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Author(s)	Endô, Yoshio; Hoshino, Ryôsuke; Nakajima, Haruo; Morita, Eiichi
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## Proton Magnetic Resonance Studies in Normal Paraffins

Yoshio ENDŌ, Ryōsuke HOSHINO, Haruo NAKAJIMA  
and Eiichi MORITA

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Studies have been made of the proton magnetic resonance absorption for three normal paraffins. Temperatures were varied from 90°K to the melting point. The experimental second moments for  $n\text{-C}_{16}\text{H}_{34}$  and  $n\text{-C}_{22}\text{H}_{46}$  at the lowest temperature were smaller than the calculated values for rigid structure, and showed no abrupt changes of the line width up to their melting points. It is concluded that the discontinuous phase transition will not occur in the paraffins of carbon numbers smaller than 18. Dicetyl showed, however, a sharp line width transition at the temperature of about 7° before melting. It was found also that the appearance of the hysteresis loop depends greatly on the volume of the sample.

### § 1. Introduction

Certain long-chain compounds such as normal paraffins and alcohols have rotational phase transition. An end view of the crystal array of paraffin molecules and a schematic side view of the carbon skeleton are shown in Fig. 1. MÜLLER<sup>1)</sup> has observed by his X-ray measurements that the crystal lattice of normal paraffins of carbon number more than 24 changes abruptly from orthorhombic to hexagonal symmetry near the melting point, and suggested that the ribbon-shaped molecules may be in a state of hindered rotation around their long axes. Experiments on abnormal specific heat of higher alcohols at transition point and on the dielectric nature of long-chain bromides were made by KAKIUCHI *et al.*<sup>2)</sup> and HOFFMAN<sup>3)</sup> and interpreted as the result of the molecular rotation.

Recently GUTOWSKY and PAKE<sup>4)</sup> have shown that the magnetic dipolar broadening of nuclear magnetic resonance absorption line width in solids is reduced by molecular motion in the crystal lattice. By this method ANDREW<sup>5)</sup> confirmed the abrupt narrowing of proton magnetic resonance line of  $n\text{-C}_{28}\text{H}_{58}$  and  $n\text{-C}_{32}\text{H}_{66}$  at transition tem-

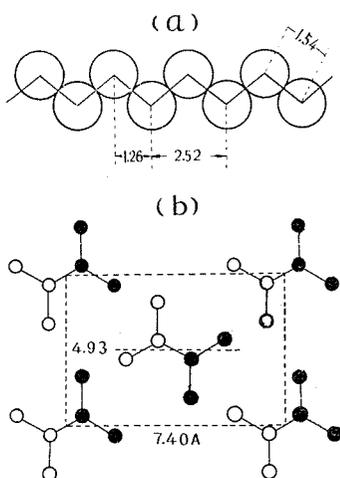


Fig. 1. (a) Side view of a paraffin molecule.  
(b) Crystal structure of n-paraffin.

a water-cooled electromagnet provided with pole pieces 13 cm in diameter. Its gap width was 3.5 cm and the field over the sample of about 1 cc was found to be uniform to within 0.1 gauss which was tested with the proton resonance in water. The best position was not always the central part of the gap. High frequency oscillator was copied after the regenerative oscillator designed by GUTOWSKY, MEYER and McCLURE<sup>7)</sup>, and operated at low power level together with a small 30 c. p. s. sinusoidal modulation of the applied field. Throughout this investigation the line shapes were displayed on the cathode ray oscillograph at constant frequency of 12 Mc/sec.

In general the signal from the oscillator is amplified by lock-in amplifier and fed to the recording meter, but it was necessary during 5 or 10 minutes to plot the whole

perature which was reasonably interpreted by supposing that the molecules are rotating as a whole. Similar experiment on  $n\text{-C}_5\text{H}_{12}$  and  $n\text{-C}_6\text{H}_{14}$  by RUSHWORTH<sup>6)</sup>, however, did not show the abrupt change of line width up to their melting point.

In this paper the writers examine whether the abrupt transition will occur in the paraffins of carbon number about 10 by means of proton resonance.

