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Zeeman Effect of NQR Lines in 2, 3, 5, 6-Tetrachloronitrobenzene

(NQR/zeeman effect/polychloronitrobenzene)

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Zeeman effect studies of ^{35}Cl NQR lines have been carried out at room temperature in a single crystal of 2, 3, 5, 6-tetrachloronitrobenzene. It was revealed that the crystal belongs to a triclinic system and contains two chemically non-equivalent molecules in the unit cell. The angles between the C—Cl bonds and the angle between the aromatic rings were determined from the directions of the efg axes. The asymmetry parameters range from 10.7 to 12.4 %. The bond characters of the C—Cl bonds were calculated from the experimental NQR parameters. The NQR lines were assigned by comparison with CNDO/2 and INDO calculations.

INTRODUCTION

A number of chlorinated aromatic compounds were studied by means of pure NQR and the Zeeman effect of the NQR lines. In most of these compounds the assignment of the NQR lines to certain chlorine atoms is comparatively easy because of the marked inductive effect. As a rule, the NQR spectra in polychloronitronitrobenzenes are spread in a comparatively narrow region.[1,2] The assignment of the resonance lines in these compounds is very difficult without the aid of information on the crystal structure. The crystal structure of 3, 4-dichloronitrobenzene alone was analyzed by X-ray diffraction,[3] so far as the auther knows.

In the compound 2, 3, 5, 6-tetrachloronitrobenzene (TCNB) eight NQR lines were observed in the range from the liquid nitrogen temperature to room temperature.[1] Needless to say, no information on the crystal structure of this compound is available. For these reasons, the NQR lines are very difficult to assign to particular chlorine atoms only by pure NQR. The Zeeman effect of ^{35}Cl NQR in a single crystal was studied in order to assign the resonance lines and clarify the C—Cl bond characters in the title compound. The assignment of the resonance lines was determined by comparison with the results of MO calculations.

EXPERIMENTAL

TCNB was obtained commercially (Tokyo Chemical Industry Co., Ltd.) and

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was recrystallized in ethanol. The single crystal of this compound was grown by the Brigdman-Stockbarger method.

The NQR spectrometer was an external-quenched Dean-type superregenerative oscillator with frequency modulation,[4] and the absorption lines were displayed on an oscilloscope. The Zeeman effect was examined at room temperature using the zero-splitting cone method.[5] A magnetic field of ca. 200 G was applied by means of a Helmholtz coil.[4]

RESULTS AND DISCUSSION

In TCNB eitht resonance lines with equal intensity were observed at room temperature, as well as at the liquid nitrogen temperature.[1] The NQR spectra are given in Fig. 1. The complicated spectra indicate that the unit cell contains at least two chemically nonequivalent molecules, since four chlorine atoms are bonded to the benzene ring.

The zero-splitting patterns for TCNB are shown in Fig. 2, where Cl_1, Cl_2, ..., Cl_8 indicate the directions of the efg z axes at the chlorine atoms con-

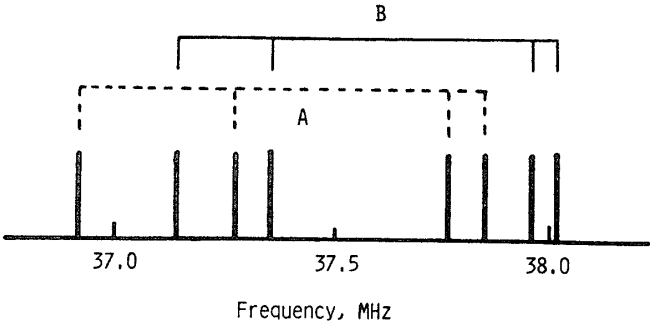

Fig. 1. NQR spectra of TCNB.

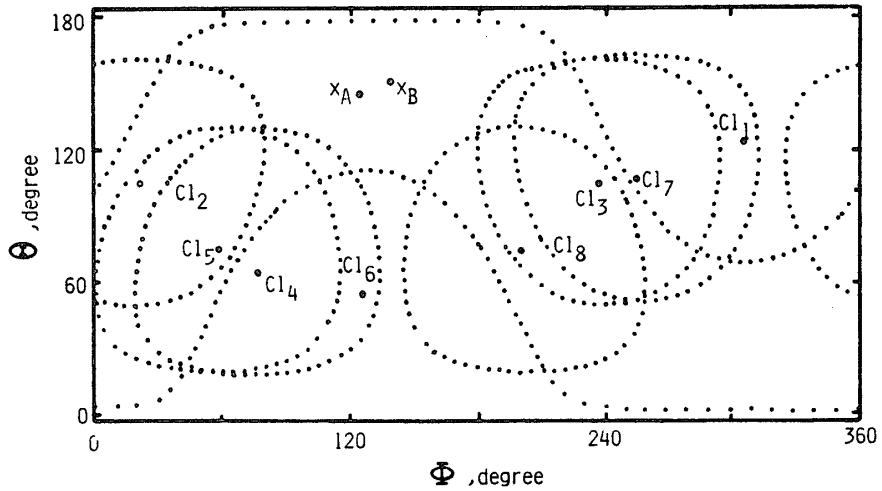

Fig. 2. Zero-splitting patterns of Zeeman lines in TCNB. The axis of $\theta=0$ is taken as the rotational axis of the sample tube. The plane of $\Phi=0$ is arbitrarily chosen.

