Structural Phase Transition and Molecular Motion of *p*-Chlorobenzamide as Studied by the Temperature Variations of ^{35}Cl NQR Frequencies, Chlorine Nuclear Quadrupolar Relaxation Times, and ^{1}H Magnetic Dipolar Relaxation Times*

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The temperature dependences of ^{35}Cl NQR frequencies, ^{35}Cl (^{37}Cl) nuclear quadrupolar relaxation times ($T_{1\mathrm{Cl}^{\mathrm{Q}}}$), ^{1}H NMR absorption, and of ^{1}H NMR relaxation times were observed for *p*-chlorobenzamide, *p*-$\mathrm{ClC_6H_4CONH_2}$ and its *N*-deuterated analog. The existence of three ^{35}Cl NQR lines already reported was confirmed for the known low temperature phase below 316 K. A single sharp ^{35}Cl NQR line was detected in the high temperature phase up to 447 K just below the melting point 451 K. At lower temperatures, three different ^{35}Cl $T_{1\mathrm{Cl}^{\mathrm{Q}}}$ values attributable to the fluctuation of the electric field gradient due to rotational oscillation were observed. With increasing temperature, these $T_{1\mathrm{Cl}^{\mathrm{Q}}}$ decreased rapidly and yielded almost the same value immediately below T_{tr} suggesting the onset of a slow motion. The ^{1}H T_1 of the high temperature phase gave a T_1 minimum and could be explained through the 180° flip motion of the phenyl ring with an activation energy of 44 kJ mol^{-1}.

Introduction

According to Taniguchi et al. [1], *p*-chlorobenzamide (*p*-$\mathrm{ClC_6H_4CONH_2}$) undergoes a structural phase transition at 317 K and forms triclinic crystals in the low temperature phase (abbreviated as LTP), space group P$\bar{1}$, $Z = 6$. In this crystal lattice, two amide molecules are held together by two N–H $\cdots$ O type hydrogen bonds forming a dimeric unit. Two kinds of crystallographically nonequivalent dimers exist in the crystal: one centrosymmetric dimer and two asymmetric ones, the latter ones being equivalent through the inversion center. These three dimeric units are periodically linked together to form endless chains equivalent to each other in the crystal. Accordingly, there are three kinds of crystallographically nonequivalent chlorines in the crystal with an abundance ratio of 1 : 1 : 1. The high temperature phase (abbreviated as HTP) has a structure belonging to the same space group and $Z = 2$, in which all of the dimers are centrosymmetric and crystallographically equivalent [2].

Kondo et al. [3] studied the temperature dependence of the ^{35}Cl NQR frequencies and found three fairly close spaced lines with equal intensity at a given temperature, in agreement with the cited X-ray results. These lines showed normal negative temperature coefficients and faded out at 316 K; no resonance could be observed above this temperature. It was reported [3] that the fade-out phenomena of the NQR lines and the disappearance of NQR signals in HTP are due to the increase of the thermal motion near the transition temperature T_{tr} and the disordered structure in HTP already reported, respectively. A disordered structure was assumed to explain diffuse scattering observed among many reflections in the Weissenberg photographs [2].

The molecular dynamics of the amide molecules is interesting because it is expected to play an important role in the occurrence of the phase transition. Therefore, the present investigation of *p*-chlorobenzamide by means of chlorine NQR and ^{1}H NMR techniques has been undertaken to obtain information about the molecular motion and the phase transition.

Experimental

Commercially available *p*-chlorobenzamide was twice purified by recrystallizations from ethanol.

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The crystals were obtained in each case by slowly evaporating the solvent over sodium hydroxide used as an absorbent in a desiccator. Two crystalline modifications, named α and β, were reported to be obtained by crystallizing the compound from ethanol and acetone solutions, respectively, at room temperature [1, 4]. Our crystals were proved to be α by taking X-ray powder patterns. We tried several times to obtain the β form from the acetone solution. However, the α form was always obtained. Moreover, the crystals obtained by slow cooling from the melt were also α. Thus we failed to prepare the β form, the successful preparation of which is reported only once [4].

