Zeeman Effect of ^{35}Cl and ^{81}Br NQR in 2, 6-Dichlorobenzyl Bromide

(NQR／Zeeman effect／polychlorobenzyl bromide)

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The ^{35}Cl and ^{81}Br nuclear quadrupole resonances of 2,6-dichlorobenzyl bromide have been observed and the Zeeman effect on a single crystal has been examined at room temperature. This compound yields two ^{35}Cl resonance lines and a single ^{81}Br line at room temperature. ^{35}Cl NQR parameters ($|e^2Qqh^{-1}|=68.65$ MHz ; $\eta=0.108$) and (69.74 MHz ; 0.101) and ^{81}Br parameters (435.57 MHz ; 0.008) were obtained. The relatively large η values for the Cl atoms are caused by the π-bonding character of the C－Cl bond. It has been found that the angle between the C－Cl bonds was 125.1° within 1° and the C－Br bond orients to the two C－Cl bonds at angles of 78.5° and 79.5°. From the distribution of the zero-splitting loci, it has been determined that the crystal of this compound belongs to a monoclinic system.

Introduction

In the course of a NQR study of 2, 6-dichlorobenzyl bromide, a spectrum consisting of a single ^{81}Br line at about 219 MHz and two ^{35}Cl lines in the frequency range of 34 to 35 MHz was obtained at room temperature. Despite the simple chemical structure, this compound has not been the subject of NQR studies. Surprisingly, the NQR frequencies of any other benzyl bromides have not been reported. Furthermore, no information on the crystal structure of 2, 6-dichlorobenzyl bromide is available. The interest in studying this compound is to get information about its molecular shape and bond character.

Zeeman effect of the ^{35}Cl and ^{81}Br NQR was studied to determine the principal axes of the electric field gradient (efg) tensor and the asymmetry parameter related to the fractional importance of the bond character. The molecular structure and the bond angles would be deduced based on these parameters.

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Experimental

The NQR spectrum of ^{35}Cl was obtained with an externally quenched superregenerative oscillator and that of ^{81}Br with an externally quenched superregenerative Lecher-line oscillator[1]. The absorption lines were displayed on an oscilloscope. The resonance frequencies were determined by the use of a signal generator and a frequency counter with an accuracy of 0.001 MHz. The resonance lines due to four isotypes : ^{35}Cl, ^{37}Cl, ^{79}Br and ^{81}Br were assigned on the basis of the known quadrupole moment ratios, $Q(^{35}Cl)/Q(^{37}Cl) = 1.2688$ and $Q(^{79}Br)/Q(^{81}Br) = 1.1970$. The Zeeman effect was examined by means of the zero-splitting cones method. The procedure of analysis is described elsewhere[2]. The Zeeman field was applied by means of a Helmholtz coil described previously[2].

2, 6-Dichlorobenzyl bromide was obtained from Tokyo Kasei Kogyo Co., Ltd. A single crystal of this compound, 15 mm in diameter and 30 mm in length, was grown from the melt by the Bridgman-Stockbarger method.

Results and Discussion

The NQR frequencies in 2, 6-dichlorobenzyl bromide are listed in Table 1. At room temperature the NQR spectrum consists of two ^{35}Cl lines and a single ^{81}Br one. This suggests that there exists only one molecular species in the unit cell of the crystal and the two chlorine atoms at the *ortho* positions are physically nonequivalent. Therefore, the molecular shape is presumed to be somewhat distorted. For convenience, the chlorine atom corresponding to the lower frequency line and the other one corresponding to the higher frequency line are designated, respectively, as Cl(1) and Cl(2).

Table 1. NQR Parameters for 2, 6-Dichlorobenzyl bromide at 296 K

Line	Frequency/MHz	η	e^2Qqh^{-1}/MHz
Cl (1)	34.393	0.108	68.652
Cl (2)	34.930	0.101	69.742
Br (3)	218.790	0.008	435.573

