^{35}Cl Nuclear Quadrupole Resonance of 2,6-Dichlorobenzaldehyde

(NQR/Zeeman effect/polychlorobenzaldehyde)

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Two ^{35}Cl resonance frequecies were measured as a function of temperature ranging from 77 to 320 K for 2,6-dichlorobenzaldehyde. The frequencies of the lines were 34.974 and 35.754 MHz at 298 K. An analysis of the Zeeman effect on the lines using a single crystal revealed that the crystal belongs to the monoclinic system. The angle between the C-Cl bonds belonging to a molecule was estimated to be $128.98 \pm 0.01°$ on the basis of the directions of the efg axes. NQR parameters ($|e^2Qqh^{-1}|$ =67.82 MHz ; η=0.01) and (71.24 MHz ; 0.15) were obtained, respectively, for the lower-frequency line and the higher-frequency one. The resonance lines were assigned with the aid of semi-empirical MO calculations. The orientations of the efg axes were explained on the basis of intramolecular interaction between the Cl atoms and the CHO group.

Introduction

It was previously reported that 2,6-dichlorobenzylbromide gave two widely split NQR lines irrespective of the highly symmetrical molecular structure.[1] The splitting of the absorption line was revealed as arising from intermolecular intraction on the basis of the Zeeman experiment.[1] In the present study, 2,6-dichlorobenzaldehyde (DCBA) was chosen as the target compound out of the derivatives of 2,6-dichlorobensene. It is presumed that there are two kinds of intramolecular interactions in DCBA, $i.e.$, van der Waals repulsion between one of the Cl atoms and the O atom of the aldehyde group and weak hydrogen bonding between another Cl atom and the aldehyde H atom. This compound is therefore predicted to yield two resonance lines. However, the ^{35}Cl resonances in DCBA heve not been observed yet, although the resonance frequencies were reported for such related compounds as 2,4-dichlorobenzaldehyde,

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3,4-dichlorobenzaldehyde[2] and 4-dichlorobenzaldehyde.[3] In addition, it is unfavorable for assigning the resonance lines to particular Cl atoms that the crystal structure of DCBA is unknown. Neverthelss, DCBA is an interesting compound in that the repulsive interaction between the Cl and O atoms may twist the CHO group from the benzene plane.

In order to shed light on the molecular structure and bond character of DCBA, the Zeeman effect on the NQR lines was examined using a single crystal. The NQR spectra and the directions of the electric field gradient (efg) axes were simulated by the CNDO/2[4] and INDO/S[5,6] molecular orbital calculations for the purpose of assigning the resonance lines and examining the molecular shape of DCBA.

Experimental

The compound, DCBA, was obtained commercially and was purified by recrystallizing from ethanol. A single crystal of this compound was grown from melt using the Bridgman technique. The NQR spectrometer used is described elsewhere.[7] The Zeeman effect was examined at room temperature by means of the zero-splitting cones method. The temperature dependence of the NQR frequencies was measured in the range of 77 to 320 K. The temperature was determined by means of a copper-constantan thermocouple inserted into the pit of a sample vial.

Results and Discussion

The NQR spectrum on DCBA consists of two ^{35}Cl lines in the range of 77 to 320 K. The absorption lines became broad near 310K and faded out near 320K. The resonance frequencies for DCBA are plotted as a function of temperature as shown in Fig. 1 and the frequencies at liquid nitrogen and room temperatures are listed in Table 1. The resonance lines are designated as Cl(h) and Cl(l) to the lower-frequency line and the higher-frequency one, respectively. The frequencies were monotonously decreased with a rise in temperature and no phase transition was found in the examined range. The two lines have almost the same temperature coefficients, suggesting that the temperature variation of the frequency depends only on the torsional motions of the whole molecule. Under the constant rf field, the line intensities decreased with lowering temperature and were completely sarurated at 77 K, where they could be detected under about half the rf intensity at room temperature. The relaxation

time is, therefore, rapidly prolonged with lowering temperature.

