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Nuclear Quadrupole Resonance of 2,5-Dichlorophenol and 2,6-Dichlorophenol

(NQR/Zeeman/chlorophenol)

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Zeeman effect studies of ^{35}Cl nuclear quadrupole resonance were carried out at room temperature in single crystals of 2, 5-dichlorophenol and 2, 6-dichlorophenol. In 2, 5-dichlorophenol two physically nonequivalent field gradients for each chlorine atom were found. The asymmetry parameters for the two chlorine atoms were 0.072 ± 0.002 and 0.080 ± 0.002 for the lower and the higher resonance lines, respectively. In 2, 6-dichlorophenol, four nonequivalent field gradients were found for each chlorine atom in the 2 and 6 positions. The crystal was identified as belonging to an orthorhombic system. The asymmetry parameters were 0.071 ± 0.001 and 0.075 ± 0.001, respectively, for the two chlorine atoms corresponding to the lower and higher resonance lines. It was revealed that in 2, 6-dichlorophenol the molecule is somewhat puckered. The bond characters of the C—Cl bonds were estimated using experimental asymmetry parameters.

INTRODUCTION

Zeeman effect studies of the nuclear quadrupole resonance (NQR) in a single crystal provide information concerning the crystal structure, the orientation of the electric field gradient (*efg*) tensor and the asymmetry parameter. The bond characters between the resonating nucleus and its neighboring atoms are estimated from NQR parameters. For the nuclei of spin 2/3, a study of

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the Zeeman effect of NQR is particularly necessary for finding the asymmetry parameter of the *efg*.

The bond character and information concerning steric distortions in polychlorinated aromatic compounds is often found to be of interest. The resonance frequencies for 2, 5-dichlorophenol[1)] and 2, 6-dichlorophenol[1-3)] have already been reported, and it was shown that the hydrogen bond between the hydroxy group and the *ortho* chlorine atom lowers the resonance frequency for the *ortho* chlorine atom.[1)]

In the present paper, some structural data are obtained for the above dichlorophenols and are compared with those of X-ray analysis on 2, 6-dichlorophenol. The bond characters are discussed on the basis of the hydrogen bond.

EXPERIMENTAL

The NQR signals were detected by means of a home-made Dean type Spectrometer.[4)] The frequencies were determined with a VHF signal generator, NJM-501C, from Japan Radio Co. Ltd. and a frequency counter, TR-5142G, from Takeda Riken Industry Co. Ltd. The Zeeman effect was examined by means of the zero-splitting cone method used in a low magnetic field. The magnetic field of about 200 G was applied by means of a Helmholtz coil, and the patterns of the zero-splitting loci were determined at room temperature.

The samples of 2, 5-dichlorophenol and 2, 6-dichlorophenol were purchased from Nakarai Chemical Industry Co. Ltd. The single crystal was grown employing the Bridgman-Stockbarger method.

RESULTS AND DISCUSSION

Each of 2, 5-dichlorophenol and 2, 6-dichlorophenol has two resonance lines,[1-3)] as is shown in Table I. The doublet lines in

TABLE I. *NQR Parameters for Dichlorophenols at Room Temperature*

Compound	$\nu^{a)}$, MHz	η, %	e^2Qq_{zz}, MHz
2, 5-$Cl_2C_6H_3OH$	34.664	7.2±0.2	69.278
	35.303	8.0±0.2	70.501
2, 6-$Cl_2C_6H_3OH$	34.723	7.1±0.1	69.504
	35.441	7.5±0.1	70.948

a) The frequency at 24°C

each compound are designated as ν_1 and ν_2, respectively, for the lower and the higher resonance lines, and the chlorine atoms contributing to ν_1 and ν_2, as Cl_1 and Cl_2, respectively.

