

^{35}Cl NQR in 2, 4, 6-Trichloronitrobenzene

(NQR/Zeeman effect/polychloronitrobenzene)

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2, 4, 6-Trichloronitrobenzene (TCNB) was examined by means of ^{35}Cl NQR, and two modifications (α - and β -forms) were found. In the α -form two resonance lines were observed at room temperature and 77 K, and in the β -form two resonance lines were also found. The lower frequency and the higher frequency lines in each of the modifications were assigned to the chlorine atoms at the para- and ortho-positions, respectively. Zeeman study of ^{35}Cl NQR lines was carried out at room temperature in a single crystal of β -TCNB. It was revealed that the crystal of β -TCNB belongs to a tetragonal system with D_{2d} or D_{4h} symmetry. The angles between the C—Cl bonds and the angles between the plane of the benzene ring and the crystal planes were determined on the basis of the directions of the principal efg axes. The values of the quadrupole coupling constants and the asymmetry parameters were determined. The bond characters of the C—Cl bonds were calculated from the NQR parameters.

INTRODUCTION

The crystal structures of a few dichloronitrobenzenes were determined by X-ray diffraction.^{1,2)} In most polychloronitrobenzenes, however, the crystal and molecular structures are not established in detail. The Zeeman effect of NQR on single crystals of chlorinated nitrobenzenes has given useful information on the crystal structures and the bond characters.¹⁻⁴⁾ 2, 4, 6-Trichloronitrobenzene (TCNB) gives two resonance lines with the intensity ratio of 1:2 at room temperature and at liquid nitrogen temperature. At room temperature the NQR spectrum of a recrystallized sample was different from that of a single crystal grown from melt. This suggests that there are at least two modifications in the crystal and that a phase transition of some type occurs between room temperature and melting point. This was verified by examining temperature dependence of the resonance frequencies.

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No information on the crystal structures of TCNB is available. The Zeeman effect of ^{35}Cl NQR lines was investigated to obtain information on the crystal structure of β -TCNB and to clarify bond characters of the C—Cl bonds. The angles between the C—Cl bonds were determined from the directions of the efg axes on the chlorine atoms. The orientation of the efg x axis at the chlorine atom and the bond characters were discussed by comparison with the results of a semiempirical SCF-MO calculation.

EXPERIMENTAL

TCNB was obtained commercially (Tokyo Chemical Industry Co., Ltd.) and was recrystallized in ethanol. A single crystal of this compound was grown from the melt by Bridgman's method. The sample container was Pyrex glass tube with 14.5 mm inner diameter.

A Dean-type superregenerative spectrometer with frequency modulation was used for detecting the NQR lines. The absorption line was observed on an oscilloscope. The resonance frequencies were determined with a VHF signal generator, NJM-501, from Japan Radio Co., Ltd. and a frequency counter, TR-5142, from Takeda Riken Co. Ltd. The Zeeman effect was examined at room temperature using the zero-splitting cones method. The Zeeman field was supplied by means of a Helmholtz coil. Temperature was determined by use of a copper-constantan thermocouple.

RESULTS AND DISCUSSION

The sample recrystallized from ethanol (sample-1) gave two absorption lines at room temperature and at liquid nitrogen temperature. These resonance frequencies were 35.82 and 37.21 MHz, with an intensity ratio of 1:2, at room temperature. In the single crystal of TCNB grown from the melt (sample-2) two resonance lines were also observed at room temperature. The relative intensity of the higher frequency to the lower frequency line is 2 or above. The spectrum of sample-1, however, differs from that of sample-2 in resonance frequency. A week after completion of crystal growth sample-2 suddenly changed opaque and gave the same spectrum as sample-1. This fact appears to correspond to a phase transition between room temperature and melting point. This was confirmed by examining temperature variations of the resonance frequencies. The results are shown in Fig. 1. It can be seen from this figure that a first order phase transition occurs at 51°C.