## § 2. Experimental Procedure

The block diagram of the apparatus is shown in Fig. 2. The necessary static magnetic field was supplied from

a water-cooled electromagnet provided with pole pieces 13 cm in diameter. Its gap width was 3.5 cm and the field over the sample of about 1 cc was found to be uniform to within 0.1 gauss which was tested with the proton resonance in water. The best position was not always the central part of the gap. High frequency oscillator was copied after the regenerative oscillator designed by GUTOWSKY, MEYER and McCLURE<sup>7)</sup>, and operated at low power level together with a small 30 c. p. s. sinusoidal modulation of the applied field. Throughout this investigation the line shapes were displayed on the cathode ray oscillograph at constant frequency of 12 Mc/sec.

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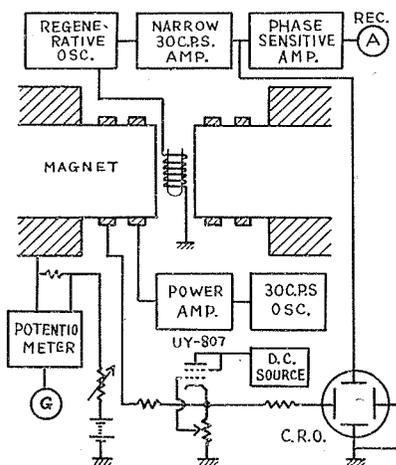


Fig. 2. Block diagram of apparatus.

derivative curve of the absorption line.

In the present experiment the line width variation with temperature was important, so it was often necessary to record the absorption line during relatively short times. To accomplish this necessity, the phase-sensitive amplifier was omitted and the output of the narrow band amplifier was fed directly to the vertical plate of the Brown tube, and at the same time the spot on the Brown tube swept from left to right in accord with the current of the second auxiliary coil around the poles. This current was varied smoothly across the resonance condition for a few seconds by controlling the grid bias of 807 tube. As this way the figure in Fig. 3 was obtained from which it is clear that the distance between two maxima shows the half width of absorption line. On the other hand the narrow line width near the melting point was measured at maximum slope of the absorption line itself.

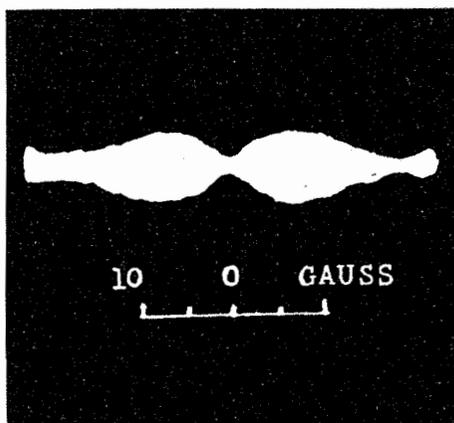


Fig. 3. Photograph of the figure on the oscilloscope screen for n-dicetyl at 20°C.

The temperature range of measurement was from 90°K to melting point. Low temperature was obtained by cooling a block of brass containing the sample and radio-frequency coil. The temperature was measured by means of a copper-constantan thermocouple inserted directly in the sample. Above room temperature the head was warmed or cooled at desired rate or maintained at a constant temperature by a circulating water bath with large

heat reservoir.

The probable error in a line width measurement was estimated at  $\pm 1$  gauss for the broader lines, and that in temperature was about  $1^\circ$  in low temperature and  $0.5^\circ$  near the room temperature.

The samples investigated were prepared in the Biochemical Laboratory, Hokkaidô University.

$n\text{-C}_{32}\text{H}_{66}$ : Dicetyl. Melting point:  $70^\circ\text{C}$ . This was obtained by polymerisation of high grade cetyl alcohol.

$n\text{-C}_{16}\text{H}_{34}$ : Cetane. Melting point:  $17.5^\circ\text{C}$ . It was prepared by adding hydrogen to cetyl alcohol. The same sample was obtained also by the reaction of hexadecyl iodide with acetic acid.

$n\text{-C}_{12}\text{H}_{26}$ : Dodecane. Melting point:  $-12^\circ\text{C}$ . This sample was prepared from pure lauryl alcohol by adding hydrogen.

