# NMR Study on Phase Transitions in n-heptadecane $C_{17}H_{36}$

by

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## Abstract

Phase transitions in n-heptadecane $C_{17}H_{36}$ have been studied by ^{1}H- and ^{13}C-NMR. Proton second moment and ^{13}C spin-lattice relaxation times show that n-heptadecane molecules rotate around their molecular long axes in the rotator phase. The rotational motion is found to freeze in the ordered phase and absence of pre-rotator phase is concluded.

***Key Words***：　*n-heptadecane, phase transition, rotator phase, NMR*

## 1. Introduction

Normal paraffins (n-paraffins) $C_nH_{2n+2}$ have extensively been studied owing to the typical zigzag-chain compound of repeated methylene unit and variety of packing structures. Just below melting point, odd numbered paraffins with *n* ranging from 9 to 43 are found to exist in orientationally disordered state, called as a rotator phase[1]. In the rotator phase, the molecules rotate around their long molecular axes. In addition, these paraffins are found to transform to an ordered phase, when temperature is lowered from the rotator phase. Dynamical and structural properties of the rotator and ordered phases have been studied by X-ray diffraction[2,3], ^{1}H-NMR[4] and neutron inelastic scattering[5]. The space group of the rotator phase is convinced as *Ccmm* for the n-paraffins with *n* = 17, 19 and 21. In the rotator and ordered

phases, moreover, these paraffins are found to take a bilayer structure with all molecules orienting their molecular long axes parallel to the *c*-axis, and the cell parameter *c* approximately agrees with twice of length of all-trans heptadecane[2,3]. Thus, these paraffins are thought to have an all-trans conformation in the rotator and ordered phases. Although the rotator phase has mainly been identified by symmetry consideration and width of ^{1}H-NMR resonance line, no definite experimental evidence has been given for this phase so far.

Stohrer and Noack have studied phase transitions in n-nonadecane ($C_{19}H_{40}$) by using ^{1}H-NMR. They proposed that an intermediate phase, named as a pre-rotator phase, exists between the rotator and order phases[4]. Thus, the phase transitions in n-nonadecane are more or less complicated in the sense that the phase transition between the rotator and ordered phases occurs *via* the pre-rotator phase. Thus, it is interesting to decide whether such the phase also exist or not in the other odd-numbered

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paraffins. In order to clarify the phase transitions in odd numbered paraffins, molecular motions of n-heptadecane ($C_{17}H_{36}$) has been examined by $^1$H- and $^{13}$C-NMR.

## 2. Experiment

Commercially obtained n-heptadecane contained impurity to some extent, and was purified through two times of recrystallization from an acetone solution. Volatile impurity such as acetone was removed by pumping for 12 hours with a rotary pump.

NMR measurements were made for the $^1$H nucleus at 300 MHz and $^{13}$C nucleus at 76 MHz using a Chemagnetics spectrometer CMX-300. Tetramethylsilane was used as a reference for resonance frequency of the $^1$H nucleus, and hexamethylbenzene as a reference for resonance frequency of the $^{13}$C nucleus. The NMR spectrum of the $^1$H nucleus was measured with a solid echo method. The spectrum of the $^{13}$C nuclei was measured by an ordinal $\pi$/2 pulse method combining magic angle spinning (MAS) and proton-decoupling, where MAS speed was 2.7 kHz and proton-decoupling power approximately 80 W. Spin-lattice relaxation times of the $^{13}$C nuclei were determined from the time evolution ($\tau$) of magnetization measured with an inversion recovery method, where the number of $\tau$ values was 12. Sample temperature was regulated within $\pm$0.5 K with a Chemagnetics temperature controller. The NMR measurements were made on cooling started from the liquid phase.
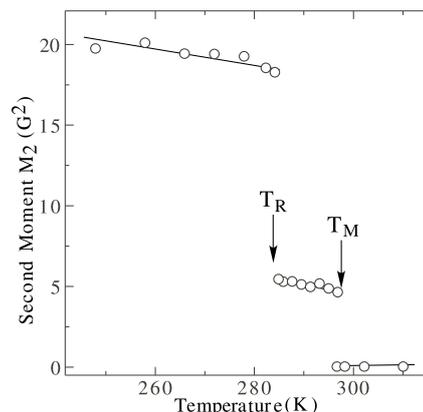
## 3. Results and discussion



Fig. 1. Temperature dependence of proton second moment $M_2$ (G$^2$). Arrows indicate phase transitions at $T_M$ (296 K) and $T_R$ (284 K).

