

Zeeman Effect of ^{35}Cl NQR on A Low Temperature Phase of 2,4,6-Trichloronitrobenzene

(NQR/Zeeman effect/trichloronitrobenzene)

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^{35}Cl NQR frequencies in the title compound have been observed as a function of temperature in the range of 77 K to the melting point. A discontinuity in the NQR signals has been observed at 321 K, suggesting a phase transition. The Zeeman effect on resonance lines in the low temperature phase has been studied at room temperature. The asymmetry parameter for the Cl atom at 2- or 6-position is 0.094, whereas that for the Cl atoms at the 4-position is 0.080. The angles between the C—Cl bonds are determined on the basis of the orientations of the axes of the electric field gradients. The phase transition is revealed to be accompanied with change in molecular shape.

Introduction

In a previous report[1], a preliminary observation of the temperature dependence of the ^{35}Cl NQR frequencies provided the evidence for the existence of two modifications in 2,4,6-trichloronitrobenzene (TCNB). The phase transition between the low temperature (α -TCNB) and high temperature phases (β -TCNB) was found to occur around 323 K. The crystal structures of these modifications are unknown. The angles between the C—Cl bonds in β -TCNB were estimated by Zeeman analysis on a single crystal[1]. These angles were very close to those in 1,3,5-trichlorobenzene(TCB)[1,2]. On the basis of these angles, the nitro group in β -TCNB was presumed to be considerably twisted against the ring plane.

It is of interest to know what rearrangement of the molecules occurs as a result of the phase transition and whether α -TCNB differs from β -TCNB in molecular geometry. The Zeeman effect on a single crystal is a useful probe to obtain information on bond directions. However, it is difficult to obtain a large single crystal of

α -TCNB, because it is formed through the phase transition from β -TCNB. For this reason, this problem has been laid aside up to now.

In the present investigation, both the asymmetry parameters and the directions of the electric field gradients (EFG) of the Cl atoms in α -TCNB are determined on the basis of the Zeeman effect of ^{35}Cl lines. The molecular shape of α -TCNB and the bond nature of the C—Cl bonds are discussed.

Experimental

A single crystal of β -TCNB that was used in the previous Zeeman study changed into a polycrystalline α -form after the observation of the Zeeman effect[1]. This sample changed gradually into a single crystal of α -TCNB with the lapse over ten years. The single crystal obtained thus was used in the present investigation. The Zeeman effect was examined by means of the zero-splitting cone method[3]. The ^{35}Cl NQR spectra were recorded with a super-regenerative spectrometer[4]. The resonance frequency was determined with an accuracy of 1 KHz by a frequency counter. Temperature was determined by use of a copper-constantan thermocouple.

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This paper is respectfully dedicated to the memory of the late professor Isao Taguchi.

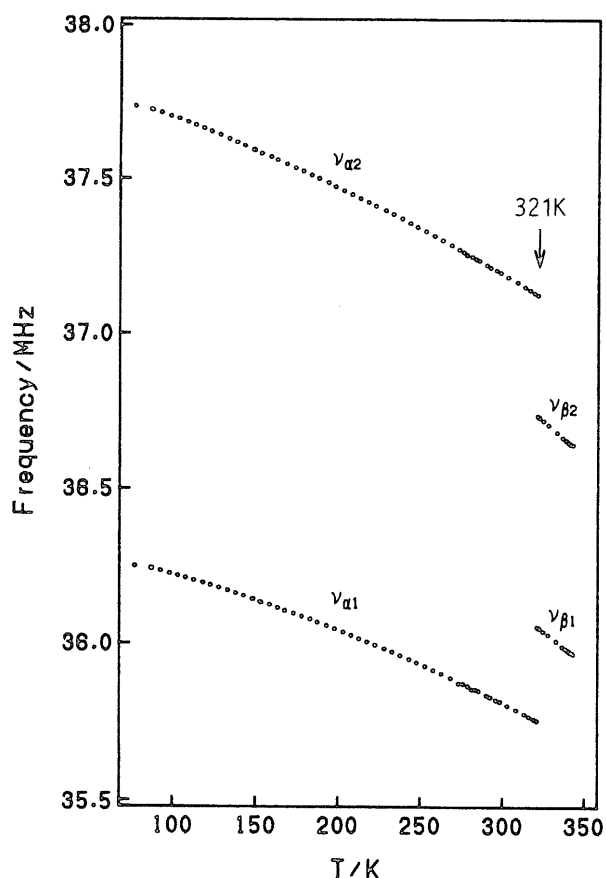


Fig. 1. Temperature dependence of ^{35}Cl resonance frequencies of 2,4,6-trichloronitrobenzene.