A partially deuterated analog *p*-$ClC_6H_4COND_2$ was prepared by refluxing a tetrahydrofuran solution of the amide and heavy water. This exchange reaction was repeated four times. Further purification was made by slowly crystallizing from the melt. The crystals thus obtained are α as confirmed by X-ray diffraction. From the disappearance of the $\tilde{\nu}_{NH}$ bands of the IR spectra the degree of *N*-deuteration was found to be quite high.

Differential thermal analysis (DTA) and measurements of the second moment (M_2) of ^{1}H NMR absorption and of ^{1}H NMR spin-lattice relaxation times (T_{1H}) were carried out employing the usual methods [5–7]. The temperature variation of the ^{35}Cl NQR frequencies (ν_Q) and of the ^{35}Cl quadrupolar spin-lattice relaxation times (T_{1Cl^Q}) were determined using a frequency-variable pulsed spectrometer [7]. In HTP, ^{37}Cl T_{1Cl^Q} was also observed. T_{1Cl^Q} was determined by observing the free induction decay (FID) of an echo signal appearing after a $\pi - \tau - \pi/2 - \tau' - \pi$ pulse sequence, where τ and τ' denote delay times. Temperatures in these studies were measured by use of a chromel-alumel thermocouple for the superregenerative NQR experiments and a copper-constantan thermocouple for the other experiments; the accuracy was ± 1 K.

Results and Discussion

The temperature dependence of the ^{35}Cl NQR frequencies observed for *p*-$ClC_6H_4CONH_2$ is shown in Fig. 1 and the frequencies for several temperatures are listed in Table 1. All of these data were determined by the pulse method. Below ca. 400 K, the NQR frequencies were determined also by the superregenerative method; identical results were obtained. The ^{35}Cl spin-spin relaxation time T_2^* estimated from the FID signals was (75 ± 20)μs for the three LTP lines and (115 ± 10)μs for the HTP line. T_2^* of all the lines was almost temperature independent even in the vicinity of T_{tr}.

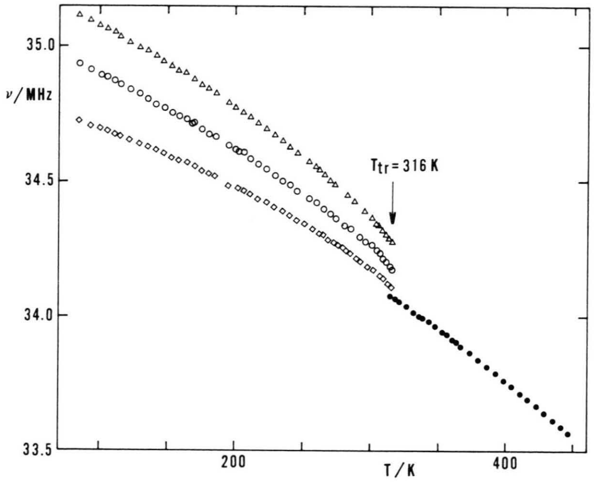

Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies observed for both the low and high temperature phases of *p*-chlorobenzamide.

Table 1. ^{35}Cl NQR frequencies observed at various temperatures for *p*-$ClC_6H_4CONH_2$ in the low and the high temperature phases.

Phase	T/K	Frequency (± 0.002)/MHz	
LTP	195	34.487, 34.634, 34.792	
LTP	288	34.224, 34.309, 34.428	
LTP	316	34.110, 34.177, 34.279	
HTP	318		34.068
HTP	356		33.932
HTP	423		39.670

The three LTP ^{35}Cl NQR lines, having equal intensity at a given temperature, were already reported [3]. Although the present ν_Q values below ca. 250 K agree well with those previously reported, the values obtained in a narrow temperature range below T_{tr} disagree with those given by Kondo et al. [3]. The almost equally spaced three lines decreased smoothly and came closer together with increasing temperature up to 316 K, where a single new sharp line immediately below the lowest LTP line appeared. The three lines became suddenly weak at ca. 316 K and disappeared in the noise level. The intensity of the new line was ca. three times stronger than that of each LTP line. The HTP line, sharper than those of LTP, decreased in frequency smoothly and almost linearly with increasing temperature and was clearly observed up to 447 K (melting point: 451 K). The intensity of the HTP line was practically unchanged up to this temperature, above which it weakened very rapidly. With decreasing temperature of the HTP, ν_Q increased reversibly and could be observed down to 314 K. In a narrow range of temperatures, the coexistence of signals attributable to both HTP and LTP could be observed. Below 314 K, only the three LTP lines could be recorded, and they followed the curves determined with increasing temperature.