All these samples were distilled many times at reduced pressure. The effect of the impurity will be given below.

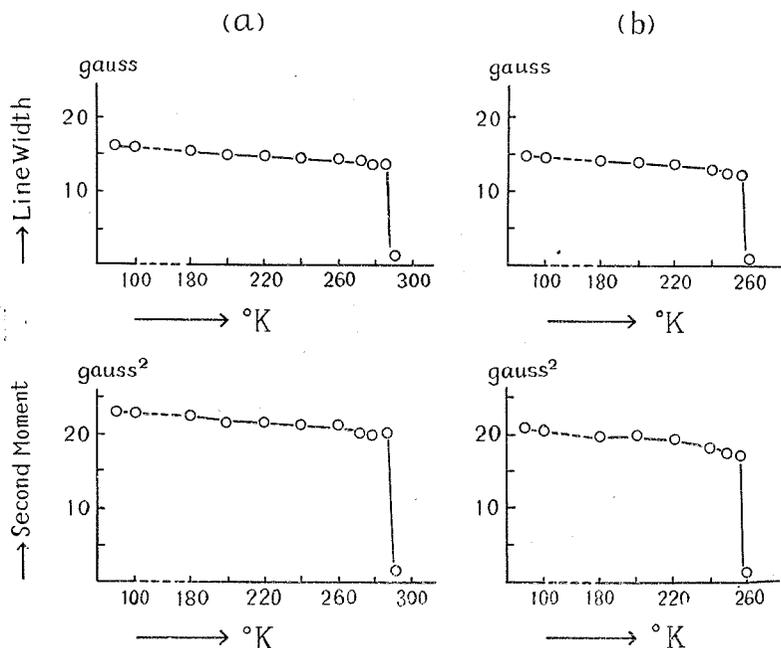


Fig. 4. The variations of line width and second moment vs. temperature.  
(a) n-hexadecane. (b) n-dodecane.

## § 3. Results and Discussion

The line width and second moment for  $n\text{-C}_{16}\text{H}_{34}$  and  $n\text{-C}_{12}\text{H}_{26}$  are plotted against temperature in Fig. 4. The sample was cooled previously to lowest temperature possible and warmed to melting point measuring the absorption line. The warming rate was about  $5^\circ$  per minute below  $200^\circ\text{K}$  but it was reduced to about  $1^\circ$  per minute above  $250^\circ\text{K}$ .

The second moment at lowest temperature  $90^\circ\text{K}$  was  $23.5 \pm 1$  gauss<sup>2</sup> and  $20.5 \pm 1$  gauss<sup>2</sup> for  $n\text{-C}_{16}\text{H}_{34}$  and  $n\text{-C}_{12}\text{H}_{26}$  respectively. These values were compared with the theoretical second moments. The second moment  $\langle \Delta H^2 \rangle$  of a crystal powder containing one magnetic nuclear species is given as follows<sup>9)</sup>

$$\langle \Delta H^2 \rangle = \frac{6}{5} \frac{I(I+1)}{N} g^2 \beta^2 \sum_{j>k} r_{jk}^{-6},$$

where  $I$  is the spin of the nucleus considered,  $g$  the nuclear  $g$ -factor,  $\beta$  the nuclear magneton,  $N$  the number of nuclei whose interactions are taken in calculation and  $r_{jk}$  the internuclear distance between nuclei  $j$  and  $k$ .  $g\beta I$  is equal to the magnetic moment of the nucleus. For protons it reduced to

$$\langle \Delta H^2 \rangle = 7.16 \times 10^{-46} N^{-1} \sum_{j>k} r_{jk}^{-6} \quad (\text{gauss}^2).$$

Inserting the value of  $r$  that is obtained by X-ray<sup>9),10)</sup> and spectroscopic data<sup>11)</sup>, the intra- and intermolecular contributions are found as shown in Table I.