Table 1. ^{35}Cl NQR parameters for 2,4,6-trichloronitrobenzene

Line	Frequency/MHz			η^a	e^2Qqh^{-1}/MHz^b
	77K	294K	321K		
α -form					
$\nu_{\alpha 1}$	36.249	35.823	35.754	0.080	71.571
$\nu_{\alpha 2}$	37.735	37.213	37.127	0.094	74.317
β -form ^{b)}					
$\nu_{\beta 1}$		36.175 ^{c)}	36.054	0.114	72.161
$\nu_{\beta 2}$		36.843 ^{c)}	36.736	0.101	73.570

a) Values at room temperature.

b) Ref. 1.

c) The resonance frequencies in a supercooled sample.

Results and Discussion

The temperature dependence of the NQR frequencies in TCNB was investigated in the range of 77 K to the melting point. The results are shown in Fig. 1. The resonance frequencies at representative temperatures are listed in Table 1. No phase change was found below room temperature. The phase transition on going from

low to high temperatures occurs at 321 K, which is 2K lower than the value in the previous work[1]. This discrepancy presumably results from the higher rate of the rise of temperature in the previous work. The phase transition was sluggish in the cooling directions and β -TCNB was readily supercooled down to room temperature. In each of α -TCNB and β -TCNB, the lower-frequency and higher-frequency lines are to the Cl atoms at the para and ortho positions, respectively, from the intensity ratio[1].

The Zeeman effect on the ^{35}Cl resonance lines in α -TCNB was observed in order to obtain information on the orientations of the EFG axes and the asymmetry parameters. Figure 2 shows the loci of the zero-splitting patterns for α -TCNB at room temperature. The lower-frequency line ($\nu_{\alpha 1}$) gave only one locus, and the higher-frequency one ($\nu_{\alpha 2}$) a pair of loci. By contrast, in β -TCNB a pair of loci were obtained for the lower-frequency line and four loci for the higher-frequency line[1]. In α -TCNB only one two-fold axis of the crystal was determined from the distribution of the Zeeman patterns. Accordingly, the crystal of α -TCNB belongs to a monoclinic or a higher symmetric system[5], whereas β -TCNB belongs to an orthogonal system[1].

The asymmetry parameter (η) was determined using the following equation:

$$\sin^2 \theta_0 = 2/(3 - \eta \cos 2\phi_0), \quad (1)$$

where θ_0 and ϕ_0 are polar and azimuthal angles, respectively. The quadrupole coupling constants (e^2Qqh^{-1}) were calculated from the following relation;

$$\nu = (1/2)e^2Qqh^{-1}(1 + \eta^2/3)^{1/2}. \quad (2)$$

The details are listed in Table 1. Table 2 lists the relative orientations of the significant EFG axes on the Cl atoms in α -TCNB. As seen in Fig. 2, the y and z axes lie on the same plane within an experimental error and the x axes related to the directions of π -bondings are normal to this plane. The angles between the C—Cl bonds were estimated, assuming that the EFG z axis coincides

Table 2. Angles ($^{\circ}$) between the EFG principal axes.

Axis	x_i	z_i	x_{2A}	z_{2A}
x_{2A}	3.72	90.63		
z_{2A}	93.52	118.96		
x_{2B}	3.49	89.03	1.64	91.05
y_{2B}	93.41	118.92	91.56	122.13

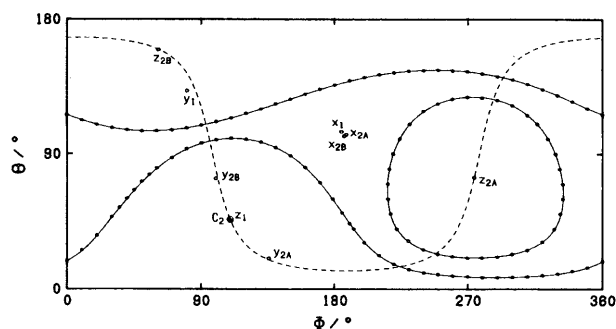


Fig. 2. Zero-splitting patterns of ^{35}Cl NQR lines in α -form of 2,4,6-trichloronitrobenzene. x_i , y_i , and z_i indicate the directions of the principal EFG axes at the halogen nucleus giving a $\nu_{\alpha i}$ line. The dashed line indicates the ring plane assumed from the directions of the EFG axes.