The above NQR results indicate the following: The compound undergoes a structural phase transition of first order at 316 K, in agreement with previous reports [2, 3]. There are three nonequivalent chlorines in the LTP, agreeing well with the results of the X-ray analysis [1]. In the HTP, all of the chlorines are crystallographically equivalent, in accordance with the average structure proposed by Takaki et al. [2]. However, the fact that a sharp ^{35}Cl NQR signal with a continuous temperature dependence of the resonance frequency can be observed over the whole temperature range of the HTP, strongly suggests that there is no static disorder in the solid and no phase transition occurs at 343 K. Our DTA experiments showed no heat anomaly at 343 K. The presence of a disordered structure and the occurrence of a phase transition at 343 K, however, had been proposed from X-ray data [2]. Moreover, the authors interpreted the diffuse scattering patterns observed in the Weissenberg X-ray photographs in terms of a random distribution of four different kinds of "domains" in the crystal. Accordingly at least four kinds of crystallographically nonequivalent chlorines would exist in the crystal. Our NQR results are inconsistent with this interpretation of the structure of the HTP.

To obtain information about the molecular dynamics of the amide in the crystal and also to get more detailed information about the phase transition, we carried out ^{1}H NMR and ^{35}Cl (^{37}Cl) $T_{1\mathrm{Cl}^{\mathrm{Q}}}$ experiments.

The temperature dependences of $T_{1\mathrm{H}}$ for the amide observed at 12.5 and 20 MHz and for its *N*-deuterated analog at 20 MHz are shown in Figure 2. Increasing the temperature, from ca. 300 K on, a discontinuity of $T_{1\mathrm{H}}$ was found at 316 K for the amide and at 312 K for its *N*-deuterated crystals. The latter temperature was confirmed by DTA. Although both compounds gave different T_{tr}, they melted at the same temperature, 451 K. The decrease of T_{tr} by *N*-deuteration suggests that the motion of NH_2 groups and/or the N–H $\cdots$ O type interdimer H-bonds participate in the mechanism of the phase transition.

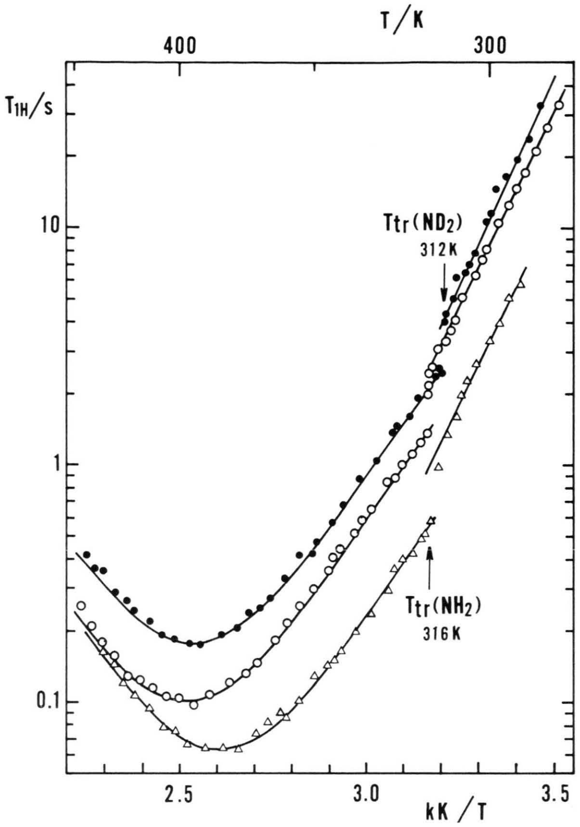

Fig. 2. Temperature dependence of the proton spin-lattice relaxation time $T_{1\mathrm{H}}$ observed at the Larmor frequencies of 12.5 (△) and 20 (○) MHz for *p*-chlorobenzamide and at 20 MHz (●) for its *N*-deuterated analog. Solid curves are obtained from the BPP theory by fitting calculations.

