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Proton Magnetic Resonance of Solid 1, 1, 1, 2-Tetrachloro-2-methylpropane

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The molecular motion in the crystal lattice of 1, 1, 1, 2-tetrachloro-2-methylpropane was studied, by proton magnetic resonance absorption measurements, over the temperature range between 30°C and −190°C. The absorption-line witdhs changed at −62°C. The second moments remain almost constant, about 5 gauss^2, between from −63°C to about −150°C, whereas above −62°C the values fall suddenly to 0.5 gauss^2. From the analysis of the proton second moment, it was found that, in the high-temperature phase, the molecules rotate almost freely in the crystal lattice, while in the low-temperature phase, the major molecular motion is the rotation of the methyl groups about the C–CH_3 bonds in the molecule.

Our previous thermal analysis revealed that 1, 1, 1, 2 - tetrachloro - 2 - methylpropane, Cl_3C–$C(CH_3)_2Cl$, showed a phase transition in the solid state.[1] By X-ray study using a single crystal,[1] the high-temperature crystal structure was found to possess a body-centered cubic lattice of $a=7.46$ Å with two molecules in the unit cell. From symmetry considerations of the crystal structure,[1] the molecules were found to orient themselves randomly in the crystal with a violent thermal motion.

A birefringence of the crystal was found in low-temperature optical observations,[1] suggesting that the molecular orientation in the low-temperature phase is an ordered one. In this paper, the detailed molecular motion in both phases, above and below the transition point, will be studied by the method of proton magnetic resonance absorption.

Experimental and Results

Sample. The preparation and the purification of the sample were the same as have been described in our previous paper.[1]

1) T. Koide, T. Oda and I. Nitta, This Bulletin, **29**, 738 (1956).

Nuclear Magnetic Resonance (NMR). The powder sample, placed in a thin-walled Pyrex glass ampoule (10 mm in diameter and 30 mm long), was sealed quickly under a pressure of about 2 mmHg in order to prevent the loss of sample due to its high volatility. The cryostat is shown in Fig. 1. The desired temperatures were attainable by controlling the amount of liquid air in the Dewar vessel and heating current. The thermal equilibrium between the specimen and the surroundings was kept within± 2°C. The temperature of the specimen was measured by a calibrated copper-constantan thermo-couple, located on the sealed-off neck of the ampoule. The temperature varied from 30°C to −190°C.

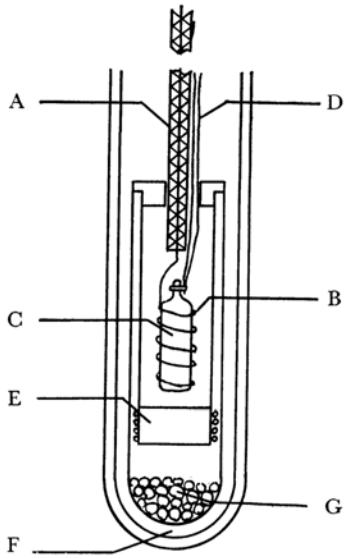

Fig. 1. The cryostat.

A) Electric shield-tube
B) R. f. coil
C) Sample
D) Thermo-couple
E) Electric heater
F) Ccoling material
G) Silica gel

The experiments were carried out using a Pound-Watkins r. f. spectrometer[2] operated at a fixed frequency of 8.5 Mc/sec and with a magnetic field sweep. The applied magnetic field was modulated with a small amplitude at 80 c/sec, and the derivative of the absorption line was recorded on a pen recorder, preceded by a sensitive detector and a narrow-bands amplifier.

The line widths are shown in Fig. 2 as a function of the temperature. From room temperature to the transition temperature, the absorption line width has a constant value of 2 gauss (peak to peak). At temperatures below the transition point (−62°C), the absorption line has shoulders and becomes broader with a decrease in the temperature. Below −100°C, these shoulders are discriminated as a fine structure on the line. Even at the lowest temperature measured, the line width does not reach a constant value but shows further broadening.

