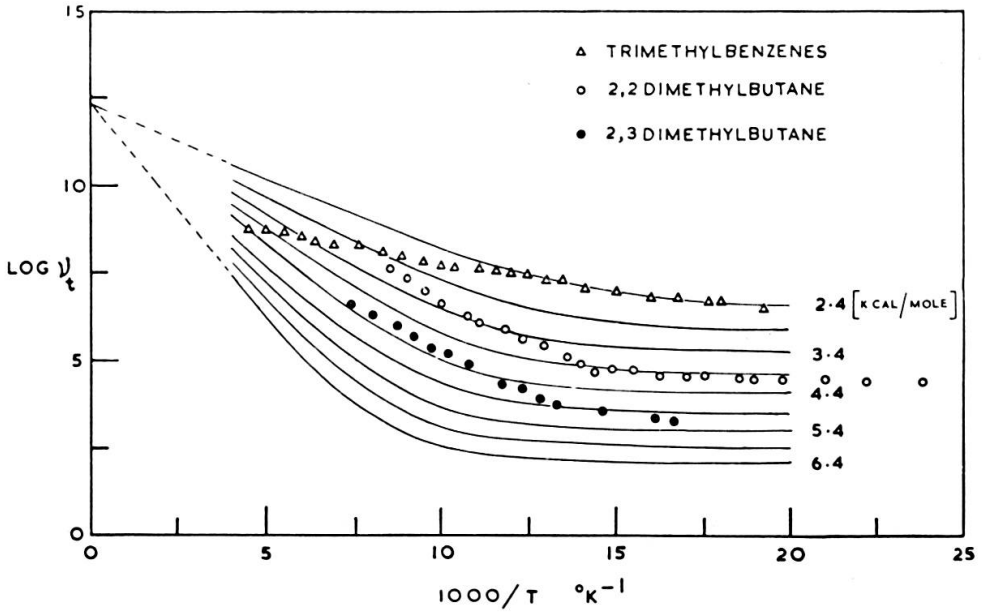

Figure Caption. The variation of reorientation rate with temperature for the dimethylbutanes and the trimethylbenzenes. The full lines show the theoretical behaviour for various barrier heights for the methyl groups. At the lowest temperatures tunnelling leads to a constant reorientation rate.

The continuous reduction of second moment between 4° and 220° K may well be due mainly to the combined effects of lattice expansion and increased

amplitude of molecular oscillations. In the case of the 1.2.3 isomer there is a linewidth transition at 219° K and above this temperature motion of the whole molecule reduces the second moment to 4.5 G^2.

Reorientation of the methyl groups can account for the observed spin-lattice relaxation over much of the temperature range studied. The relaxation times for all three isomers exhibit minima, and as with the dimethylbutanes the derived values of reorientation rate do not fit a simple activation law. However, as the figure shows, the values for all three isomers between 50° and 100° K can be approximately accounted for by assuming a barrier height of 2.5 k cal/mole. The corresponding ground-state tunnelling frequency is about 2 Mc/s, thus explaining why the spectra remain narrow even at 4° K. Irregularities have been observed in the values of T_1 at the lowest temperatures which cannot be explained in terms of the simple tunnelling model with a temperature-independent barrier.

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Résonance magnétique a basse température du proton de solides contenant des groupes CH_3

Résumé.

Les spectres de résonance magnétique du proton et les temps de relaxation spin-réseau ont été mesurés entre 4° K et le point de fusion pour les cinq solides hydrocarbonés suivants: 2.2 et 2.3 diméthyl-butane, 1.2.3, 1.2.4, et 1.3.5 triméthylbenzène. Dans ces cinq composés la réorientation du groupe méthyl provoque un rétrécissement du spectre, rétrécissement qui persiste même aux plus basses températures observées. L'effet tunnel de la mécanique quantique semble contribuer appréciablement à la relaxation spin-réseau. On rapporte d'autres formes de réorientation moléculaire à plus haute température dans le cas des diméthylbutane et du 1.3 triméthylbenzène.