The low temperature (sample-1) and the high temperature phases (sample-2) are tentatively termed α -form and β -form, respectively. In each of the

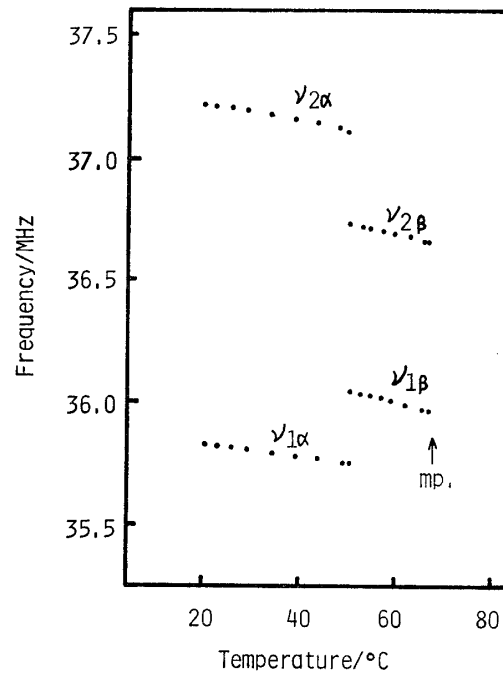


Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in TCBN.

two phases the lower frequency (ν_1) and the higher frequency lines (ν_2) can be assigned to the chlorine atoms at the para- and ortho-positions, respectively, on the basis of the intensity ratio. The two chlorine atoms at the ortho-positions are chemically equivalent. It is apparent from the NQR spectra of the two modifications of TCNB that there are considerable differences in bond character between the chlorine atoms at the ortho- and para-positions. The spectra, however, suggest that the crystal field affects considerably the resonance frequencies. Therefore, this crystal field effect veils a slight difference in bond character.

The Zeeman effect on the ^{35}Cl nucleus in β -TCNB was observed in order to obtain the orientation of the electric field gradient and the crystal axes. The zero-splitting patterns are shown in Fig. 2. The symbols Z_1 and Z_2 indicate the directions of the z axes of the electric field gradient (efg) tensors at the chlorine atoms contributing to the resonance lines ν_1 and ν_2 , respectively. Four loci were obtained for ν_1 and eight for ν_2 . This indicates that there are at least four crystal sites in a unit cell. The subscript A, B, C or D indicates that these chlorine atoms belong to the molecule situated at the different crystal sites. The observed cones were analyzed by the method of least squares to yield the directions of the principal efg tensors and the asymmetry parameters (η). The cone is expressed for ^{35}Cl nucleus as follows;⁵⁾

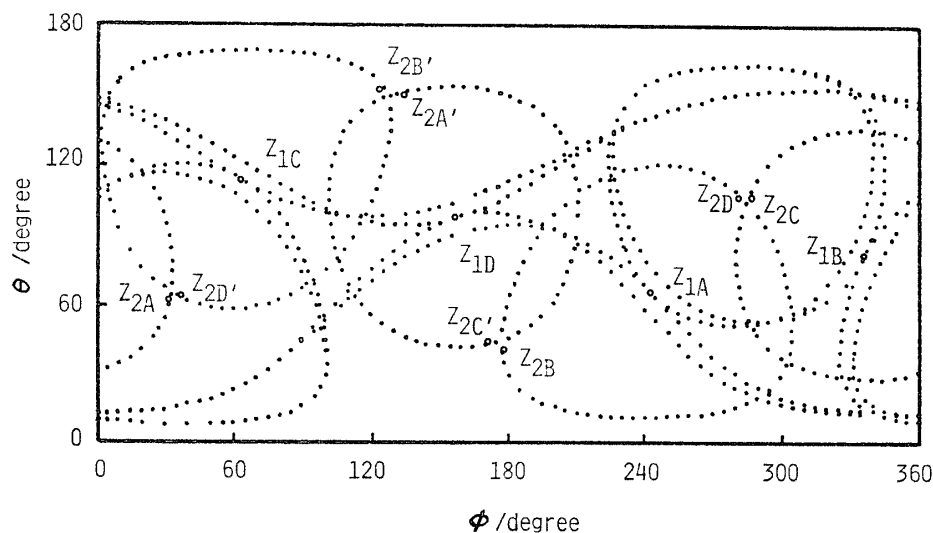


Fig. 2. Zero-splitting cones of ^{35}Cl Zeeman lines in β -TCBN. The angles θ and ϕ are given with respect to the laboratory system.