Discussion

The experimental second moments are shown in the last column of Table 1, while their temperature dependence is shown in Fig. 3. The modulation broadening for the second moment was corrected by the method of Perlman and Bloom.[3] By the formula given by Gutowsky and Pake,[4] the analysis of the second moments may be carried out if information on the molecular configuration and on the molecular motion in the crystal is available.

According to the results of the X-ray study[1] of the high-temperature phase, two molecules are located at the lattice points, 0, 0, 0 and 1/2, 1/2, 1/2 of a body-centered cubic lattice of $a=7.46$ Å. Statistically, the molecular axis will be oriented parallel to the four body-diagonal directions of the unit cell with equal probabilities.

Since no crystal data have been given for the low-temperature phase, the present authors have tentatively assumed that the molecular volume and the packing of the molecules in the crystal lattice

Table 1. The experimental and theoretical second moments

Mode of motion	Temp.-range, °C	Interaction: Between three protons in a methyl group gauss²	Between the protons belonging to two methyl groups in a molecule gauss²	Between the intermolecular protons gauss²	Total second moment gauss²	Experimental second moment gauss²
Fix.	−190	21.79	3.21	0.8	25.8	14.0
C_3-Rot.	−160—−63	5.43	1.22	0.8	7.5	5.5—4.9
C_3+C_3'-Rot.	−65— 20	0.55	0.31	0.2	1.1	0.5
$C_3+C_3'+C_2'$-Rot.		0.35	0.19	0.3	0.8	
Free-Rot.		0	0	0.3	0.3	

2) C. D. Watkins, Thesis (Harvard, 1952).
3) M. M. Perlman and M. Bloom, *Phys. Rev.*, **88**, 1920 (1952).
4) J. G. Powles and H. S. Gutowsky, *J. Chem. Phys*, **21**, 1695 (1953); **21**, 1704 (1953).

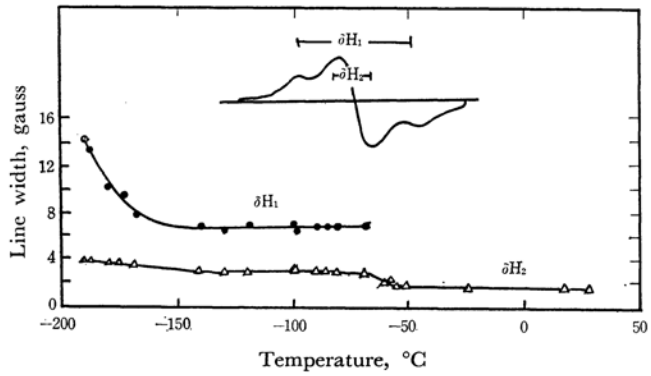

Fig. 2. The line width of Cl_3C-$C(CH_3)_2Cl$.

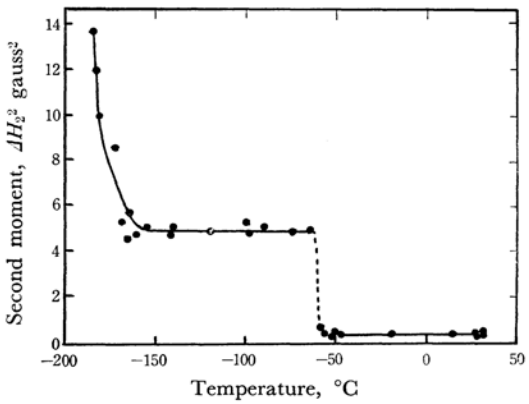

Fig. 3. The second moments of Cl_3C-$C(CH_3)_2Cl$ as a function of the temperature.

are not much changed through the phase transition; the unit cell length and the molecular axis orientation are taken as nearly the same as those of the high-temperature phase.