Table 1. NQR Parameters for 2,6-Dichlorobenzaldehyde at 298 K

Line	Frequency/MHz		e^2Qqh^{-1}/MHz	η
	77 K	298 K		
Cl(l)	35.490	34.974	69.816	0.106±0.001
Cl(h)	36.273	35.754	71.242	0.150±0.001

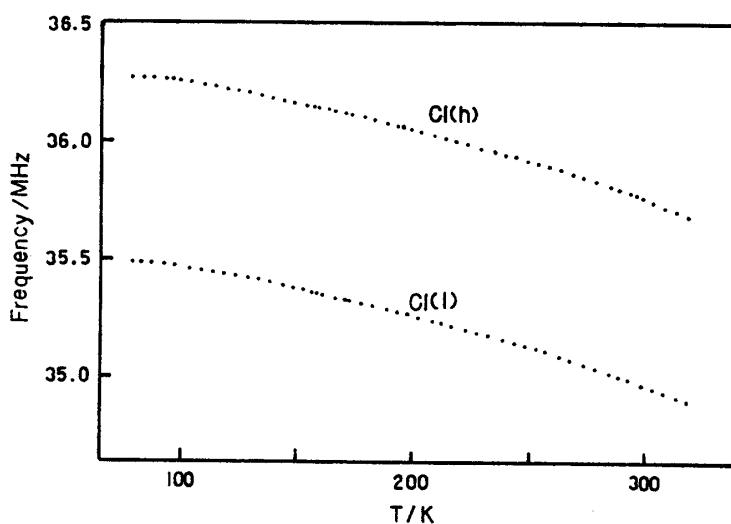Fig. 1. Temperature dependence of the ^{35}Cl resonance frequencies in 2,6-dichloroenzaldehyde.

The zero-splitting patterns on the ^{35}Cl lines in DCBA and the directions of the efg axes are illustrated in Fig. 2. Each line gave two patterns, suggesting that a crystal of DCBA belongs to the monoclinic system.[8] From the distribution of these patterns, a twofold axis (C$_2$) was determined. The efg axes with the subscript, h or l, belong to the Cl(h) and Cl(l) lines, respectively, while the subcript a or b indicates that each Cl atom is situated in a different crystal site.

The NQR parameters determined from the Zeeman analysis are listed in Table 1. The Zeeman lines were analyzed by the least squares method using Dean's relation.[9] Each Cl atom has a compatatively large asymmetry parameter (η) and it is noted that the η-value for the Cl(h)
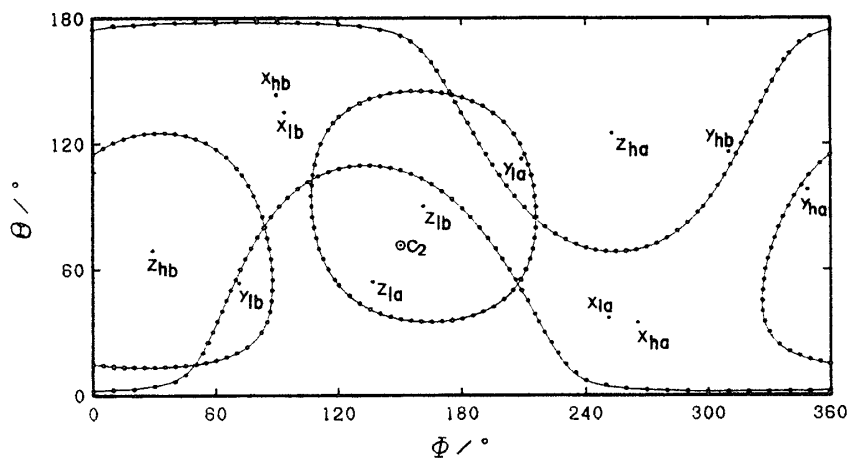
Fig. 2.   Zero-splitting   patterns   on   the   [35] Cl   resonance   lines   in   2,6-dichlorobenzaldehyde.

line   is   5   percent   greater   than   that   for   the   Cl(1)   line.