Figure 1 shows temperature dependence of proton second moment $M_2$. $M_2$ shows presence of two discontinuous phase transitions at $T_M$ (296 K) and $T_R$ (284 K). Three phases are temporarily denoted by phases I, II and III in order of decreasing temperature. Phase I is in liquid state since $M_2$ shows extremely small value; $M_2$ is 5 G$^2$ on average in phase II; $M_2$ shows a discontinuous increase at $T_R$ and increases from 18 to 20 G$^2$ in phase III on lowering temperature. The ratio of the $M_2$ values in phases II and III is almost equal to 4:1. It is well known that $M_2$ is reduced to a quarter of the value for the rigid lattice by a fast uniaxial rotation when vectors connecting protons are perpendicular to the rotation axis[6]. Since n-heptadecane is thought to have an all-trans conformation in the rotator and ordered phases[2,3], the vectors connecting the nearest-neighbor protons is approximately perpendicular to the molecular long axis. As a consequence, the behavior of $M_2$ shows that n-heptadecane molecules undergo the rotation around their molecular long axes in phase II, and this rotational motion freezes in phase III. Thus, the behavior of $M_2$ shows that phases II and III are, respectively, the rotator and ordered phases and the pre-rotator phase proposed by Stohrer and Noack[4] is absent.
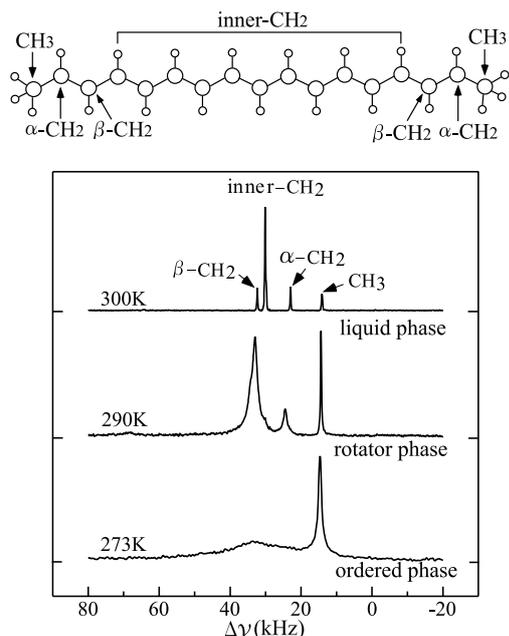
Fig. 2. $^{13}$C-NMR spectra in the liquid phase (300 K), rotator phase (290 K) and ordered phase (273 K), together with molecular structure of n-heptadecane.



Fig. 3. $^{13}$C spin-lattice relaxation times $T_1$ (s) of the $CH_2$ groups (a) and the $CH_3$ groups (b). For the $CH_2$ group, only the mean value is shown in the liquid and rotator phases. Solid lines indicate calculated $T_1$ values.

Figure 2 shows typical $^{13}$C-NMR spectra observed in three phases, together with molecular structure of all-trans n-heptadecane. As shown in the figure, the first and second nearest-neighbor $CH_2$ groups from the $CH_3$ end groups are, respectively, designated $\alpha$- and $\beta$-$CH_2$ groups, and the other $CH_2$ groups inside the $\beta$-$CH_2$ groups inner-$CH_2$ groups. The spectrum of the liquid phase consists of well separated four lines which can be assigned to the resonances of the $^{13}$C nuclei in the $\beta$-$CH_2$, inner-$CH_2$, $\alpha$-$CH_2$ and $CH_3$ groups from upfield[7]. In the rotator phase, the resonance lines of the $\beta$- and inner-$CH_2$ groups become too hard to resolve due to broadening, probably caused by reduction of proton decoupling efficiency and/or spin-spin relaxation time. Finally, the resonance lines of all the $CH_2$ groups turn into a broad peak centered at 33 kHz in the ordered phase.
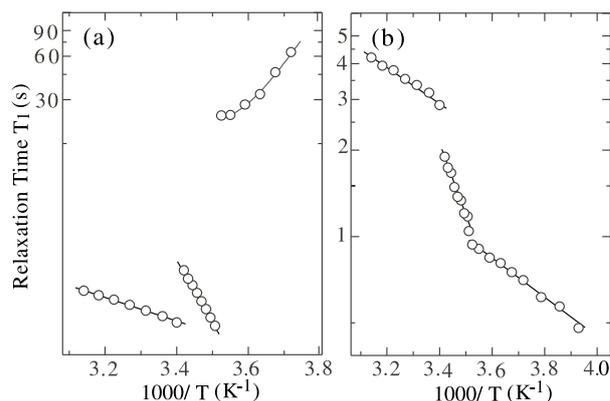
Figure 3 shows temperature dependence of $^{13}$C spin-lattice relaxation times $T_1$ of the $CH_2$ and $CH_3$ groups. In the liquid and rotator phases, $\log T_1$'s of the $CH_2$ and $CH_3$ groups both decrease linearly with increasing inverse temperature $1/T$, showing that the motions are in the fast limit. The same situation is found in $T_1$ of the $CH_3$ group in ordered phase. In addition, $T_1$ of the $CH_2$ groups shows a discontinuous increase at $T_R$ skipping over a minimum and increases on lowering temperature in the ordered phase. This discontinuous increase is consistent with the fact that the rotational motion around the molecular long axis freezes in the ordered phase.