The patterns of the zero-splitting were obtained from the Zeeman effect on the resonance lines at room temperature and are shown in Figs. 1 and 2. Here, z_{iA} and z_{iB} indicate the directions of the z axes of the field gradients at the chlorine atom showing ν_i resonance line. The loci were analyzed by the method of least squares using the following relation,$^{5)}$

$$\sin^2\theta = 2/(3-\eta\cos 2\phi), \tag{1}$$

where θ and ϕ are the polar and azimuthal angles of the Zeeman magnetic field with respect to the coordinates of the principal axes (x, y and z) of the field gradient tensor at the resonating nucleus. The asymmetry parameter, η, was determined at the same time. Consequently, the quadrupole coupling constant, e^2Qq_{zz}/h, of the ^{35}Cl atom was calculated using

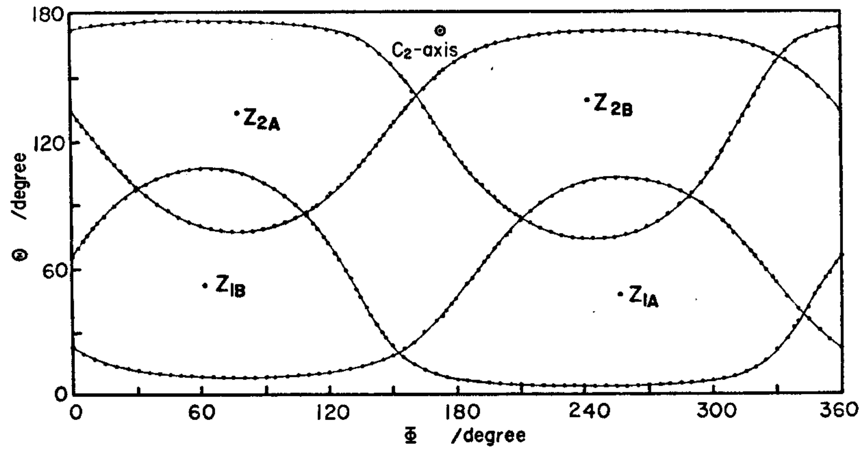

Fig. 1. Zero-splitting patterns of the Zeeman lines of 2, 5-dichlorophenol. θ and ϕ are polar and azimuthal angles, respectively, in the coordinates fixed to the sample.

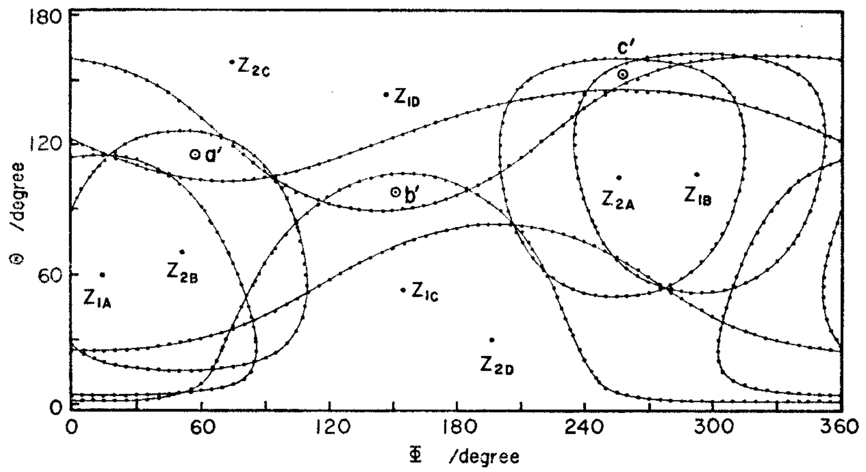

Fig. 2. Zero-splitting patterns of the Zeeman lines of 2, 6-dichlorophenol. θ and ϕ are polar and azimuthal angles, respectively, in the coordinates fixed to the sample.

$$h\nu=(e^2Qq_{zz}/2)\,(1+\eta^2/3)^{1/2}, \qquad (2)$$

where ν is the NQR frequecy. The values of η and e^2Qq_{zz}/h derived in this way are listed in Table I.

The angles between the C-Cl bonds can be calculated by assuming that the z-axis of the *efg* of chlorine is parallel to the C-Cl bond. The results thus obtained are listed in Table II.

TABLE II. *Angles between the Principal Axes and the b-Axis in* 2, 5-*Dichlorophenol*

	z_1-z_2	z_1-b	z_2-b	x_1-x_2	y_1-y_2
NQR	179°18′±1′	130°55′±1′	48°26′±1′	7°36′±12′	172°24′±12′
X-ray[a)]	178.8°	128.9°	49.0°	—	—

a) These values were calculated from the atomic positions of the crystal. (Ref. 6).

