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Nuclear Quadrupole Resonances of 2,4,6-Trichlorobenzonitrile

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2,4,6-Trichlorobenzonitrile was examined by means of the nuclear quadrupole resonances (NQR) resulting from ^{14}N and ^{35}Cl nuclei. One ^{14}N resonance line (the higher line of the pair) and three ^{35}Cl resonance lines were observed. The Zeeman effect on a single crystal was studied in an attempt to predict the lower ^{14}N line. Thus, $|e^2Qq|=3936.7$ kHz and $\eta=0.1298$ were calculated for the nitrogen atom; the frequency of the lower line was estimated at 2824.8 kHz. On the other hand, ($\eta=0.130$; $|e^2Qq|=71.209$ MHz), (0.128; 72.594), and (0.116; 73.720) were determined for the chlorine atoms in the order of increasing frequencies by studying the Zeeman effect of ^{35}Cl NQR on the single crystal.

Short intermolecular distances between nitrogen and halogen atoms have been known from structural studies of X-ray diffraction in the cyanogen halides and *p*-halobenzonitriles.[1,2] These results have been interpreted as indicating donor-acceptor interaction between adjacent molecules. The crystal structure of 2,4,6-trichlorobenzonitrile was recently determined to be as is shown in Fig. 1,[3] where the intramolecular bonds are represented by the solid lines, while the intermolecular bonds are represented by the broken lines. The shortest distance between the nitrogen and chlorine atoms in this crystal is 3.22 Å, which is shorter by 0.08 Å than the sum of their van der Waals radii. Therefore, there should be a weak interaction between the cyanide groups and *ortho* chlorine atoms, both of which serve to form the dimer. In this respect it seemed that it would be interesting to examine and discuss the chemical bonding in this crystal.

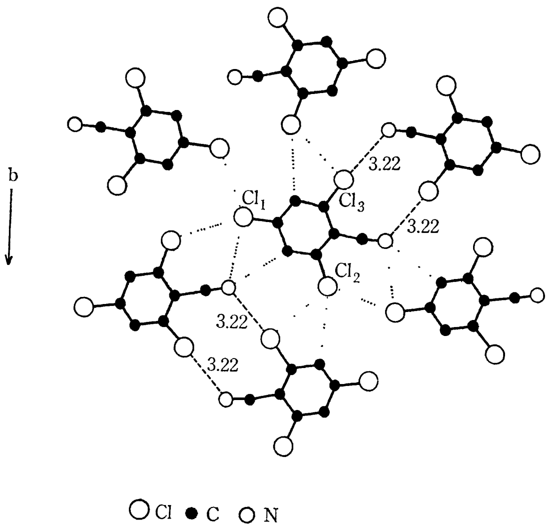

Fig. 1. The projection to the layer of 2,4,6-trichlorobenzonitrile. (Space group $P2_1/c$)

Experimental

The ^{14}N NQR spectrum of 2,4,6-trichlorobenzonitrile was obtained at 77 K by the use of a frequency-modulated spectrometer described previously,[4] whereas the ^{35}Cl NQR spectra of this compound were obtained by the use of a superregenerative spectrometer at 290 K. The resonance frequencies were measured by means of two kinds of heterodyne-type frequency meters, whose frequencies were checked by means of a frequency counter, TR-5578, of the Takeda Riken Co. The Zeeman field was supplied by a Helmholz coil described previously.[5,6]

2,4,6-Trichlorobenzonitrile was prepared from 2,4,6-trichloroaniline *via* 2,4,6-trichloroiodobenzene. This compound was identified by means of its infrared spectrum, its mass spectrum, and its melting point. About a 10-g portion of the sample was used, and a single crystal, 15 mm in diameter and 35 mm in length, was prepared by the Bridgman-Stockbarger method.

Results and Discussion

Our sample of 2,4,6-trichlorobenzonitrile revealed one weak ^{14}N resonance line and three fairly strong ^{35}Cl resonance lines.