$$\sin^2\theta_0 = 2 / (3 - \eta \sin 2\phi_0) \quad (1)$$

where θ_0 and ϕ_0 are polar and azimuthal angles, respectively, with respect to the normal coordinate system. From the zero-splitting cones and the resonance frequencies in zero field the nuclear quadrupole coupling constants ($e^2Qq_{zz}h^{-1}$) are determined from the following relations ;

$$\begin{aligned} \nu &= (1/2)e^2Qq_{zz}h^{-1}(1 + \eta^2/3)^{1/2}, \\ \eta &= (q_{xx} - q_{yy})/q_{zz}, \\ |q_{xx}| &\leq |q_{yy}| \leq |q_{zz}|, \end{aligned} \quad (2)$$

where q_{ii} 's are the field gradient tensors. The calculated NQR parameters are listed in Table I. The η -values for β -TCNB are almost the same as those for 3,5-dichloronitrobenzene ($\eta = 0.11$)⁵⁾ and 2, 3, 5, 6-tetrachloro-

Table 1. ^{35}Cl NQR parameters for 2, 4, 6-trichloronitrobenzene

Line	Frequency/MHz		η	e^2Qqh^{-1}/MHz
	77 K	294 K		
α -form				
ν_1	36.248	35.823		
ν_2	37.643	37.213		
β -form				
ν_1		36.157	0.114 ± 0.001	72.161
ν_2		36.843	0.101 ± 0.002	73.570

nitrobenzene (0.11 to 0.12)⁴⁾ and are somewhat smaller than those for 2, 3-dichloronitrobenzene (0.13 and 0.15)²⁾ and 3, 4-dichloronitrobenzene (0.13 and 0.15).¹⁾ Molecular symmetry appears to affect to some extent the η -value for the chlorine atom bonded to the aromatic ring.

Crystal System. Three mutually perpendicular axes of the crystal were determined from the zero-splitting patterns. The directions of these axes are shown in Fig. 3. From the number of the non-equivalent directions

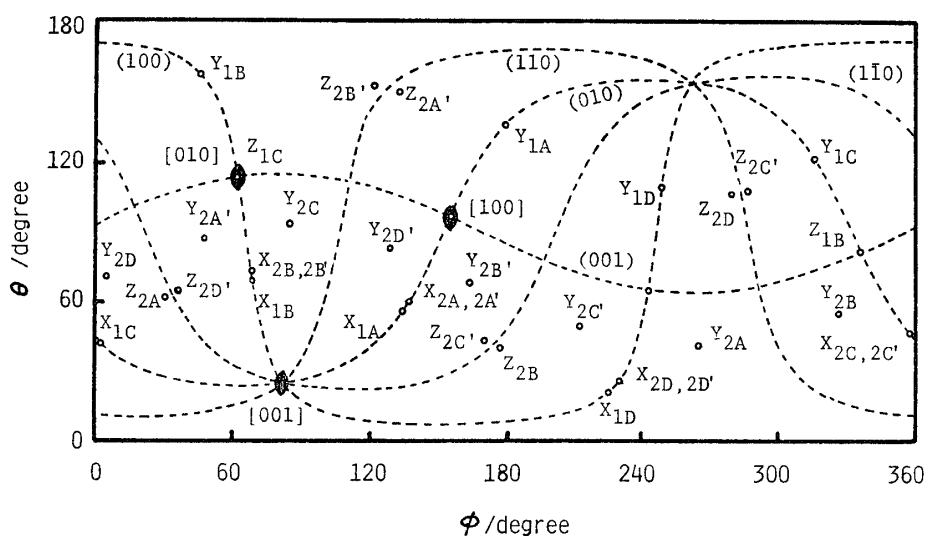


Fig. 3. Directions of the principal efg axes at the chlorine atoms in β -TCNB. The angles θ and ϕ are given with respect to the laboratory system.

