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Nuclear Magnetic Resonance in some solid Hydrocarbons

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Résumé.

On examine les spectres de résonance magnétique nucléaire des protons du cyclohexène et des triméthylbenzènes 1-2-3 et 1-3-5 entre 80° K et 220° K.

Dans le cyclohexène le réseau est vraiment rigide au-dessous de 100° K et le second moment S de la raie de résonance est en bon accord avec la valeur théorique calculée pour une structure moléculaire en anneau sans tensions. La transition de phase à 139° K se traduit par une diminution importante de S , indiquant l'apparition soudaine de mouvements moléculaires importants. On discute les réorientations possibles.

A 85° K, les spectres des deux triméthylbenzènes ont des seconds moments beaucoup plus petits que les valeurs calculées pour des réseaux rigides. Le mouvement moléculaire responsable de la diminution de S est probablement la réorientation des groupes « méthyl ». Le temps de relaxation spin-réseau du triméthylbenzène 1-2-3 est nettement plus petit que celui du triméthylbenzène 1-3-5 dans tout l'intervalle de températures 84° K-220° K. Ceci est en bon accord avec l'existence d'un blocage d'ensemble des groupes méthyl dans le triméthylbenzène 1-2-3.

Abstract.

The nuclear magnetic resonance spectra of protons in cyclohexene, 123-, and 135-trimethylbenzene have been examined between 80° K and 220° K.

In cyclohexene the lattice is effectively rigid below 100° K and the second moment S of the resonance line is consistent with that calculated for a molecular structure based on a tension-free ring. The phase transition at 139° K results in a large reduction in S indicating the sudden onset of considerable molecular motion. Possible reorientations are discussed.

At 85° K the spectra from the two trimethylbenzenes have second moment values which are considerably lower than those calculated for rigid lattices. The molecular motion responsible for the reduction in S is undoubtedly the reorientation of the methyl groups. The spin-lattice relaxation time in 123-trimethylbenzene is significantly lower than that in the 135-specimen at all temperatures between 84° K and 220° K. This is consistent with the existence of cooperative hindering of the methyl groups in the 123- specimen.

The nuclear magnetic resonance spectra of solid cyclohexene, 135-trimethylbenzene and 123-trimethylbenzene are simple lines showing no fine

structure. The samples examined were obtained from the National Bureau of Standards, Washington, and were of the highest purity available (about 99.8 mole %). The apparatus was a standard radio frequency bridge employing field modulation and phase-sensitive detection. The required temperature was obtained by a cryostat similar to that described in [1].

CYCLOHEXENE.

The variation with temperature of the nuclear magnetic resonance spectrum of solid cyclohexane proved particularly interesting [2]. At that time we examined two specimens of cyclohexene; some inconsistencies, however, pointed to the possibility of impurity effects (see for example, [3]) and the work was not continued.

The variation of the second moment of the spectrum with temperature obtained with the very pure NBS sample is shown in figure 1. The discontinuity at 139° K (which was not observed with the impure samples) occurs at the temperature of the polymorphic change [4]. Measurements taken with the temperature decreasing indicate that the solid supercools through the phase transition temperature by some 40° C before changing to the lower temperature modification.

Since the second moment is constant from 84° K to 139° K, it may be assumed that the mean experimental value of 21.7 ± 0.4 gauss² represents the rigid lattice value. The lattice contains only one species of magnetic nuclei, and the line broadening originates entirely from the dipolar interaction of the protons. Van Vleck's second moment formula [5] can therefore be used to calculate a theoretical value provided (*a*) the molecular structure is known or can be proposed and (*b*) the crystal structure below the phase transition is known.

The larger part of the theoretical second moment will be the intramolecular contribution. The molecular structure we have assumed is based on evidence obtained from both chemical reaction rate experiments and spectroscopic studies [6, 7, 8]. In [6] it is shown in a velocity of oxidation experiment that cyclohexene and hexene-3 behave identically. This is indicative of the absence of any appreciable ring-tension, and rules out the possibility of a planar structure. The evidence from spectroscopic studies [7, 8] is in favour of a model having C₂ symmetry; such a model is shown in figure 2 alongside the more symmetrical cyclohexane. The carbon

atoms E and B lie in the plane containing A and F, the double-bonded carbon atoms. Atom C is above and atom D is below the plane. All the angles at E, D, C, and B are assumed tetrahedral, and the angles EFA and BAF are adjusted to make the ring-tension zero. The required value of these angles is $123^{\circ} 29'$ and the atoms C and D lie 0.425 \AA above and below the plane EFAB.