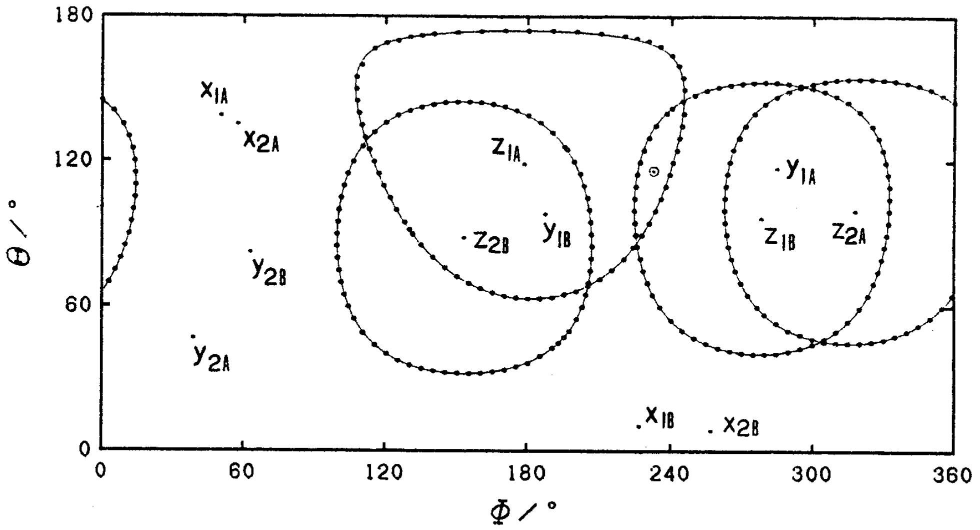

Fig. 1. Zero-splitting patterns on the ^{35}Cl resonance lines in 2, 6-dichlorobenzyl bromide.

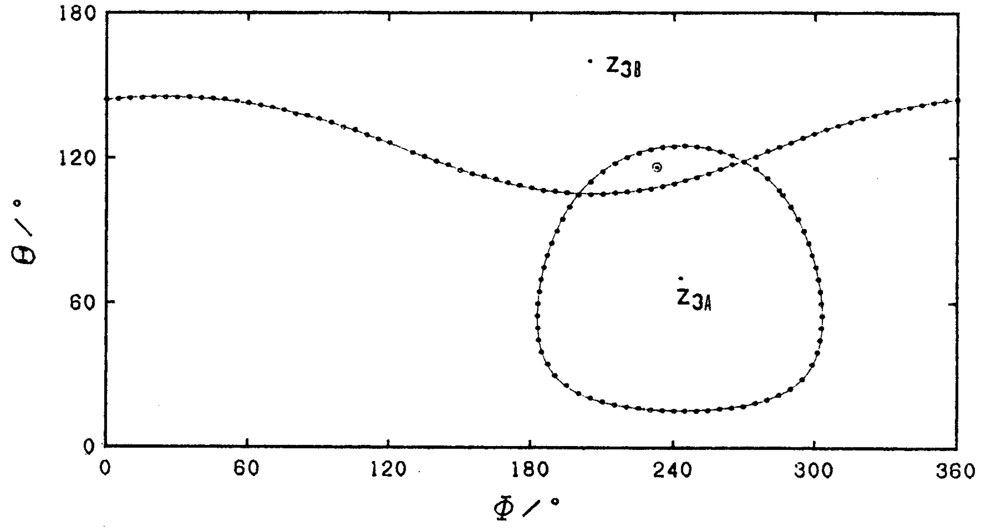

Fig. 2. Zero-splitting patterns on the ^{81}Br resonance line in 2, 6-dichlorobenzyl bromide.

The zero-splitting patterns obtained from the Zeeman effect of the resonance lines for the ^{35}Cl and ^{81}Br nuclei in the 2, 6-dichlorobenzyl bromide are shown in Figs. 1 and 2. Here x_i, y_i, and z_i are the directions of the axes of the efg tensor at the ^{35}Cl or ^{81}Br nucleus contributing to a Cl (i) or Br (3) resonance line. The zero-splitting loci were analyzed by the least squares method to obtain the directions of the efg tensor axes and the asymmetry parameter (η). The locus is expressed for ^{35}Cl and ^{81}Br nuclei as follows ;3)

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

where ϕ_0 and θ_0 are the polar and azimuthal angles, respectively.

The quadrupole coupling constant (e^2Qqh^{-1}) may be determined from the following equation ;

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

The NQR parameters are listed in Table 1. A pair of zero-splitting loci were obtained for each line. This indicates that there are two molecules in a unit cell related by the twofold axis. From the number of the nonequivalent directions of the efg axes, the crystal belongs to a monoclinic class[4]. The twofold axis was determined from the distribution of the efg axes.

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

(a) Angles between the Z axes

axis	Z_{1B}	Z_{2A}	Z_{2B}	Z_{3A}[a)]	Z_{3B}
Z_{1A}	95. 12	125. 14	39. 20	78. 58	43. 78
Z_{1B}		39. 21	125. 14	43. 83	78. 51
Z_{2A}			162. 98	79. 51	88. 86
Z_{2B}				88. 866	79. 49
Z_{3B}					93. 83

(b) Angles between the X axes

axis	X_{1B}	X_{2A}	X_{2B}	P(A)[b)]	P(B)
X_{1A}	148. 82	6. 03	145. 71	6. 64	35. 67
X_{1B}		145. 03	5. 21	36. 13	5. 92
X_{2A}			142. 59	1. 21	38. 85
X_{2B}				38. 60	1. 46
P(A)					40. 05

a) Z_{3i} represents the direction of the efg Z axes at the bromine atom. b) P(i) indicates the plane formed by the efg axes Z_{1i} and Z_{2i}.