The   angles   between   the   efg   axes   are   summarized   in   Table   2.   Assuming   that   the   direction   of   the   efg   z   axis   is   parallel   to   the   C–Cl   bond,   the   angle   between   the   two   C–Cl   bonds   calculated   in   the   case   of   each   molecule   is   found   to   be $128.98° \pm 0.01°$,   as   there   are   two   chlorine   atoms   in   a   molecule   with   two   C–Cl   bonds   oriented   at   an   approximate $120°$ to   each   other.   The   calculated   angle   considerably   greater   than $120°$ presumably   results   from   steric   hindrance   between   the   Cl   atoms   and   the   CHO   group.   Unless   the   CHO   plane   is   perpendicular   to   the   ring   plane,   the   Cl   atom   at   the   2-position   is   nonequivalent   to   the   one   at   the   6-position,   because   it   is   presumed   that   one   of   the   Cl   atoms   interacts   repulsively   with   the   O   atom   of   the   CHO   group   and   anothor   attractively   with   the   aldehyde   H   atom.   The   orientation   of   the   aldehyde   group   is,   therefore,   considered   to   affect   significantly   the   bond   character   of   the   C–Cl   bonds.

Interesting   features   of   the   orientations   of   the   x   and   y   axes   are   seen   in   Table   2.   The   maganitude   of   the   discrepancy   in   the   orientation   of   the   x   axes   belonging   to   a   molecule   is   estimated   to   be $8.64° \pm 0.08°$.   In   determining   the   molecular   plane   it   is   convenient   to   assume   that   the z_l and z_h axes   in   the   bond   directions   are   coplanar   to   the   ring   plane.   The   orientations   of   the   x   and   y   axes   with   respect   to   the   molecular   plane   are   given   in   Table   3.   Here   we   can   see   that   they   axes   make   fairly   large   angles   of   about $10°$ with   the   ring   plane   which   are   far   beyond   experimeatal   error.

Table 2. Angles ($/°$) between the efg Axes in 2.6-Dichlorobenzaldehyde

(a) Angles between the z axes

axis	Z_{la}	Z_{lb}	Z_{ha}
Z_{lb}	42.75 (137.25)		
Z_{ha}	128.99 (51.01)	91.08 (88.92)	
Z_{hb}	91.06 (88.94)	128.97 (51.03)	139.30 (40.70)

(b) Angles between the x axes

axis	X_{la}	X_{lb}	X_{ha}
X_{lb}	16.61 (163.39)		
X_{ha}	8.52 (51.01)	169.59 (11.41)	
X_{hb}	168.94 (11.06)	8.75 (171.25)	176.89 (3.11)

(c) Angles between the y axes

axis	Y_{la}	Y_{lb}	Y_{ha}
Y_{lb}	140.90 (39.10)		
Y_{ha}	129.79 (50.21)	89.27 (90.73)	
Y_{hb}	89.25 (90.75)	129.81 (50.19)	40.83 (139.17)

a) The value in parentheses represents the supplemetary angle.

Table 3. Orientations ($/°$) of the efg x and y axes with respect to the ring plane.

Plane	X_l	X_h	Y_l	Y_h
$Z_l Z_h$	80.57 ± 0.07	79.49 ± 0.16	9.5 ± 0.07	10.51 ± 0.16

The main cause of these inclinations is probably intramolecular interaction between the Cl atoms and the nearest CHO group. A twist of the CHO group around the C–C bond appears to change the directions of the x and y axes.   To solve this problem,   the dependence of the

orientations of the x and y axes on the twist angle of the CHO group was analyzed with the approximate molecular orbital theories.[4-7] The results are shown in Fig. 3. The field gradients were determined by the method devised by Sichel and Whitehead.[10] Since the molecular geometry of DCBA in unknown, geometrical parameters were assumed by reference to related compounds. The dimensions used are r_{CC}=2.6154a.u., r_{CH}=2.0409a.u., r_{CCl}=3.2882a.u,. and $\angle$CCC=120° for the benzene ring and r_{CH}=2.1543a.u., r_{CO}=2.2866a.u., r_{CC}=2.7968a.u., $\angle$CCO=123.3° and $\angle$CCH=144° for the aldehyde group. The experimental value was used for the angle between the C-Cl bonds.
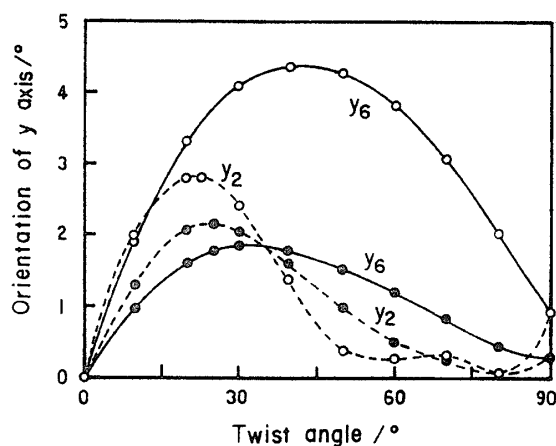

Fig. 3. Dependence of the orientation of the efg y axis with respect to the ring plane on the twist angle of the CHO group. The open and shaded circles correspond to the INDO/S and CNDO/2 calculations, respectively.