2, 5-Dichlorophenol. Two zero-splitting patterns were determined, as shown in Fig. 1. According to the crystal structure of 2, 5-dichlorophenol as determined by X-ray analysis,[6)] the space group is $P2_1/m$. Therefore, the two-fold axis obtained from the Zeeman patterns corresponds to the b axis of the crystal. The angles between the C-Cl bonds and those between the crystal axis and the C-Cl bonds which were calculated from the atomic positions of the crystal are listed in Table II. The results obtained from the NQR are in good agreement with those of the X-ray study. The value of the angle between the y-axes indicates a negligible deviation from planarity of the C–Cl bond vectors. This is in accordance with the results of the X-ray analysis. Therefore, the x-axis of either of the chlorine atoms is twisted about the C–Cl bond axis by 7.6°. The disagreement of the direction between the two x-axis perhaps results from the intermolecular interaction.

Unambiguous assignment of the resonance lines is difficult to make from the angles alone, since the two C–Cl bond vectors form a nearly straight line. Therefore, the assignment of the resonance lines must rely on chemical considerations. Pies and Weiss[1,7] have previouly associated the lower line with the *ortho*

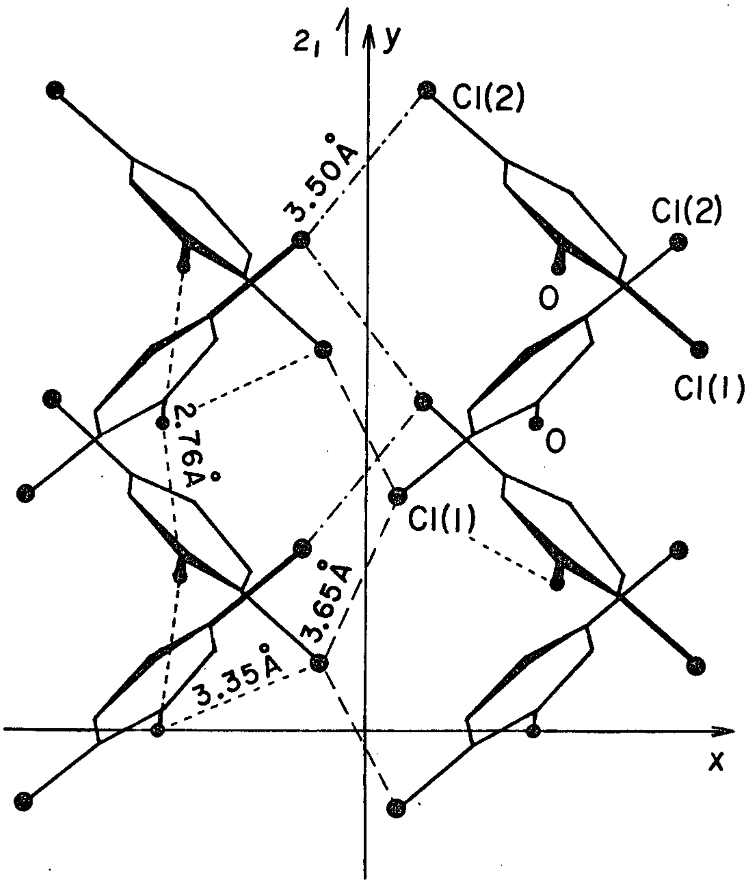

Fig. 3. The crystal structure of 2, 5-dichlorophenol projected onto the ab plane.

chlorine atom by assuming the hydrogen bond between the *ortho* chlorine atom and the hydroxy group.

The intermolecular O...O distance in 2, 5-dichlorophenol⁶⁾ is 2.76 Å which is about 0.2 Å less than the corresponding distances in pentachlorophenol⁸⁾ and tetrachlorohydroquinone.⁹⁾ The hydrogen-bonded Cl...O distances in pentachlorophenol and tetrachlorohydroquinone are 3.28 Å and 3.29 Å respectively. On the other hand, in 2, 5-dichlorophenol the intermolecular atomic distance between the *ortho* chlorine and oxygen atoms is 3.35 Å which is greater than the normal van der Waals approach. However, this distance is comparable to the hydrogen-bonded Cl...O distances in $HICl_4 \cdot 4H_2O$ (3.35 Å)¹⁰⁾ and $HAuCl_4 \cdot 4H_2O$ (3.35 Å).¹¹⁾ The *meta* chlorine atom is at a great distance from the oxygen atoms. This indicates that a weak bifurcated hydrogen bond $\mathrm{O{-}H}\langle{}^{\mathrm{O}}_{\mathrm{Cl}}$ is formed in 2, 5-dichlorophenol as well as in pentachlorophenol⁸⁾ and tetrachlorohydroquinone,⁹⁾ though Bavoux and Perrin⁶⁾ did not mention the matter. It was shown that the NQR frequency of chlorine is decreased by hydrogen bonding.⁸⁾ Consequently, the lower frequency line is assigned to the *ortho* chlorine atom and the higher to the *meta* chlorine atom.