Molecular Shape and Molecular Plane. The angles between the efg axes are listed in Table 2. Although no X-ray data is available for this compoun the efg axes of the chlorine atoms can be easily assigned to a particular molecule on the basis of a bond angle. The two C-Cl bonds in a molecule are inclined at an approximate angle of 120° to one another. Usually, when the halogen atom under consideration does not bridge surrounding atoms, the direction of the efg z axis is assumed to be parallel to a sigma bond axis. Furthermore, the efg x axes of the Cl atoms belonging to the same molecule are presumed to be nearly parallel to each other, since they are connected with the orientations of the π bond orbitals of the benzene ring. The directions of the significant efg axes are shown in Fig. 3. The two planes, P (A) and P (B), consisting of the z_1, z_2 and y_2 axes were obtained. These planes were assumed to be parallel to the aromatic rings. This is equivalent to assuming that the two C–Cl bonds lie in the ring plane. The two molecules tentatively were termed Molecule A and Molecule B. In each molecule the x_2 axis is normal to the ring plane allowing for experimental error. The x_1 axis deviates by about 5.6°±0.4° from the direction of the x_2 axis and the y_1 axis is out of the ring plane. This may result from intermolecular interaction through the Cl (1) atom. In this connection, it is noteworthy that the resonance frequency of the Cl (1) atom is lower by 0.5 MHz than that of the Cl (2) atom. The angle between these planes are 40.0°. These planes make the angle of 70.0° to the twofold axis.

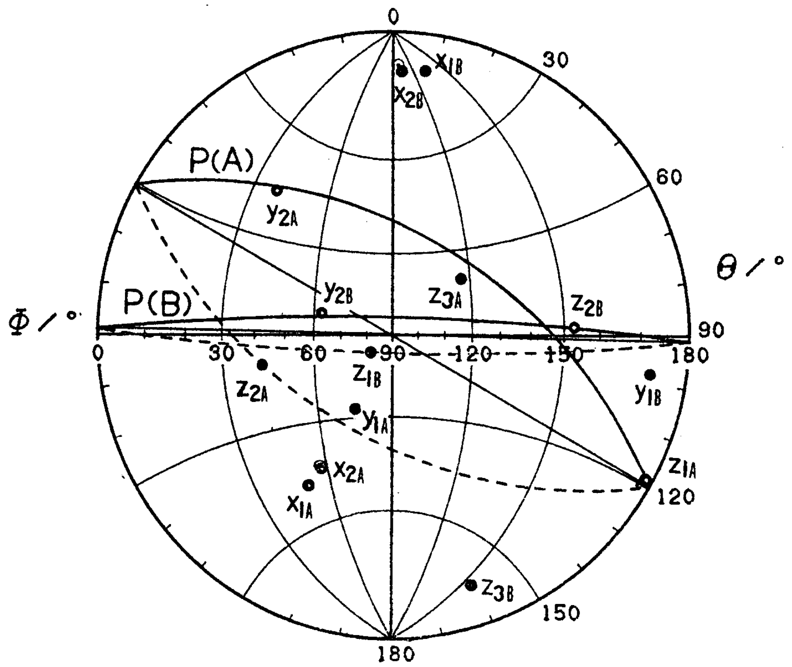

Fig. 3. Stereogram of the ring planes in 2, 6–dichlorobenzyl bromide, as deduced from the directions of the efg axes.

By contrast, there is no reason that the C–Br bond of the $-CH_2Br$ group orients at particular angles to the two C–Cl bonds. Therefore, the efg z axes of the bromine atom cannot be assigned unequivocally to the molecule at a particular crystal site. The C–Br bond should orient at an angle of about 110° to the C–C bond between the carbon atom at the α position and .the one at the 1–position. The direction of this C–C bond cannot be determined accurately because of the unknown crystal structure of this compound. This direction, however, can be approximated by the bisector of the angle between the two C–Cl bonds, taking the symmetry of the molecule into account. The angles between the bisector and the C–Br bond are listed in Table 3.

Table 3. Angles (/°) between the C–Br bonds and the Bisector of the C–Cl Bonds or the Ring Planes

Bond	B(A)[a]	B(B)[b]	P(A)[b]	P(B)[b]
C–Br(A)	65.63 (114.37)	36.37 (143.63)	65.63	26.23
C–Br(B)	36.76 (143.24)	65.50 (114.50)	26.33	65.52

a) B(*i*) is the direction of the bisector between the Z_{1i} and Z_{2i} axes. b) P(*i*) is the plane formed by the Z_{1i} and Z_{2i} axes.