the crystal belongs to a tetragonal system.⁶⁾ It is apparent from the NQR spectrum and the Zeeman patterns that each molecule in the β -phase possesses a twofold axis. The p -Cl—C bond and the twofold axis are colinear.

The twofold axes of four TCNB molecules are parallel or perpendicular to one another. These twofold axes are parallel to the crystal plane (001) and coincide in direction with the crystal axis [100] or [010]. Accordingly, the crystal possesses two mutually perpendicular twofold axes and the symmetry class is restricted to D_{2d} or D_{4h} .⁷⁾ It is impossible to determine from the NQR Zeeman effect whether the axis [001] is a twofold axis or a fourfold axis. Assuming that the axis [001] is a twofold axis, the crystal belongs to the symmetry D_{2d} . Figure 2 shows the directions of the efg axes based on this assumption. The symmetry operation due to three twofold axes and the mirror planes $(\bar{1}10)$ and (110) reproduces completely the observed directions of the efg axes.

The zero-splitting cones are indistinguishable from the those connected with the operation of inversion. If all the inverted cones are added to the

patterns in Fig. 2, the axis [001] is changed into a fourfold axis. The operation newly brings about two twofold axes [110] and $[\bar{1}10]$ and three reflection planes (100), (010) and (001). In this case the symmetry class of the crystal is D_{4h} .

Molecular Structure. The assignment of the efg z axes to the chlorine atoms are based on the directions of x axes and the angles between the z axes. The direction cosines of the principal efg axis in the molecule at one of the crystal sites are given in Table II, with respect to the crystal axes.

Table II. Direction cosines of the principal axes of the efg tensors with respect to the crystal axes system in β -TCNB

Atom	q_{ii}	λ	μ	ν
Cl _{1A}	q_{xx}	0.0003	0.7066	0.7107
	q_{yy}	-0.0004	0.7108	-0.7034
	q_{zz}	1.0000	0.0001	-0.0001
Cl _{2A}	q_{xx}	-0.0026	0.7586	0.6515
	q_{yy}	0.8674	-0.3228	0.3785
	q_{zz}	-0.4971	-0.5658	0.6579
Cl _{2A'}	q_{xx}	0.0026	0.7586	0.6515
	q_{yy}	-0.8674	-0.3228	0.3785
	q_{zz}	-0.4971	0.5658	-0.6579

Assuming that the principal z axis of the efg tensor is parallel to the direction of the C—Cl bond, the angles between the C—Cl bonds were calculated. These angles are listed in Table III. The angles between the C—Cl bonds is quite close to the angles for 2, 4, 6-trichlorobenzene (119.8, 119.9 and 120.3°).⁸⁾ The bond angles are little affected by the nitro group lying between the ortho-chlorine atoms. This suggests that repulsion of electron clouds between the nitro group and the ortho-chlorine atoms is considerably small. It is inferred that the nitro group is twisted about the

Table III. Angles between C—Cl bonds in β -TCNB (in degree)

Bond ^{a)}	C—Cl(2)	C—Cl(6)
C—Cl(6)	120.33±0.02	
C—Cl(4)	119.84±0.03	119.84±0.03

a) The numbers in parentheses indicate the positions of the chlorine atoms.