As is well known, the values of the second moment are influenced greatly by the mode of the molecular motion. Four modes of molecular motion have, therefore, been taken into account in the calculation of the second moments observed. In the first mode, two methyl groups of the molecule are assumed to rotate around their own C_3-axes (named as C_3-Rot.*1); in the second one, the molecules are considered to rotate axially as a whole around the molecular axes, namely, the central C-C bond axis (C_3'-Rot.), while in the third one, the over-all rotational motion of the molecule is about the axis vertical to the central C-C axis (C_2'-Rot.) In the last mode, the free spherical rotation of the molecule as a whole around its center of gravity is assumed.

The molecular configuration and the assumed molecular rotational modes mentioned above are shown in Fig. 4. The values of the second moments calculated for these modes are given in Table 1.

*1 Following Ref. 4.

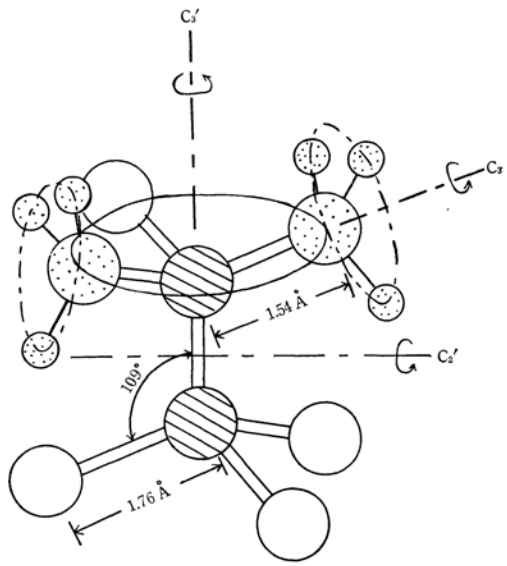

Fig. 4. The assumed molecular configuration and the assumed molecular motions. The circle shows chlorine, hached one shows carbon atom and dotted one shows methyl group.

The method of calculation used for the free-rotation mode was that of Andrew.[5]

Above the transition temperature, −62°C, the observed second moment of about 0.5 gauss² is less than the calculated value of 1.1 gauss² for the C_3+C_3'-Rot. mode, that is, the methyl groups rotating around their own C_3-axis (C_3-Rot.) and also about the molecular C-C axis (C_3'-Rot.). In order to reduce the calculated value to the observed value, 0.5 gauss², an additional motion, the C_2'-Rot. motion must be considered ($C_3+C_3'+C_2'$-Rot.). This procedure gives a value of 0.8 gauss². If the free rotation mode is assumed, 0.3 gauss² is obtained. The experimental second moment of 0.5 gauss² lies between the value of

5) E. R. Andrew and R. G. Eades, *Proc. Roy. Soc.*, **A**216, 398 (1953).

0.3 gauss^2 of the free rotation and the value of 0.8 gauss^2 of the $C_3+C_3'+C_2'$-Rot. mode. Thus, it may be concluded that, in the high-temperature phase, the molecules rotate almost freely about the center of gravity at the body-centered lattice points.

Below the transition point, $-62°C$, the experimental values, 5.5—4.9 gauss^2, are nearly equal to those calculated assuming only the C_3-Rot. mode (7.5 gauss^2). The slight disagreement between the experimental and theoretical values may be explained mainly by the uncertainty of the low-temperature crystal structure used in the calculations. Thus, in the phase between $-63°C$ and $-150°C$ the methyl groups may be said to rotate around their own C_3 axes, although the molecular axes are fixed in the crystal lattice.

At temperatures below $-160°C$, the C_3 axis rotation of methyl groups may become more restricted. However, even at the lowest temperature observed (about $-190°C$), there may still be some degree of rotational motion, since the observed second moment does not reach a constant value (see Fig. 3).

The results of NMR measurements are consistent with those of X-ray study[1] and optical observation.[1]

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