2, 6-*Dichlorophenol.* The crystal structure of 2, 6-dichlorophenol appears not to be known. Four zero-splitting loci were obtained for each of the resonance lines, as shown in Fig. 2. From these data, it follows that there are four nonequivalent C–Cl directions for each chlorine atom. The directions of three mutually perpendicular two-fold axes were easily determined from the distributions of the z-axis. Therefore, the crystal of this compound belongs to an orthorhombic system.¹²⁾ The calculated angles between the C–Cl bonds within a molecule are listed in Table III, along with those between the crystal axes and the C–Cl

TABLE III. *The Angles between the Principal Axes and the Crystal Axes in 2, 6-Dichlorophenol*

z_1-z_2	x_1-x_2	y_1-y_2
120°59′±1′	5°24′±24′	120°43′±3′

	Crystal axes		
	a′	b′	c′
z_1	77°30′±1′	44°54′±1′	47°51′±1′
z_2	45°32′±1′	69°22′±1′	51°38′±1′

bonds. This value is in accordance with expectations based on molecular shape. In the crystal, each plane of the benzene rings of four molecules orients at the angles 90.34±0.01°, 96.13±0.01° and 152.53±0.04°. The x_1-axis is not parallel to the x_2-axis. The angle between the yz plane of one side and the z-axis of the other side is calculated to be 2.6±0.5°. Assuming that one of the two C–Cl bonds lies in the plane of the benzene ring, the other bond is out of the plane. Such a deviation from planarity was observed in 2, 6-dichloro-4-nitroaniline.[13)]

The lower frequency line was assigned to the chlorine atom which is connected by hydrogen bond to the hydroxy group.[1,7)] Babushkhina *et al.*[3)] demonstrated that the hydrogen bond decreases the resonance frequency to the *ortho* chlorine atom associated with the hydrogen bond in the 2, 6-dichloro-X-substituted phenols. This assignment is supported from hydrogen-deuterium isotope effects in 2, 4, 6-trichlorophenol.[1)] Accordingly, a later discussion is based on this assignment.

Bond Character. The number of the umbalanced p electrons, U_p, is given by the followlng relation :

$$U_p = e^2Qq_{zz}/e^2Oq_{atom}\,, \qquad (3)$$

where e^2Qq_{atom}/h is the atomic quadrupole coupling constant, which is 109.74 MHz for ^{35}Cl. The relation between the bond characters and U_p is given by the following equations :

$$U_p=[(1-s)(1-i-f)-f/2],^{14)} \tag{4}$$

$$f=\frac{2}{3}U_p\eta, \tag{5}$$

where i is the ionic character, s is the fractional s character of the sigma bonding orbital—assumed to 0.15 in accordance with Dailey and Townes[15)]—, and f is the double bond character. The bond characters obtained by using these relations are given in Table IV.

TABLE IV. *Bond Parameters*

Compound	U_p	i, %	f, %
2, 5-$Cl_2C_6H_3OH$	0.6310	21.0	3.0
	0.6423	19.0	3.4
2, 6-$Cl_2C_6H_3OH$	0.6324	20.9	3.0
	0.6459	18.9	3.2

In *p*-chlorophnol[16,17)] the chlorine atom hydrogen-bonded to the hydroxy group of a neighboring molecule has a very high value of η compared with the chlorine atom not affected by the hydrogen bond. In pentachlorophenol, on the contrary, η for the hydrogen-bonded chlorine atom is much lower than those for the other chlorine atoms.[8)] These are in contrast to the case of 2, 6-dichlorophenol. In this compound the double bond character is mostly uninfluenced by hydrogen bonding, although the C–Cl_1 bond is somewhat more ionic than the C–Cl_2 bond. This means that few charges transfer from the chlorine atom to the hydroxy group, since the apparent double bond character is changed if a part of $3p_x$ or $3p_y$ electrons of chlorine is transferred.

