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Zeeman effect of ^{35}Cl NQR in 2,6-Dichlorobenzyl Chloride

(NQR／Zeeman effect／polychlorotoluene)

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The Zeeman effect of the ^{35}Cl NQR of 2,6-Dichlorobenzyl chloride was observed. The three absorption lines were assigned to the three chlorine atoms, referring to the bond directions which were determined on the basis of the orientations of the principal z axes. The locations of the principal z axes of the field gradient were determined with uncertainty below 0.1°. The asymmetry parameters of the electric field gradients were found to be 0.120 ± 0.002, 0.110 ± 0.002, 0.008 ± 0.002, respectively, for the three chlorine atoms corresponding to the resonance lines in order of decreasing frequency. The two higher-frequency lines were assigned to the chlorine atoms bonded to the ring and the lower-frequency line was assigned to the chlorine atom bonded to the side chain.

Introduction

It was previously revealed in the Zeeman study on ^{35}Cl and ^{81}Br resonances that 2,6-dichlorobenzyl bromide (DCBB) had a highly symmetrical molecular structure in a crystalline state and the CH_2Br group was slightly twisted about the C−C bond[1]. Nevertheless, the ^{35}Cl resonance spectrum of the bromide was widely split into two lines. The main cause of the splitting was ascribed to intermolecular interaction. It is of interest how the molecular shape is changed by replacing the bulky bromine atom in DCBB with the less bulky chlorine atom. For this reason, 2,6-dichlorobenzyl chloride (DCBC) was chosen as the target compound.

No NQR spectrum of DCBC has been observed, although resonance frequencies were reported for such related compounds as 2,4-dichlorobenzyl chloride[2] and 3,4-dichlorobenzyl chloride[2]. In addition, neither morphological data nor X-ray data are available for this compound. In organic compounds, the principal z-axes of the electric field gradients (efg) coincide with the bond axes with good accuracy[3,4]. Therefore resonance lines can be assigned to particular atoms using the NQR Zeeman effect in a single crystal.

The directions of the efg axes and the efg asymmetry parameters will be determined using the method of zero-splitting cones in order to obtain information on the mutual angles between the C−Cl bonds and the bond characters.

Experimental

Commercially available DCBC, supplied by Tokyo Kasei, was recrystallized from ethanol. A single crystal was grown from melt in a Pyrex tube using the Bridgman technique. The NQR spectrometer used is described elsewhere[5]. The Zeeman effect was studied at room temperature by means of the zero-splitting cones method. The magnetic field for the Zeeman study was furnished by an air-cooled Helmholtz coil[6].

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This paper is respectfully dedicated to the memory of the late Professor Masami Kurokawa.

Results and Discussion

The NQR spectrum on DCBC consists of three ^{35}Cl lines at room temperature. The resonance frequencies for DCBC are listed in Table 1. The resonance lines were designated as Cl_1, Cl_2 and Cl_3 in order of decreasing frequency.

The zero-splitting patterns of the ^{35}Cl Zeeman lines in DCBC are shown together with the significant directions of the principal efg axes in Fig. 1. The axes, x_i, y_i, and z_i are the directions of the efg axes contributing to the Cl_i resonance lines and the subscript a or b indicates that each chlorine atom is situated in a different crystal site. These directions and the asymmetry parameters (η) were determined through analyzing the zero-splitting loci by the least squares method. The locus is expressed for the nuclear spin $I=3/2$ as follows ; [7]

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

where θ_0 and η_0 are the polar and azimuthal angles, respectively. Each line gave two patterns, suggesting that the DCBC crystal belongs to the monoclinic system[8]. From the distribution of these patterns, a twofold axis (C_2) was determined. The quadrupole coupling constant (e^2Qqh^{-1}) and the asymmetry parameter are related to the resonance frequency (ν) by the following relation ;

$$\nu=(e^2Qq/2h)(1+\eta^2/3)^{1/2}. \qquad (2)$$

The calculated parameters and the mutual angles between the efg axes are listed in Tables 1 and 2, respectively.

Table 1. NQR Parameters for 2,6-Dichlorobenzyl Chloride at 295 K

Line	Frequency /MHz	e^2Qqh^{-1}/MHz	η
Cl_1	34.776	69.38	0.120±0.002
Cl_2	34.592	69.04	0.110±0.002
Cl_3	34.266	63.53	0.008±0.002

The efg axes of the Cl atoms can be easily assigned to a particular molecule on the basis of the bond angle. The two C−Cl bonds at the ortho positions make an approximate angle of 120° to one another and thier x axes connected with the *pi* bond directions are nearly parallel. The C−Cl bond of the side chain can be presumed to be inclined at an angle of about 80° to the two C−Cl bonds lying on the ring plane, when the C−C−Cl angle of the side chain is tetrahedral and the C−C−Cl plane is nearly perpendicular to the ring plane. Actually, the angles of 78.5° and 79.5° were found in DCBB[1].