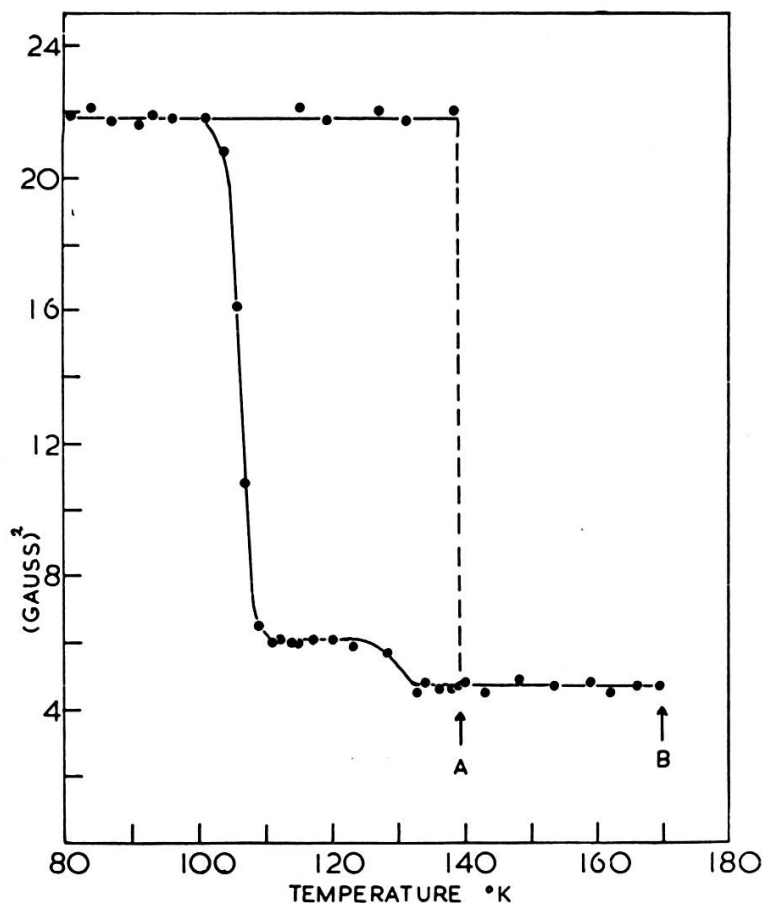


Fig. 1.

Variation with temperature of the second moment of the absorption line in cyclohexene.

A: phase change; B: melting point.

The only relevant X-ray data comes from [9]. There a brief account is given of work on δ -pentachlorocyclohexene where the carbon atom skeleton is found to be essentially that proposed here.

This model gives an intramolecular contribution of 13.9 gauss^2 . The inter-contribution has to be estimated from the more detailed knowledge of the related cyclohexane and benzene. These give an inter-contribution

of 8.0 ± 1.0 gauss² and a total theoretical second moment of 21.9 ± 1.0 gauss². The agreement with experiment is satisfactory and the nuclear magnetic resonance data certainly confirms the correctness of the model based on the results reported in [6, 7, 8 and 9].

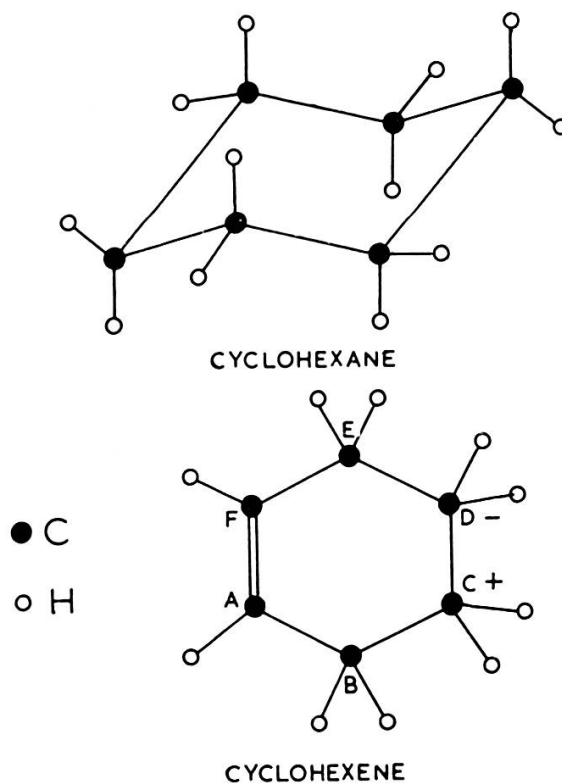


Fig. 2.
Molecular configuration of cyclohexene.