For the HTP, the amide yielded a single $T_{1\mathrm{H}}$ minimum of 63 ms at 383 K and of 98 ms at 397 K at the Larmor frequencies of 12.5 and 20 MHz, respectively, while the *N*-deuterated one yielded 175 ms at 394 K (ν = 20 MHz). From the frequency dependence of $T_{1\mathrm{H}}$ in the amide, $T_{1\mathrm{H}}$ is thought to be governed by a magnetic dipolar relaxation mechanism.

By assuming that a single motional process is involved in the relaxation, the T_{1H} values observed for the HTP can be analyzed by the BPP theory [8]. For the system studied, the theoretical T_{1H} can be written as [9]

$$T_{1H}^{-1} = \tfrac{2}{3}\gamma^2 \Delta M_2 \{\tau_C/(1+\omega^2\tau_C^2) + 4\tau_C/(1+4\omega^2\tau_C^2)\}\,. \quad (1)$$

Here, γ, ΔM_2, τ_C, and ω denote the gyromagnetic ratio of the proton, the reduction of M_2 due to the molecular motion in question, the correlation time of this motion, and the angular Larmor frequency, respectively. An Arrhenius relationship between τ_C and the activation energy E_a for the motion, was assumed:

$$\tau_C = \tau_0 \exp(E_a/kT)\,. \quad (2)$$

Equations (1) and (2) were least-squares fitted to the observed T_{1H} values using the SALS program [10] at the Computation Center of Nagoya University. The best fitted values of the parameters ΔM, τ_0, and E_a are given in Table 2. The calculated curves using these values are shown in Fig. 2 by solid curves.

To assign of the motional mode, we measured M_2 in the temperature range (280−400)K. M_2 turned out to be ca. 8 G^2, almost independent of temperature, although a small decrease with increasing temperature could be seen. At T_{tr} no change in M_2 was observed, showing that the motion responsible for T_{1H} in the HTP is probably the dominant relaxation process in the LTP too.

Since the frequency dependence of T_{1H} in the LTP is positive, we have the condition $\omega\tau_C \gg 1$ applicable to the LTP. Therefore (1) becomes

$$T_{1H}^{-1} = \frac{4}{3}\gamma^2 \Delta M_2 \omega^{-2} \tau_C^{-1}\,. \quad (3)$$

From (2) and (3) we could roughly calculate the foregoing parameters using the same method as above. In this calculation, however, the ΔM_2 value obtained for the HTP was assumed to be valid also for the LTP. The most probable values determined for τ_0 and E_a are given in Table 2, and the calculated curves by use of these parameters are shown in Fig. 2 by solid lines. Since E_a and τ_0 for both analogs are very close to each other, it can be concluded that the same motional process governs T_{1H} of both compounds. This indicates that the motion such as the 180° flip of the NH_2 group cannot explain the T_{1H} minimum observed.

Table 2. Motional parameters (the reduction of the 2nd moment ΔM_2, the correlation time τ_0, and the activation energy E_a for the 180° flip motion of the phenyl rings) obtained from observed ^{1}H spin-lattice relaxation times using fitting calculations by a least-squares method. The theoretical values of ΔM_2 are given in parentheses.

	$\Delta M_2/G^2$	$-\log(\tau_0/s)$	E_a [kJ mol^{-1}]
p-$ClC_6H_4CONH_2$			
low temp. phase	–	17.1	64 ± 5
high temp. phase	1.8 ± 0.1 (1.75)	14.1	44 ± 5
p-$ClC_6H_4COND_2$			
low temp. phase	–	17.9	68 ± 5
high temp. phase	1.0 ± 0.1 (1.08)	14.0	43 ± 5

From the following discussion, the motion responsible for the T_{1H} of these compounds can be assigned to the 180° flip of the phenyl ring about the C−Cl bond axis. The small ΔM_2 values derived from the fitting calculation support this assignment because approximately the same ΔM_2 values were calculated by use of the average structure of the HTP [2] assuming usual C−H and N−H distances in the amide molecule. The calculated values are given in Table 2. Although the 180° flip motion has a large amplitude, the atomic arrangement in the crystal remains unchanged, and it is expected that the transient time of the reorientation is so short that the average EFG produced at the chlorine nucleus is well-defined. The large E_a values can be understood by considering that the amide group attached to the phenyl group has a C−C bond shorter than the usual C−C single bond [11] indicating the formation of a conjugated system. Very short τ_0 values of the order of 10^{-17} s were obtained in the LTP. Such short τ_0 values were also determined for the 180°-flip of phenyl rings in anilinium halides [12] exhibiting large activation energies.