C—N bond and the two oxygen atoms are outside the ring plane, as well as 3, 4-dichloronitrobenzene¹⁾ and 2, 3-dichloronitrobenzene.²⁾

The efg axes at the ortho-chlorine atoms and that at the para-chlorine atoms are coplaner, and the x axes at the ortho-chlorine atoms are perpendicular to all the z axes within an accuracy of experimental error. It is, therefore, presumed that the three C—Cl bonds lie in the plane of the aromatic ring. The ring plane is inclined at $49.3 \pm 0.1^\circ$ to the crystal plane (001). The efg x axis at the para-chlorine atom is oriented at $85.4 \pm 0.3^\circ$ to the ring plane and at $44.7 \pm 0.3^\circ$ to the plane (001). This twist in the x axis perhaps results from the intermolecular van der Waals interaction or the intramolecular interaction with the twisted nitro group. This will be discussed below.

Bond Character. The bond characters of the C—Cl bonds obtained from the experimental NQR parameters are tabulated in Table IV. These values are estimated by the following relations;⁹⁾

$$\begin{aligned} (e^2Qq_{zz}h^{-1}) &= (e^2Qq_{zz}h^{-1})_{\text{atom}}(1-s)(1-i) - f/2, \\ f &= (2/3)(e^2Qq_{zz}h^{-1}) / (e^2Qq_{zz}h^{-1})_{\text{atom}}, \end{aligned} \quad (3)$$

where the atomic coupling constant, $(e^2Qq_{zz}h^{-1})_{\text{atom}}$, is 109.74 MHz.¹⁰⁾ s and f are fractional s character of the atomic orbital of the chlorine atom and the double bond character, respectively. s is assumed to be 0.15, following Dailey and Townes.¹¹⁾

The difference in the double bond character between the two kinds of chlorine atoms is very small, whereas the ionic character of the chlorine atom at the para-position is somewhat greater than that at the ortho-position. The difference in the bond character between the ortho- and

Table IV. Bond parameters for β -TCNB

Atom	$U_p^a)$	$i^b)$	$f^c)$	Net charge
NQR				
Cl ₄	0.6575	0.204	0.043	-0.161
Cl _{2,6}	0.7604	0.191	0.039	-0.142
MNDO ^{d)}				
Cl ₄	0.867	0.116	0.019	-0.063
Cl _{2,6}	0.900	0.073	0.023	-0.017

a) The ratio of $(e^2Qq)_{\text{obs}} / (e^2Qq)_{\text{atom}}$.

b) Ionic character

c) Double bond character.

d) The twist angle of the nitro group is assumed to be 45° .

para-chlorine atoms is therefore characterized mainly by the sigma electron densities. This was examined by a calculation of MNDO SCF-MO.¹²⁻¹⁴⁾ The MNDO calculations yield physical properties, such as heats of formation, molecular geometries and dipole moments, quite close to the experimental values. This method was applied to calculations of quadrupole coupling constants and charge densities. The NQR parameters were estimated using the method of Kaplansky and Whitehead.¹⁵⁾ The results are listed in Table IV, where the framework of nitrobenzene is assumed for TCNB with C—Cl=1.74 Å and C—H=1.08 Å.⁴⁾

The bond characters were little affected by the twist of the nitro group. The values for the twist angle of 45° are shown in Table IV. Comparison of the results of NQR with those of the MNDO calculation gave qualitative agreement, except for the double bond character. The results of NQR and MNDO indicate that there is not a significant difference in the double bond character between the ortho- and para-chlorine atoms. The value of the asymmetry parameter depends not only on the pi density but also on the intermolecular interaction. A slight difference in the double bond character cannot be discussed in detail.

The dependences of the orientation of the efg x axis and the binding energy on the twist angle of the nitro group in an isolated molecule were examined by a calculation with the MNDO method. The results are shown in Fig. 4. The direction of the x axis at the ortho-chlorine atom varies with the twist of the nitro group. The inclination of the x axis against the ring plane is minimum, when the twist angle is about 20°. If the angle for 2,3-dichloronitrobenzene (53.4°) is applied to TCNB, the twist of the x