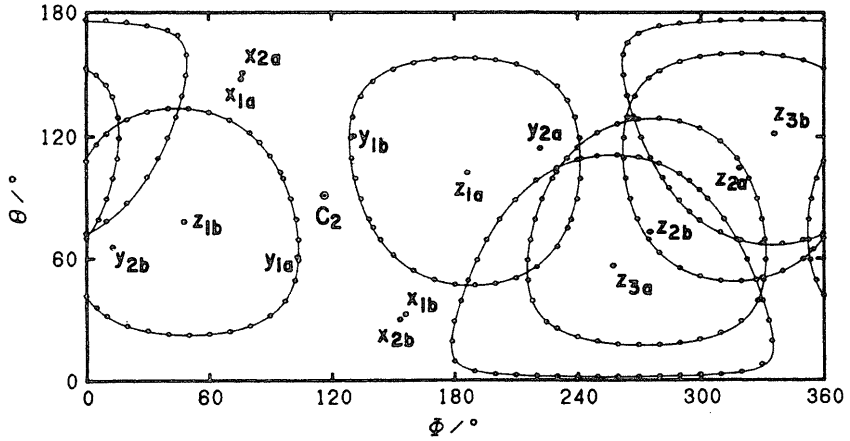

Fig. 1. Zero-splitting patterns on the ^{35}Cl resonance lines in 2,6-dichlorobenzyl chloride. The twofold axis is referred to C_2.

Table 2. Mutual Angles (/°) between the efg Axes in 2,6-Dichlorobenzyl Chloride

(a) Angles between the z axes

axis	z_{1b}	z_{2a}	z_{2b}	z_{3a}	z_{3b}
z_{1b}	139.82	125.24	92.15	81.43	126.77
z_{1a}		92.10	125.20	126.70	81.34
z_{2a}			53.34	75.71	23.10
z_{2b}				23.07	75.74
z_{2a}					98.51

(b) Angles between the x axes

axis	x_{1b}	x_{2a}	x_{2b}
x_{1a}	131.55	3.06	132.44
x_{1b}		133.35	2.99
x_{2a}			134.30

(c) Angles between the y axes

axis	y_{1b}	y_{2a}	y_{2b}
y_{1a}	64.70	125.14	79.09
y_{1b}		78.70	125.13
y_{2a}			153.80

Since the values of the asymmetry parameters are not so large, it can be assumed that the directions of the z axes coincide with those of the C−Cl bonds. The calculated mutual angles between the C−Cl bonds are shown in Fig. 2. The angle between the C−Cl bonds attached to the ring is larger by 5° than the expected value. This angle is almost identical to the corresponding angle, 125.1°, in DCBB. Accodingly, the Cl_1 and Cl_2 lines were assigned to the chlorine atoms bonded to the ring, and hence

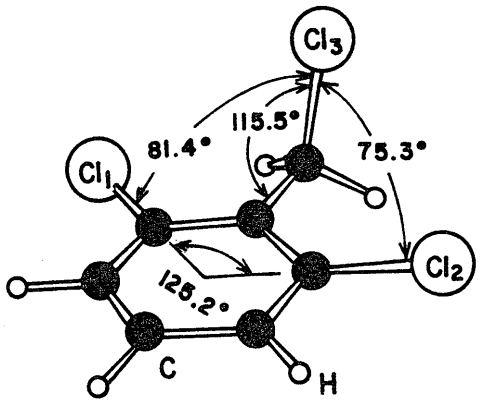

Fig. 2. Molecular shape of 2,6-dichlorobenzyl chloride.

the remaining line Cl_3 to the chlorine atom bonded to the side chain. This assignment is consistent with the magnitudes of the asymmetry parameters for the chlorine atoms expected from the *pi* bond character.

It is interesting to know whether the chlorine atoms bonded to the ring are out-of-plane or not. Since the crystal structure of DCBC is not known, we cannot solve this problem exactly. However, an approximate solution can be obtained from the orientations of the efg axes. It is noted that the discrepancy in orientation between the x_1 and x_2 axes is very slight, as can be seen in Table 2. For convenience, the plane which is made up of the z_1 and z_2 axes was assumed to be coplanar to the ring. The angles between the x_1 and x_2 axes and the assumed ring plane are calculated to be $89.0° \pm 0.5°$ and $87.7° \pm 0.4°$, respectively. The x axes of the chlorine atoms at the 2- and 6-positions in DCBC are almost perpendicular to the ring plane. It is therefore presumed that the two C−Cl bonds are almost coplanar to the ring plane.