The Cl atom on the side of the O atom in the aldehyde group is assumed to be situated in the 2-position and another in the 6-position. The y axes on these Cl atoms are referred to as y_2 and y_6, corresponding to the position of each Cl atom. The calculated orientations of the y axes do not quantitaively reproduce the experimental ones and in particular, concerning the y axis at the 6-position, the curve calculated by the INDO/S method is considerably different from that calculated by the CNDO/2 method. The INDO/S that calculated by the CNDO/2 method.

The INDO/S approximation appears to overestimate the interaction between the H and Cl atoms.

In angles of less than 25°, however, the curves calculated by the different methods behave qualitatively in similar manners. The y axis at the 2-position is roughly parallel to the Cl···O direction, whereas the one at the 6-position orients in such a way that the relation between the H ···Cl and the y axis is just like that the incident and reflected light beams on the ring plane. These orientations of the y axes are very similar to the experimental ones, as can be seen from the detailed examination of the angle between the axes in Table 1 and Table 3.

As can be understood from Fig. 3, the short-range repulsion makes the y axis at the 2-position out-of-plane. By contrast, the relatively long-range attraction due to weak hydrogen bonding between the Cl atom and the aldehyde H atom makes the y axis at the 6-position out-of-plane. These different interactions cause the charge distribution around the individual Cl atom to be distorded in a different manner, so that the y axes at the two sites are different in direction. A predominant factor determining the directions of the x and y axes is conjugation between the Cl atom and the aromatic $p\pi$ system in any chlorinated benzene derivative. In DCBA, a second factor appears to be intramolecular interaction between the CHO group and the Cl atoms.

Table 4. Comparison of the calculated NQR parameters with the experimental ones.

Atom	Method	Frequency/MHZz	η	Population [a]	
				Nz	Nx
Cl (2)	CNDO/2	39.34	0.048	1.267	1.972
	INDO/3	36.32	0.040	1.328	1.981
	Experimental	36.27	0.150	1.318	1.935
Cl (6)	CNDO/2	38.75	0.045	1.278	1.974
	INDO/5	35.83	0.035	1.337	1.982
	Experimental	35.49	0.106	1.324	1.955

a) Nz and Nx are the electronic population of the p_z and p_x orbitals. respectively. The experimental values were determined according to the Townes-Dailey theory (Ref. 11).

The resonance lines cannot be unequivocally assigned to particular Cl atoms on the basis of the Zeeman effect. The MO calculation serves as a useful tool for the assignment. The NQR parameters can be estimated from the calculations on the field gradient as described above. The results are listed in Table 4. Here the calculations are based on the structure having a twist angle of $10°$, because the parmeters were not so dependent on the twist angle of the CHO group in the small angle region and because the more twisted structure is disadvantageous for conjugation between the CHO group and the benzene ring.

The INDO/S theory gives fairly good predictions of the frequencies, whereas the asymmetry parameters are not satisfactorily predicted. The frequencies calculated by the CNDO method are too high compared with the experimental ones. In either calculation, however, the Cl atom bonded to the 1-position yields the higher frequency and a greater asymmetry parameter than anothor atom. Thus the higher-frequency line is assigned to the Cl atom adjacent to the O atom and the lower-frequency line to the one adjacent to the aldehyde H atom. Furthermore, the phenomenon that the steric repulsion between the adjacent Cl atoms enlarges the asymmetry parameters for the related Cl atoms is also seen in the compounds such as 1,2,4,5-tetrachlorabenzene[12] and 2,3,5,6-tetrachloronitrobezene[13] and supports these findings. The bond characters were calculated by the method suggested by Kojima, et al.[14] The single bond, ionic and double bond characters are in the ratio 73.0:23.1:3.9 for the Cl(1) atom and 73.7:20.7:5.6 for the Cl(h) atom.

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