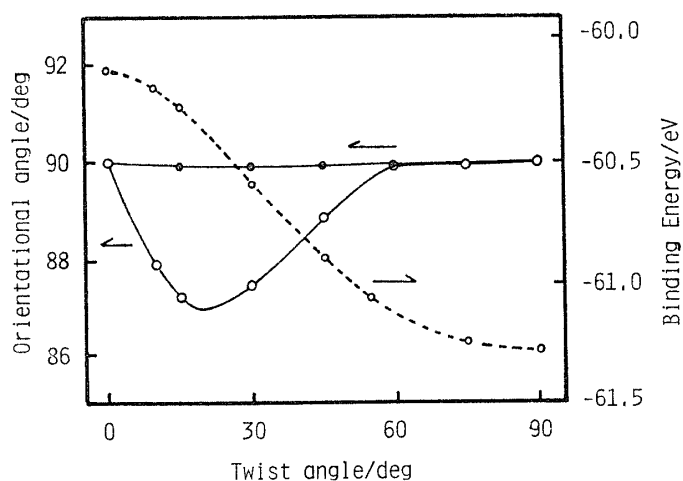


Fig. 4. Dependences of the orientation of the efg x axis and the binding energy on the twist angle of the nitro group around the N—C bond. The orientational angle of the x axis is given against the ring plane.

axis on the ortho-chlorine atom is negligibly small. On the other hand, the direction of the x axis at the para-chlorine atom is almost independent of the orientation of the nitro group. Taking into account the fact that the experimental x axes at the ortho-chlorine atoms are perpendicular to the ring plane, it may be concluded that the twist of the nitro group does not affect the orientation of the x axes at the chlorine atoms bonded to the aromatic ring. It is therefore presumed that the twist of the efg x axis at the para-chlorine atom arises not from the intramolecular interaction but from the intermolecular interaction.

Figure 4 shows that the molecule is energetically the most stable when the plane of the nitro group is perpendicular to that of the aromatic ring. This indicates that repulsion of electron clouds between the nitro group and the chlorine atoms at the ortho-position contributes more effectively to the orientation of the nitro group than delocalization of pi electrons on the nitro group. It is therefore considered that the twist angle of the nitro group about the N—C bond is determined by the competition of steric hindrance between the nitro group and the two chlorine atoms at the ortho-positions and the problem of packing in the crystal lattice. Of course, the crystal structure of TCNB must be determined by X-ray analysis to prove this presumption.

REFERENCES

- 1) S. Kumura and Y. Kuroishi, *Bull. Chem. Soc. Jpn.*, **56**, 1541 (1983).
- 2) S. Sharma, H. Paulus, N. Weiden, and A. Weiss, *Z. Naturforsch.*, **41a**, 134 (1986).
- 3) V. D. Ramanamurti, P. Venkatacharyulu, and D. Premaswarup, *Indian J. Pure Appl. Phys.*, **17**, 234 (1979).
- 4) Mishima, *Bull. Shimane Med. Univ.*, **8**, 27 (1985).
- 5) C. Dean, *Phys. Rev.*, **96**, 1053 (1954).
- 6) K. Shimomura, *J. Phys. Soc. Jpn.*, **12**, 657 (1957).
- 7) R. W. G. Wyckoff, "The structure of Crystals," 2nd. ed. Chem. Cat. Co. Inc., New York (1931). pp. 28–31.
- 8) Y. Morino, M. Toyama, K. Itho, and S. Kyono, *Bull. Chem. Soc. Jpn.*, **35**, 1667 (1962).
- 9) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, New York (1969). Chap. 7.
- 10) V. Jaccarino and I. G. King, *Phys. Rev.*, **63**, 471 (1951).
- 11) B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1955).
- 12) M. S. J. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977).
- 13) M. S. J. Dewar, M. L. Mckee, and H. S. Rzepa, *J. Am. Chem. Soc.*, **100**, 3607 (1978).
- 14) M. S. J. Dewar and H. S. Rzepa, *J. Comput. Chem.*, **4**, 158 (1983).
- 15) M. Kaplansky and M. A. Whitehead, *Trans. Faraday Soc.*, **65**, 641 (1969).