The only reasonable value for the ∠CCBr angle is 114.4°. Accordingly, the Br(A) atom is assigned to Molecule A and the Br (B) atom to Molecule B. On the basis of this assignment the angles between the C–Br bond and the two C–Cl bonds can be determined to be 78.5° and 79.5° from the values in Table 1 (a). The C–Br bond is inclined at an angle of 65.6° to the aromatic ring. The molecular structure thus determined is illustrated in Fig. 4. The molecular shape of 2, 6–dichlorobenzyl bromide seems to be more symmetric than predicted from the pattern of the NQR spectrum.

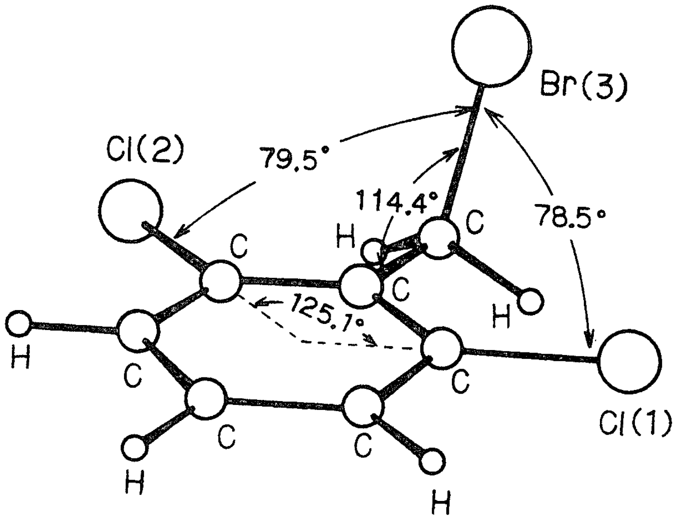

Fig. 4. Molecular shape of 2, 6–dichlorobenzyl bromide.

Bond Character of the C-X bond. The number of the unbalanced p-electron, U_p, is given by[5)]

$$U_p = |e^2Qq_{\mathrm{obs}}| / |e^2Qq_{\mathrm{atom}}|, \qquad (3)$$

where e^2Qq_{atom}/h is the quadrupole coupling constant for the free halogen atom (109.746 MHz for ^{35}Cl 643.032 MHz for ^{81}Br). U_p is related to the ionic character, i, and the double bond character, f, of the C-X bond by the following relations ;[6, 7)]

$$U_p = (1-s)(1-i) - f/2, \qquad (4)$$

and

$$f = (2/3)\eta U_p, \qquad (5)$$

where s is the fractional s character of the C-X bond and is assumed to be 0.15 according to the Dailey-Towns theory[8)].

The values of the bond parameters thus calculated are given in Table 4. The double bond character of the bromine atom bonded to the side chain bond is negligibly small in contrast to the case in 4-chlorobenzotrichloride ($\eta = 0.072$ for Cl at the 4-position and $\eta = 0.04$ for Cl of the CCl_3 group)[9)]. It has been suggested that in 4-chlorobenzotrichloride charge migration interaction occurs between the chlorine atoms of the -CCl group and the π system of the benzene ring[9)]. In 4-chlorobenzyl chloride ($\eta = 0.07$ for Cl at the 4-position)[10)], and 4-chlorobenzotrichloride, the double bond characters of the chlorine atoms bonded to the ring are calculated to be 3.0 percent. The C-Cl bonds in 2, 6-dichlorobenzyl bromide gain additional double bonding compared with the corresponding bonds in these chlorinated toluene derivatives.

There is no significant difference in π character for the aromatic C-Cl bond between 2, 6-dichlorobenzyl bromide and α, α, α, 2, 4-pentachlorotoluene ($\eta = 0.11$ for Cl at the 4-position and $\eta = 0.10$ for Cl at the 2-position)[11)], although the aromatic chlorine atoms are somewhat more ionic in the former than in the latter. These compounds have, in common, the two chlorine atoms situated at the meta position to each other. The halogenated methyl group appears not to play an important role in π electron distribution. The arrangement of the two chlorine atoms seems to be a dominant factor in the bond character for the in-plane C-Cl bonds, as yet not fully understood for lack of other relevant data.

Table 4. Bond Parameters

Atom	U_p	Single bond (%) character	Double bond (%) character	Ionic (%) character
Cl (1)	0.6255	66.4	4.5	29.1
Cl (2)	0.6355	65.4	4.3	30.3
Br (3)	0.6773	79.7	0	20.3

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