TABLE I. The second moment of solid cetane and dodecane

	Intramolecular contribution (gauss <sup>2</sup> )	Intermolecular contribution (gauss <sup>2</sup> )	Total (gauss <sup>2</sup> )	Observed second moment (gauss <sup>2</sup> )
$\text{C}_{16}\text{H}_{34}$	19.5	8.1	27.6	$23.5 \pm 1$
$\text{C}_{12}\text{H}_{26}$	19.8	8.3	28.1	$20.5 \pm 1$

The calculated second moment is appreciably higher than the observed value. This suggests that the molecules are not quite stationary and there is still some motion such as the rotational oscillation of the molecules as a whole about their long axes or

the reorientation of the methyl groups about the end C-C axis. If the former motion will occur, it must be postulated that only a fraction of the molecules are rotating to obtain the observed second moment as indicated by ANDREW. But to explain the central peak which appears at the temperature near 150°K in the center of the absorption line, the rotation of the methyl groups will be satisfactory.

As the temperature was increased the line width decreased gradually up to melting point for both samples and showed no abrupt change. From this fact and ANDREW's data it seems reasonable to state that the transition point would not exist for the normal paraffins whose carbon numbers are less than 18.

The line width for dicetyl ( $n\text{-C}_{32}\text{H}_{66}$ ) is shown in Fig. 5. The warming rate was  $0.2^\circ$  per minute. Before the measurements the sample was cooled very slowly at the rate of  $0.1^\circ$  per minute from molten state and left at room temperature for about 20 hours.

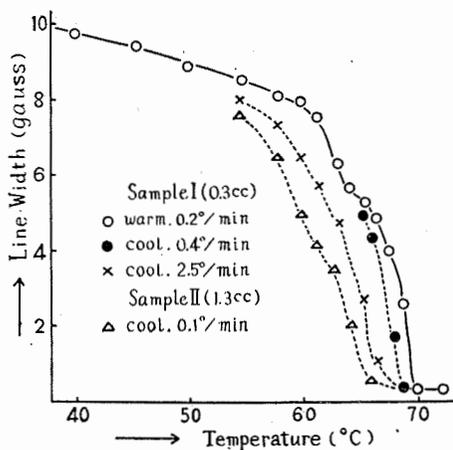


Fig. 5. Line width variation for  $n\text{-C}_{32}\text{H}_{66}$  and its hysteresis characteristics for the various cooling rates.

When this treatment was omitted, the results were not reproducible and the transition was occurred over the broader temperature range. These effects were pronounced in the presence of impurity and the transition point shifted remarkably to lower temperature as shown in Fig. 6. At transition temperature  $63^\circ\text{C}$  the second

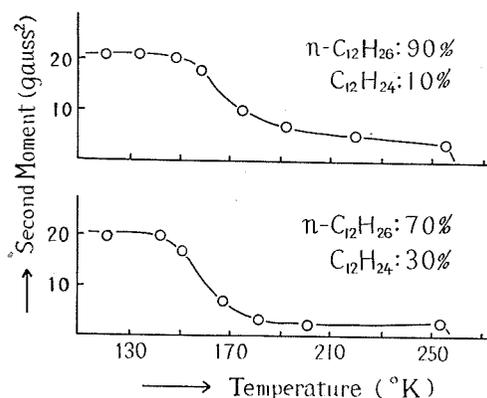


Fig. 6. The effect of impurity for the second moment.

moment changed abruptly to  $11 \pm 0.5$  gauss<sup>2</sup> from  $17 \pm 0.5$  gauss<sup>2</sup> and above this temperature the line narrowed slowly to the molten state. The value  $11 \pm 0.5$  gauss<sup>2</sup> is rather great if all the molecules are rotating, so that it must be interpreted by another crystal form such as tilted packing arrangements.

The hysteresis loop, which often appears for long-chain molecules, was affected strongly by the cooling rate as shown in Fig. 5. Furthermore, the volume of the sample gave the remarkable influence upon the loop owing to its poor heat conductivity. When the sample of volume 1.3 cc was employed, the large hysteresis was observed but in the case of 0.3 cc there was only a trace at melting point in spite of the same cooling rate. It can be said, therefore, that the hysteresis loop will not appear practically if we use the small sample and cool it slowly such as  $0.1^\circ$  per minute for normal paraffins.

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