The C−C−Cl angle of the chloromethyl group cannot be determined accurately. However, the bond angle can be roughly estimated by assuming that the C−C bond connecting the chloromethyl group with the ring is parallel to the bisector of the two C−Cl bonds at the 2- and 6-positions[1]. So long as the C−C bond lines in the ring plane, the calculated angle is

little affected by a small deviation of the C−C direction from the bisector. The calculated angle, 115.5°, which is appreciably greater than the tetrahedral angle, is comparable to the corresponding angle, 114.4°, in DCBB[1].

The angles between the twofold axis and the bond directions or the ring plane in DCBC are compared with those in DCBB in Table 3. As mentioned above, the crystals of DCBC and DCBB[1] belong to the monoclinic system. However, the orientations of the bond axes, particularly regarding the $C-Cl_1$, $C-Cl_2$, and C−C bonds, to the twofold axis in the chloride are quite different from those in the bromide. The DCBC crystal does not seem to be isomorphous with that of DCBB.

The CH_2Cl group in DCBC is more twisted around the C−C bond than the CH_2Br group in DCBB. By contrast, the difference in the resonance frequency between the Cl_1 and Cl_2 atoms in the less distorted molecule of DCBB is about 500 KHz, whereas the corresponding difference in DCBC is only about 180 KHz. If the Cl···Cl interaction in a molecule is significant with respect to the resonance frequencies for the Cl_1 and Cl_2 atoms, the resonance lines should be more spread out in DCBC than in DCBB. It can therefore be assumed that in these compiunds the spacing between the resonance lines of the chlorine atoms at the 2- and 6-positions is governed mainly by intermolecular interaction. This lends further support to the presumption that these compounds differ from one another in their crystal structures.

The bond characters which were calculated in the same manner as described previously[1] are listed in Table 4. In *α, α, α*, 4-tetrachlorotoluene[9], it has been suggested that the charge-transfer interaction occurs between the aromatic *pi* system and the trichloromethyl group. In DCBC and DCBB, such interaction is not found, because the chlorine atom of the chloromethyl group is characterized by a negligibly small asymmetry parameter.

There is no significant difference in the

Table 3. Orientations of the Bond Axes and the Ring Plane to the Twofold Axis of the Crystals in 2,6-Dichlorobenzyl Chloride (DCBC) and 2,6-Dichlorobenzyl Bromide (DCBB)

Bond or Plane	DCBC	DCBB[a]
$C-Cl_1$	69.91°±0.03°	81.49°±0.01°
$C-Cl_2$	26.67°±0.01°	47.66°±0.01°
$C-Cl_3$ (or C−Br)	49.26°±0.02°	46.91°±0.01°
C−C[b]	53.28°±0.02°	26.92°±0.01°
Ring plane[c]	23.35°±0.01°	20.02°±0.01°

a) Calculated using the data in Ref. 1.
b) The assumed C−C bond between the ring and the side chain.
c) The assumed plane is made up of the z_1 and z_2 axes.

Table 4. Bond Characters for Dichlorobenzyl Chloride (DCBC) and 2,6-Dichlorobenzyl Bromide (DCBB)

Atom	DCBC			DCBB[a]		
	s	*f*	*i*[b]	*s*	*f*	*i*
Cl_1	0.714	0.051	0.235	0.654	0.043	0.303
Cl_2	0.712	0.046	0.242	0.664	0.045	0.291
Cl_3 (or Br)	0.735	~0	0.265	0.797	~0	0.203

a) Ref. 1.
b) *s*, *f*, and *i* represent the single bond, double bond and the ionic characters respectively.

double bond character of the Cl_1 and Cl_2 atoms between DCBC and DCBB. With respect to the ionic character of these chlorine atoms, DCBC have 5 to 6 percent smaller values than DCBB. On the contrary, the chlorine atom bonded to the side chain in DCBC has additional ionic characters compared with the corresponding bromine atom in DCBB, as expected from the difference in electronegativity between the halogen and carbon atoms. It is probable that the sigma electrons of the Cl atoms bonded to the ring are indirectly drawn toward the halogen atom of the halogenated methyl group by an inductive effect. It is therefore considered that the C−Cl bonds at the 2- and 6-positions are more covalent in DCBC than in DCBB because of more inductive group.

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