In n-heptadecane, the $^{13}$C nuclei relax almost exclusively through dipolar coupling with covalently bonded protons. Based on the linear relation $\log T_1$ vs $1/T$, only the activation energies $E_a$ are determined from the $T_1$ values of the $CH_2$ groups in the liquid and rotator phases, and the $T_1$ values of the $CH_3$ group in three phases. The $T_1$ values of the $CH_2$ groups in the ordered phase are analyzed by the ordinal rotational diffusion model[8] given by

$$\frac{1}{T_1} = S\left\{\frac{\tau_r}{1+(\omega_C-\omega_H)^2\tau_r^2} + 3\frac{\tau_r}{1+\omega_C^2\tau_r^2} + 6\frac{\tau_r}{1+(\omega_C+\omega_H)^2\tau_r^2}\right\},$$

where $S$ is the scale factor related to motional

amplitude. In the above equation, $\tau_r$ is the correlation time of motion whose temperature dependence is assumed to obey the Arrhenius law given by

$$\tau_r = \tau_0 \exp\left(\frac{E_a}{k_B T}\right) \ .$$

Here, $\tau_0$ is the pre-exponential factor, and $k_B$ denotes the Boltzmann constant. Obtained activation $E_a$ are all shown in Table 1.

Table 1. Activation energies $E_a$ (kJmol$^{-1}$) in the liquid, rotator and ordered phases.

| group | $E_a$(liquid) | $E_a$ (rotator) | $E_a$(ordered) |
|-------|------|------|------|
| CH$_3$ | 11.5(6) | 47(2) | 13.4(4) |
| $\alpha$-CH$_2$ | 16.0(9) | 83.6(9) | 71(1) |
| inner-CH$_2$ | 12.9(7) | 83.4(5) | 71(1) |
| $\beta$-CH$_2$ | 14.8(6) | 83.4(5) | 71(1) |

In the rotator phase, $T_1$ of the CH$_2$ groups reflects the rotation around the molecular long axis with $E_a$ of 83.5(7) kJmol$^{-1}$. This rotation freezes and turns into the torsional one with $E_a$ of 71(1) kJmol$^{-1}$ in the ordered phase. $T_1$ of the CH$_3$ groups in the ordered phase only reflects the methyl rotation. In fact, $E_a$ of the CH$_3$ group is 13.4(4) kJmol$^{-1}$ which can be considered as a reasonable value for the methyl rotation. In the rotator phase, $T_1$ of the CH$_3$ group both reflects the methyl rotation and rotation around the molecular long axis. The obtained $E_a$ is 47(2) kJmol$^{-1}$ which almost agrees with the mean $E_a$ value of the both rotations (48 kJmol$^{-1}$).

According to NMR study on n-nonadecane[4], the proton $T_1$ shows a V-shaped minimum in the temperature region of the pre-rotator phase and decreases on lowering temperature in the ordered phase. In the present experiment, $T_1$ of CH$_2$ groups increases and $T_1$ of CH$_3$ group decreases on lowering temperature in the ordered phase. Thus, it is quite probable that the proton $T_1$ in the pre-rotator and ordered phases of n-nonadecane only

reflects the torsional motion of the CH$_2$ groups and the methyl rotation. Thus, the presence of the pre-rotator phase is quite doubtful. Further study is necessary to clarify the phase transitions in the odd numbered paraffins.

## Conclusion

The present results indicate that the molecules undergo the rotation around the molecular long axis in the rotator phase, and this rotation freezes in the ordered phase. In addition, the pre-rotator phase is absent in n-heptadecane.

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