Assuming a point-charge model, the perturbations due to the hydrogen bond can be calculated. The contribution to the field gradient of a point charge is

$$q=e(3\cos^2\theta-1)/r^3, \quad (6)$$

where θ is the angle between the z-axis and the point charge, e, and r is the distance between the resonating nucleus and the point charge. Equation (6) indicates that the positive charge of the proton contributes negatively to the *efg* if θ is in the range of 55° to 125°. Assuming a intramolecular O—H···Cl bond as well as in *o*-chlorophenol,[18] the angle between the C–Cl and H···Cl bonds is calculated at about 70° by appling the data on *o*-chlorophenol and 2, 5-dichlorophenol to 2, 6-dichlorophenol. This value satisfies the above condition. Therefore, the lowering of the NQR frequency for the hydrogen-bonded chlorine atom can be explained by the electrostatic effect rather than by the charge transfer.

2, 5-Dichlorophenol and 2, 6-dichlorophenol are alike in bond character regardless of the structural difference between them. Accordingly, the inductive and mesomeric effects which were observed in 2, 5-dichloroaniline[19] and 2, 5-dichloronitrobenzene[20] are not recognized clearly in these chlorophenols. This may result from the fact that the $C\text{–}Cl_2$ bond length substantially greater than the ordinary C–Cl bond length, 1.71 Å, in polychlorinated aromatic compounds and that the intermolecular distance is less than the sum of the van der Waals radii (3.6 Å).

REFERENCES

1) W. Pies and A. Weiss, "Advances in Nuclear Quadrupole Resonance," ed. by J. A. S. Smith, Heyden, London (1977).
2) S. L. Segal and R. G. Barnes, "Catalog of Nuclear Quadrupole Interactions and Resonance Frequencies in Solid. Part II. Halogen Resonances in Organic Compounds," U. S. Atomic Energy Commission IS-1222 (1965).
3) T. A. Babushkhina, A. P. Zhukov, L. S. Kobrina, C. K. Semin and G. G. Yakobson, *Izv. Akad. Nauk SSSR*, ser. *Khim Nauk* **5**, 93 (1969).
4) C. Dean and M. Pollak, *Rev. Sci. Instr.* **29**, 630 (1958).
5) C. Dean, *Phys. Rev.* **96**, 1053 (1954).

6) C. Bavoux and M. Perrin, *Acta Crystallogr.* **B29**, 666 (1973).
7) D. Biedenkapp and A. Weiss, *J. Chem. Phys.* **49**, 3933 (1968) ; A. Weiss, *Org. Magn. Resonance* **3**, 147 (1971).
8) T. Sakurai, *Acta Crystallogr.* **15**, 1164 (1962).
9) T. Sakurai, *Acta Crystallogr.* **15**, 443 (1962).
10) R. J. Bateman and L. R. Bateman, *J. Am. Chem. Soc.* **94**, 1130 (1972).
11) J. M. Williams and S. W. Peterson, *J. Am. Chem. Soc.* **91**, 776 (1969).
12) K. Shimomura, *J. Phys. Soc. Jpn.* **12**, 652 (1957).
13) J. L. Narayan, C. Subsrahmayasastry, P. Venkataryulu and D. Premaswarup, *Indian J. Pure Appl. Phys.* **13**, 849 (1975).
14) R. Ikeda, D. Nakamura and M. Kubo, *J. Phys. Chem.* **69**, 2101 (1965).
15) B. P. Dailey and C. H. Townes, *J. Chem. Phys.* **23**, 118 (1955).
16) C. E. Peterson and P. M. Briedenbaugh, *J. Chem. Phys.* **46**, 2644 (1967).
17) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York (1969).
18) M. Onda and I. Yamaguchi, *Bull. Chem. Soc. Jpn.* **51**, 3121 (1978).
19) D. Giardino, Thesis, University of Pittsburgh (1961).
20) N. Narajan, and C. R. K. Murty, *Cuss. Sci. India* **32**, 254 (1964).