tributing to the resonance frequency, in order from the lower to the higher. The loci observed were analyzed by the method of least squares to yield the directions of the principal efg axes and the asymmetry parameters, η. The locus is expressed for I=3/2 as follows:[5]

$$\sin^2\theta = 2/(3-\eta\cos 2\theta) \quad (1)$$

where θ and ϕ are polar and azimuthal angles, respectively. The quadrupole coupling constant, e^2Qq, may be determined from the following relation:[5]

$$\nu = (1/2)e^2Qq(1+\eta_v/3)^{1/2}. \quad (2)$$

The NQR parameters are listed in Table I. Only one locus was found for each resonance line. From the number of the nonequivalent directions of the efg z axes the crystal belongs to a triclinic class.[6] A consideration of the directions of the x axes shows that the crystal has two structurally nonequivalent molecules in the unit cell and all the C—Cl bonds in these molecules are nonequivalent. These two molecules are tentatively termed molecule-A and molecule-B. The assignment of the resonance lines to each molecule was determined by the directions of the efg x axes. The resonance lines for the chlorine atoms belonging to molecule-A and molecule-B are indicated by the symbols A and B, respectively, in Fig. 1. The x_A and x_B in Fig. 2 indicate the average directions of the x axes at the chlorine atoms belonging to molecule-A and molecule-B, respectively. The C—Cl bonds in each molecule are coplaner within an experimental error, and hence seem to be parallel to the corresponding benzene ring.

Table I. *NQR Prameters for TCNB at 297 K*

Atom	ν, MHz	η	e^2Qq, MHz
Cl_1	36.915	0.115	73.667
Cl_2	37.167	0.116	74.182
Cl_3	37.275	0.114	74.388
Cl_4	37.365	0.112	74.529
Cl_5	37.727	0.111	75.212
Cl_6	37.849	0.107	75.575
Cl_7	37.954	0.107	75.765
Cl_8	38.007	0.124	75.820

The values of the asymmetry parameters for ^{35}Cl are comparable with those in the case of the other nitrobenzene derivatives.[3,7-9] These values are almost independent of the position of the chlorine atom with respect to the nitro group, since the correlation between the asymmetry parameter and the resonance frequency cannot be found. On the other hand, the quadrupole coupling constant is apparently correlated with the frequency. The coupling constants can be roughly divided into two groups. The value of *ca.* 75 MHz forms the boundary between the two groups.

Table II. *Angles between C—Cl Bonds in TCNB (in Degree)*

	Cl_1	Cl_2	Cl_3	Cl_4	Cl_5	Cl_6	Cl_7
Cl_2	68.91 (111.09)						
Cl_3	64.10 **(115.90)**	47.25 (132.75)					
Cl_4	43.13 (131.87)	63.24 **(116.76)**	18.55 (161.45)				
Cl_5	**63.42** (116.58)	47.89 (132.11)	0.82 (179.18)	17.74 (162.26)			
Cl_6	0.58 (179.42)	69.45 (110.55)	**63.57** (116.43)	47.57 (132.43)	62.90 **(117.10)**		
Cl_7	48.63 (131.37)	**62.55** (117.45)	17.05 (162.95)	2.15 (177.85)	16.25 (163.75)	48.08 (113.92)	
Cl_8	68.33 (111.67)	0.80 (179.20)	18.55 (161.45)	**63.87** (116.13)	48.40 (131.60)	63.83 (111.13)	63.16 **(116.84)**

Assuming that the efg z axis is parallel to the direction of the C—Cl bond axis, the angles between the C—Cl bonds were deduced and collected in Table II. No X-ray data is available for this compound, as described above. It is therefore difficult to assign the NQR lines to chlorine atoms in particular positions. Furthermore, the angles between the C—Cl bonds are *ca.* 60° (or 120°) or *ca.* 180° (or 0°) and the position of the nitro group cannot be determined on the basis of the efg data for ^{35}Cl alone. However, the resonance lines are also divided into two groups according to the coupling constants. Either of these groups can be assigned to the ortho chlorine atoms and the other to the meta chlorine atoms. Taking into this and the angles between all the C—Cl bonds into accout, the arrangement of the chlorine atoms around the benzene ring was determined, as shown in Fig. 3.