When the quadrupolar spin-lattice relaxation is governed by librations involving oscillation of the principal EFG axes of the resonant nuclei, the relaxation rate $T_{1Cl^Q}^{-1}$ for quadrupolar nuclei having nuclear spin 3/2 is proportional to T^2 under the condition of $\hbar\omega_l \ll kT$, where ω_l represents the librational angular frequency [13, 14]. In the LTP, the log T_{1Cl^Q} vs. log T curves observed for the three ^{35}Cl resonance lines show a good linear relationship at lower temperatures, as depicted in Fig. 3, and

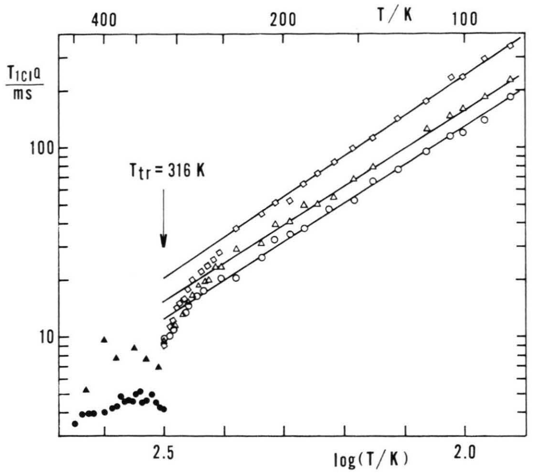

Fig. 3. Temperature dependence of the ^{35}Cl quadrupolar spin-lattice relaxation time $T_{1\mathrm{Cl}^Q}$ for the three resonance frequencies of the low temperature phase and of ^{35}Cl (●) and ^{37}Cl (△) $T_{1\mathrm{Cl}^Q}$ for the high temperature phase of p-chlorobenzamide. The symbols, □, △, and ○ denote ^{35}Cl $T_{1\mathrm{Cl}^Q}$ corresponding to the lowest, the highest, and the middle NQR frequency lines, respectively, of the low temperature phase. The solid lines are best fitted curves.

yield the relations $T_{1\mathrm{Cl}^Q}^{-1} \propto T^{2.1}$, $T_{1\mathrm{Cl}^Q}^{-1} \propto T^{2.0}$, and $T_{1\mathrm{Cl}^Q}^{-1} \propto T^{2.0}$ in the order of decreasing $T_{1\mathrm{Cl}^Q}$. Therefore, one can conclude that $T_{1\mathrm{Cl}^Q}$ of the three lines below ca. 250 K is mainly determined by vibrational fluctuation of the chlorine EFG. With increasing temperature, above ca. 250 K all $T_{1\mathrm{Cl}^Q}$ values decreased gradually and converged into the same value at T_{tr}. This $T_{1\mathrm{Cl}^Q}$ behavior is characteristic but not typical for a second order phase transition, although this transition is clearly a first order one. In the HTP, the ratios of $T_{1\mathrm{Cl}^Q}$ observed for the ^{35}Cl and ^{37}Cl nuclei at several temperatures were 1.5 ± 0.2, which value is almost equal to $\{Q(^{35}\mathrm{Cl})/Q(^{37}\mathrm{Cl})\}^2$. This indicates that the quadrupolar relaxation in the HTP is also attributable to a librational process.

Taniguchi et al. [1] proposed a structural model for the HTP. The existence of domains is assumed which have a structure similar to the LTP. This domain model may be consistent with the observation of a single NQR line in our study, if these domains are mutually exchanged by rapid reorientations of the dimers about their long axes. However, the present NQR and NMR results cannot be explained by this model mostly because $T_{1\mathrm{Cl}^Q}$ observed showed no Arrhenius type temperature dependence. Also the $T_{1\mathrm{H}}$ curves of the HTP cannot be explained by the model [1], which involves a thermally activated orientational change of the dimers mainly by rotations between orientational positions having fairly large angles, which would result in a thermal fluctuation process of the chlorine EFG.

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