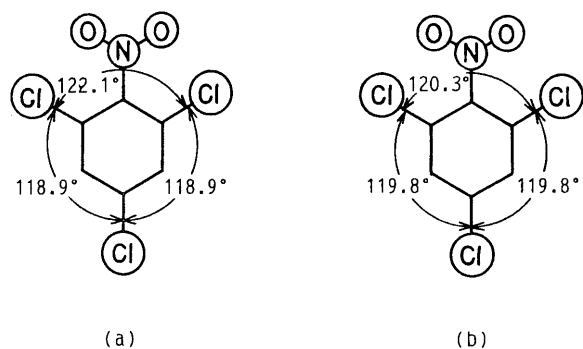


Fig. 3. Angles between the C—Cl bonds in (a) α -TCNB and (b) β -TCNB.

with the bond axis, as is generally the case. All the C—Cl bonds lie on the ring plane. The results are shown in Fig. 3. The two-fold axis of the molecule lies along the C—Cl bond at the 4-position and is consistent in direction with the two-fold axis of the crystal. Therefore the molecular symmetry of α -TCNB is C_2 or C_{2v} , depending on the orientation of the nitro group.

An interesting finding is that the angle between the C—Cl bonds at the 2- and 6-positions in the α -form is *ca.* 2° greater than that in the β -form. Apparently, the phase change is accom-

panied with change in molecular shape. By comparing the angles between the C—Cl bonds in β -TCNB with those in TCB, it is presumed that the nitro group of β -TCNB is considerably twisted about the N—C bond[1]. The twist angle of the nitro group against the ring plane is greatly affected by steric repulsion between the nitro group and its adjacent Cl atoms. For example, the twist angle in 2,3-dichloronitrobenzene is 53.4° [6], and that in 3,4-dichloronitrobenzene 8.8° [8].

In α -TCNB the nitro group appears to push the Cl atoms at 2- and 6-positions outside, compared with β -TCNB. Therefore the plane of the nitro group is presumed to be less twisted against the ring plane in α -TCNB than in β -TCNB. We made a rough estimation of the distance between the O atom of the nitro group and the Cl atom at the 2-position, assuming that the nitro group and the ring plane are coplanar. The distance in α -TCNB is calculated to be about 250 pm, using the experimental angles between the C—Cl bonds and the averaged bond parameters in 2,3-dichloronitrobenzene[6] and 3,4-dichloronitrobenzene[8]. This distance is too short compared with the sum of van der Waals radii of the O and Cl atoms[9,10]. Therefore, the nitro group must be considerably twisted about the N—C bonds in α -TCNB as well as β -TCNB, and hence the molecular symmetry is expected to be C_{2v} .

The η -values for the Cl atoms in α -TCNB are a few percent smaller than those in β -TCNB[1], as seen in Table 1. In other polychloronitrobenzenes[6-8], the η -values for the Cl atoms are in the range of 0.11—0.15. In addition to the π interaction with the aromatic ring, the deformation of electron cloud due to van der Waals contacts between the Cl atom and its neighboring atoms affects the η -value. On the Cl atom at the 4-position, intermolecular interaction probably is an important factor in the difference in the η -value, because no significant neighbors exist within a molecule. On the Cl atoms at the 2- and 6-positions, the intramolecular interaction between the Cl atom and

Table 3. Bond character of 2,4,6-trichloro-nitrobenzene.

Chlorine	s^a	i^a	f^a
α -form			
Cl(4)	0.753	0.217	0.030
Cl(2,6)	0.779	0.184	0.037
β -form ^b			
Cl(4)	0.753	0.204	0.043
Cl(2,6)	0.770	0.191	0.039

a) s, i, and f represent the sigma, ionic, and double bond characters, respectively.

b) Ref. 1.

the O atom of the nitro group is dominant, as described above. Therefore the orientation of the nitro group is attributable to the change in the η -value.

From the coupling constant and the asymmetry parameters the bond characters were estimated, using the Townes-Dailey approximation[11] and Bersohn's equation[12]. The calculated values are listed in Table 3. No appreciable differences in bond character between α -TCNB and β -form are found.

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