Figure 1 shows that the specimen supercools through the phase transition and the second moment has steady values of 4.7 gauss² between 169° K and 132° K and 6.1 gauss² between 126° K and 110° K. These reduced values result from the partial averaging out of the dipolar interaction by molecular motion. By analogy with cyclohexane [2], the most likely reorientation is about an axis perpendicular to the plane containing the four carbon atoms. This motion reduces the intra-contribution to 4.3 gauss² and the estimated inter-contribution by a factor of 4 to 2 gauss². The total 6.3 ± 1.0 gauss² indicates that this motion can well account for the main reduction in the second moment which takes place between 100° K and 110° K.

The lower value between 132° K and 169° K is probably due to the onset of another form of motion and the various possibilities are being investigated.

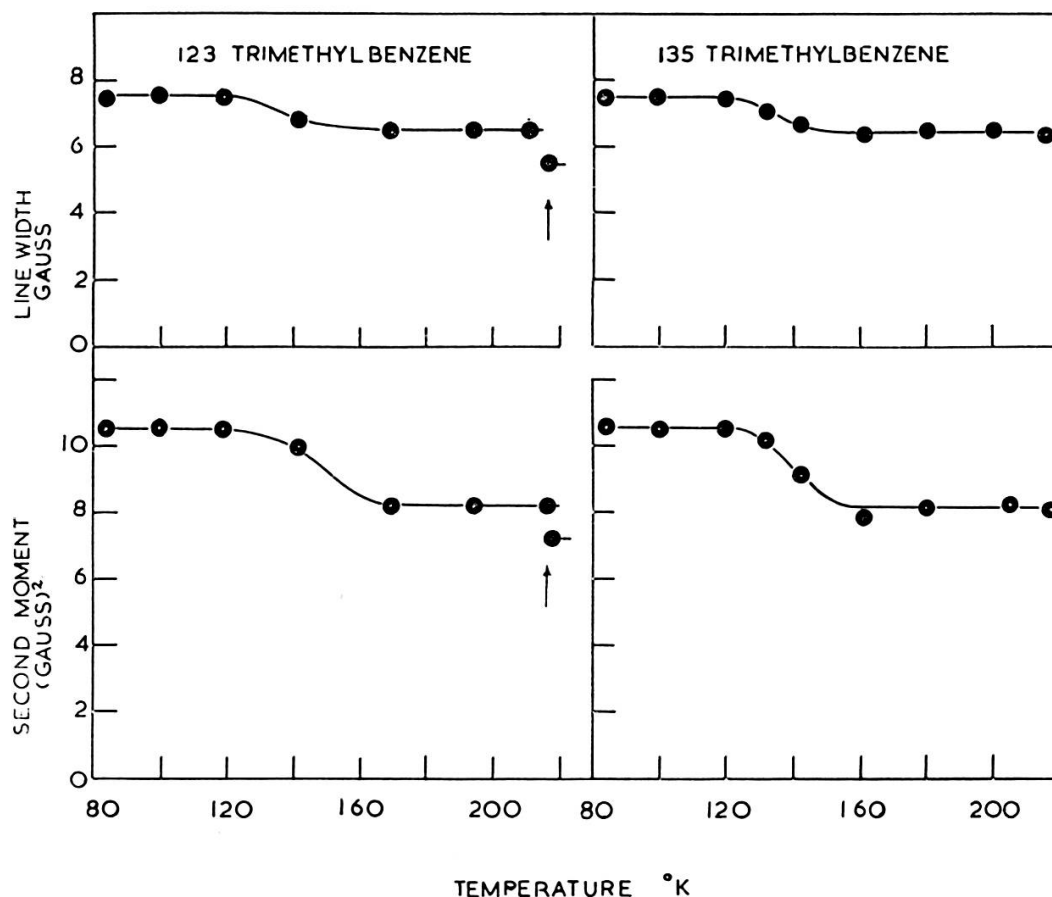


Fig. 3.

Variation with temperature of the line widths and second moments of the absorption lines in 123- and 135-trimethylbenzenes.

123- AND 135-TRIMETHYLBENZENE.