^{14}N Resonance Line. Generally a pair of ^{14}N NQR frequencies, ν_{I} and ν_{II}, are observed as follows:

$$\begin{aligned}\nu_{I} &= |e^2Qq|(3-\eta)/4,\\ \nu_{II} &= |e^2Qq|(3+\eta)/4,\end{aligned} \tag{1}$$

where $|e^2Qq|$ and η are the quadrupole coupling constant and the asymmetry parameter respectively. However, only one resonance line was observed at 3080.2 kHz; it was assigned to the higher line by observing the Zeeman shift. The frequency of the lower line was calculated from the shift of the higher line by applying the Zeeman field, using a single crystal in the same way as before.[6] Figure 2 shows the angular dependence of the Zeeman shift of the higher line when the sample is rotated about a given axis. The Zeeman field was applied along the Y-axis of the laboratory frame, and the resonance frequencies were measured at various rotating angles (Θ) about the X-axis for a constant rotating angle ($\Phi=0°$) about the Z-axis. The maximum frequency or shift was found for $\Theta=335°$. Next, the frequencies were measured at various rotating angles (Φ) about the Z-axis for $\Theta=335°$. The shift was at its maximum at $\Phi=350°$. Therefore, the procedures were repeated until a self-consistent maximum shift was obtained; the maximum frequency was determined to be 3083.4 kHz. Under this condition, the perturbed resonance frequency is at its maximum and expressed as $3083.4=K(3+\eta)+D^2/(2\eta K)$, where K is $|e^2Qq|/4$ and D^2 is 807.8 kHz^2.[6] On the other hand, the higher line in the absence of the Zeeman field is expressed by $3080.2=K(3+\eta)$. Thus, the NQR parameters are calculated as $|e^2Qq|=3936.7\pm7.0$ kHz and $\eta=0.1298\pm0.0057$. Substituting these values into Eq. 1, the frequency of the lower line is obtained as 2824.8±

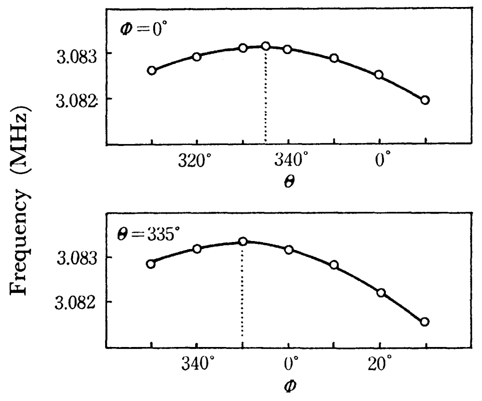

Fig. 2. The angular dependences of the Zeeman shifts.

10.6 kHz. The neighborhood of this frequency was carefully swept again, but, unfortunately, no resonance line was observed.

^{35}Cl Resonance Lines. The ^{35}Cl NQR frequency, ν, is obtained according to the following equation:

$$\nu = |e^2Qq|(1+\eta^2/3)^{1/2}/2. \qquad (2)$$

The ^{35}Cl resonance lines of the sample were observed at 35.704, 36.395, and 36.941 MHz, as is shown in Table 1. These lines are labeled as ν_1, ν_2, and ν_3 respectively. Then, referring to the crystal structure of the sample, these lines can be ascribed to the three kinds of chlorine atoms, Cl_1, Cl_2, and Cl_3, in one molecule. One of the zero-splitting patterns of the Zeeman effect on the resonance lines is shown in Fig. 3. For each of the resonance lines, ν_1, ν_2, and ν_3, two loci were obtained. The direction of the principal z-axis of the field gradient on the chlorine atom can be obtained from the zero-splitting pattern; it is assumed to be parallel to the direction of the C–Cl bond. The direction of the b-axis (C_2-axis) of the crystal can be found easily from the symmetrical distributions of the z-axis. The resonance line can be assigned by means of the angle between the b-axis and the z-axis. Thus, it is evident that ν_1, ν_2, and ν_3 originate from the *para-*, *ortho-*, and *ortho*-chlorine atoms respectively. The last interacts weakly with the cyanide group of the adjacent molecule. The condition under which the zero-splitting occurs for the ^{35}Cl nucleus is given[7] by:

$$\sin^2\theta = 2/(3-\eta\cos^2\varphi), \qquad (3)$$

where θ and φ are the polar and azimuthal angles for the Zeeman magnetic field with respect to the coordinates of the principal axes of the field gradient at the resonant nucleus. The asymmetry parameters were determined from Eq. (3) by the use of the least-squares method. If the crystal field effects are negligibly small, the quadrupole coupling constant and the double-bond character, f, can be determined from the following equation:[8]

$$f = 2|e^2Qq|\eta/(3|e^2Qq_{\text{atom}}|), \qquad (4)$$

where $|e^2Qq_{\text{atom}}|$ is 109.7 MHz.[9] These results are listed in Table 1. The f value of ν_3 is rather smaller. This suggests that the *ortho*-chlorine atom assigned ν_3 interacts with the cyanide group of the adjacent molecule, as is to be expected from the crystal structure of this compound.[3] The ∠CN···Cl angle is 122.4°, although generally the ∠CN···halogen angle is about 180°, as in the acetonitrile–bromine complex.[10] This seems to suggest that the σ-orbital of the nitrogen atom in this molecule has an s-character of less than 50%.

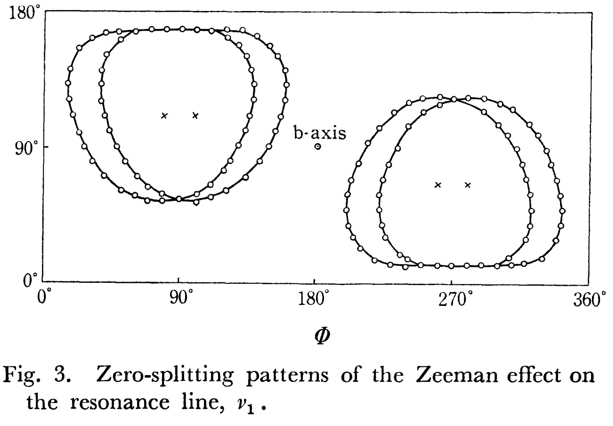

Fig. 3. Zero-splitting patterns of the Zeeman effect on the resonance line, ν_1.

Table 1. NQR parameters in 2,4,6-trichlorobenzonitrile

		ν(MHz)	$\lvert e^2Qq\rvert$(MHz)	η(%)	f(%)
^{14}N		2.8248[a)] 3.0802	3.9367[a)]	12.98[a)]	—
^{35}Cl	Cl_1	35.704	71.209	13.0	5.63
	Cl_2	36.395	72.594	12.8	5.65
	Cl_3	36.941	73.720	11.6	5.19

a) Estimated by the experiment of Zeeman effects.

References

1) R. B. Heiart and G. B. Carpenter, *Acta Crystallogr.*, **9**, 889 (1956).
2) E. O. Schlemper and D. Britton, *ibid.*, **18**, 419 (1965).
3) V. B. Carter and D. Britton, *ibid.*, **B28**, 945 (1972).
4) H. Negita, M. Hayashi, and T. Okada, *J. Sci. Hiroshima Univ., Ser. A*, **35**, 85 (1971).
5) T. Okuda, H. Terao, O. Ege, and H. Negita, This Bulletin, **43**, 2398 (1970).
6) H. Negita, K. Shibata, and T. Kubo, *ibid.*, **46**, 110 (1973).
7) C. Dean, *Phys. Rev.*, **96**, 1053 (1954).
8) R. Bersohn, *J. Chem. Phys.*, **22**, 2078 (1954).
9) V. Jaccarino and J. G. King, *Phys. Rev.*, **83**, 471 (1951).
10) K. M. Marstokk and K. O. Strømme, *Acta Crystallogr.*, **B24**, 713 (1968).