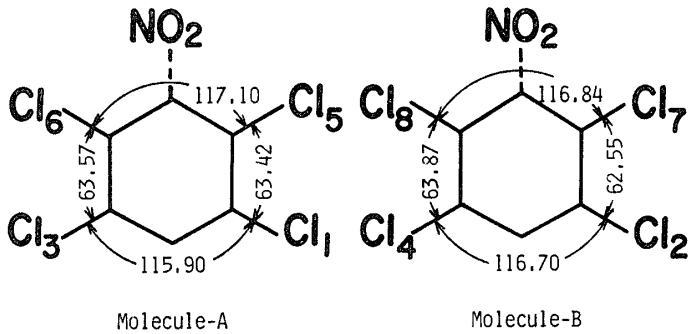

Fig. 3. The arrangement of the chlorine atoms in TCNB.

Steric repulsion by the nitro group is usually expected to enlarge the angle between the ortho chlorine C—Cl bonds, whereas such repulsion between the meta chlorine and para hydrogen atoms is relatively small. In molecule-A the resonance lines contributing to Cl_5 and Cl_6 may be assigned to the ortho chlorine atoms. In molecule-B the NQR lines cannot be assigned on the

basis of the angles alone, as can be seen in Fig. 3. The angles between the adjacent C—Cl bonds are greater than 120° and are somewhat greater than in case of 3, 4-dichlonitrobenzene.[3] This suggests that the repulsion between the chlorine atoms is more significant. The resonance lines must be assigned not on the basis of the bond angles, but on the basis of the bond characters. The bond characters obtained from the experimental NQR parameters are listed in Table III. These values were calculated using the Dailey-Townes method,[5] assuming that the fractional s character of the chlorine atom is 0.15 as has been done by others.

Table III. *Bond Parameters*

Atom	$(e^2Qq)_{obs}/(e^2Qq)_{atom}$	i, %	f, %	Net charge
Cl_1	0.671	18.7	4.5	−0.142
Cl_2	0.676	18.1	4.5	−0.136
Cl_3	0.678	17.9	4.5	−0.134
Cl_4	0.679	17.7	4.8	−0.129
Cl_5	0.687	16.9	4.4	−0.125
Cl_6	0.689	16.7	4.4	−0.125
Cl_7	0.691	16.5	4.3	−0.122
Cl_8	0.692	16.0	5.0	−0.110

Calculations of CNDO/2 and INDO[10] were carried out in order to examine the assignment of the resonance lines. The method of MINDO/3 achieved great success in quantitative calculations for nitrogen compounds.[11] This method is inapplicable to TCNB, since combinations of parameters for third period elements are limited. For this reason, the above methods were applied to TCNB, and accordingly a discussion of the bond character is qualitative. In the MO calculations the framework of nitrobenzene[12] was assumed for TCNB with C−Cl = 1.74 Å and C−H = 1.08 Å. The results are listed in Table IV.

Table IV. *Bond Character Based on MO calculations*

Position	CNDO/2			INDO		
	i, %	f, %	Net charge	i, %	f, %	Net charge
ortho	8.4	3.1	−0.05	4.4	4.4	0
meta	14.0	2.6	−0.11	9.1	3.7	−0.05

The dependence of the double-bond character (f) on the position of the chlorine atom with respect to the nitro group is not so remarkable, whereas the ionic character (i) is appreciably affected by the position of the chlorine atom. The ortho chlorine atoms are less ionic than the meta ones. The NQR lines in the higher frequency group are assumed to be assigned to the ortho chlorine atoms by comparison of the results of NQR with those of the

MO calculation, though the ionic character obtained from NQR is much greater than from the MO calculations. This discrepancy is ascribable to the crystal field effect in NQR[13] and problems of parametrizations for the semi-empirical MO calculations.

For chlorinated derivatives of benzene it has been pointed out that the influence of a substituent to the resonance frequency of a particular chlorine atom is expressed by a substituent parameter (κ_i)[14]

$$\nu = \nu_0 + \Sigma\kappa_i \tag{3}$$

According to this expression, the difference in frequency between the ortho and meta chlorine atoms is determined only by the nitro group, since the influence of the chlorine atoms as substituents is compensated for by one another. It follows for the nitro group that κ (ortho) $>$ κ (meta).[15] It is therefore presumed that the ortho chlorine atoms have higher resonance frequencies than the meta chlorine atoms. In 2, 5-dichloronitrobenzene the higher frequency line was assigned to the meta chlorine atom.[9] These suggest that the above assignment is plausible.

The molecular planes were determined from the x and z axes of the efg tensor. The aromatic rings of molecule-A and molecule-B are inclined at an angle of $7.8\pm0.8°$ to each other. Assuming that the nitro group lies on the bisector of the two ortho or meta C—Cl bonds, the angle between the C—N bonds of molecule-A and molecule-B is calculated to be $48.2\pm0.2°$. This value shows that Cl_1, Cl_3, Cl_5, and Cl_6 in molecule-A correspond to Cl_4, Cl_2, Cl_8, and Cl_7, respectively, in molecule-B (see Table II). This suggests that the resonance lines or the coupling constants are well grouped and the assignment on the basis of the bond character is reasonable.

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