We are at present examining the series 123-, 124- and 135-trimethylbenzenes and intend covering the whole temperature range from liquid helium to the melting points. Work has been completed for the 123- and 135- forms for the temperature range 84° K to 220° K. The line widths and second moment values are shown as functions of the temperature in figure 3. The results obtained for the 135- form is consistent with that previously reported in [10], and there is close agreement between the behaviour of the 123- and the 135- forms.

The calculated intramolecular contribution to the second moment is 18.7 gauss^2 for 135-, and 20.7 gauss^2 for 123-trimethylbenzene. The estimated value of the inter- contribution in each case is about 6.1 gauss^2 , giving totals of 24.8 gauss^2 and 26.8 gauss^2 for the 135- and 123- forms

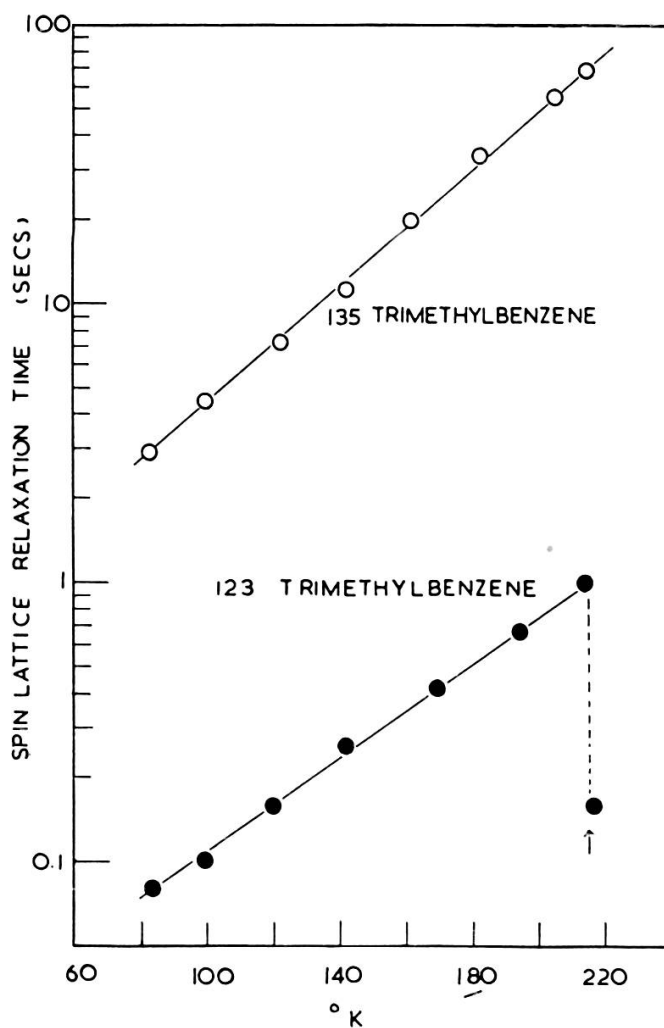


Fig. 4.

Temperature dependence of the spin-lattice relaxation times for the polymethylbenzenes.

respectively. The experimental values of about 10.5 gauss^2 for each form at 84° K can only be explained by assuming rotation or 3-fold tunnelling of the CH_3 groups about the C-C sidebonds. This reduces the contribution from the CH_3 protons by a factor of four. Although the effect of such motion on the inter-contribution cannot be calculated with any great accuracy, it can be shown that it is reduced to a figure which is consistent

with this interpretation. The cause of the further small reduction in the line width around 130° K is not easily explained: the fact that it occurs in both forms indicates that it may well involve the CH₃ groups, a view which will be supported if the same small change is found in the 124- form.

The main interest, however, in looking at these polymethylbenzenes is to establish whether or not the reorientation of the methyl groups is a cooperative process in the 123- and 124- forms. This information can be obtained from the variation of spin-lattice relaxation time T_1 with temperature. Figure 4 shows the variation of T_1 between 84° K and 220° K for the 123- and 135-forms: at all temperatures in this range the relaxation mechanism is more effective in the case of the 123- isomer.

Although any conclusions drawn from this incomplete data must be tentative, the result of applying the analysis outlined in [11], section 6, together with the assumption that

$$(T_1)_{\min}^{123} \cong (T_1)_{\min}^{135}$$

indicates that the entropy of activation associated with the reorientation process is greater for the 123 isomer. From this it would follow that the reorientation of a methyl group in the 123- form requires co-operation on the part of the neighbouring methyl groups.

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