

^{35}Cl NQR of Dimethyl Tetrachloroterephthalate

(Dimethyl tetrachloroterephthalate/NQR/Zeeman effect)

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The title compound exhibits four ^{35}Cl NQR lines. The NQR frequencies have been measured as a function of temperature between 77 and 425 K. Four lines exhibit normal negative temperature dependence. At 77 K the spectrum composed of the lines at 37.462, 37.521, 37.570, and 37.783 MHz is different from that reported previously. The Zeeman effect on ^{35}Cl NQR in a single crystal has been studied at room temperature. It is deduced on the basis of the orientations of the efg axes that there are two crystallographically nonequivalent molecules in the crystal. The angles between the adjacent C-Cl bonds are estimated to be $62.99 \pm 0.05^\circ$ in one of these molecules and $61.77 \pm 0.05^\circ$ in another.

Introduction

Interesting results on NQR of dimethyl tetrachloroterephthalate (DMTCT) have been reported.¹⁾ According to Hart et al.,¹⁾ the NQR spectrum of DMTCT at 77 K consists of four lines, one low-frequency line at 35.762 MHz and three closely spaced high-frequency lines at nearly 37.5 MHz, whereas the spectrum at 298 K consists of four lines around 37 MHz. Thus the low-frequency line exhibits a very positive temperature coefficient, which has been discussed in terms of the bond character of the C-Cl bond of DMTCT. If this is the case, DMTCT is very unique in chlorinated aromatic compounds.

Usually the positive temperature coefficient of the NQR frequency of a monovalent halogen atom is attributed to strong bonding, especially, in hexahalometallates, strong hydrogen bonding, or phase transition.²⁾ The above discussion of the bond character is based on the data only at temperatures of 77 and 298 K. More detailed data are required in order to know what causes a lowering of the frequency of the unique line.

For this reason, an attempt was made to observe the temperature dependence of the NQR frequencies of DMTCT. Furthermore, in order to obtain information on the molecular shape and bond character, the Zeeman effect of NQR was observed.

Experimental

A commercial compound (Tokyo Chemical Industry) of DMTCT was purified by recrystallization in ethanol. A single crystal was grown from the melt using the method outlined by Bridgeman. The NQR spectrometer has been described elsewhere.³⁾ The absorption lines were displayed on an oscilloscope. The frequencies were determined within an accuracy of 1 kHz by a frequency counter. The Zeeman effect was studied by means of the zero-splitting cones method. The orientations of the magnetic field for the zero-splitting was determined in polar coordinates (θ and ϕ), where θ and ϕ are polar and azimuthal angles, respectively, in the coordinate fixed to the crystal. Temperatures were determined with a Yokogawa 7563 thermometer by the use of a thermocouple (copper-constantan). The temperature dependence of the resonance frequency was measured from 77 K up to 420 K.

Results and Discussion

In DMTCT, four ^{35}Cl NQR lines with equal intensities were observed. The NQR frequencies in DMTCT at 77 K and 298 K are listed in Table 1 along with the literature values. The frequencies at 298 K agree well with those reported previously within experimental errors,¹⁾ whereas the frequencies at 77 K are considerably different from the literature values. Figure 1 presents the ^{35}Cl NQR spectrum of DMTCT as a function of temperature. The quartet lines are designated as Cl₁, Cl₂, Cl₃, and Cl₄ in the order of decreasing frequency. The frequencies of the Cl₃ line

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Table 1. ^{35}Cl NQR parameters for dimethyl tetrachloroterephthalate

T/K	Frequency/MHz	$e^2Qq_{zz}h^{-1}$ /MHz	Ref.
77	37.577		b
	37.530		
	37.466		
	35.762		
298	37.383		c
	37.095		
	36.950		
	36.831		
77	37.783(29.778) ^{a)}		c
	37.570(29.611)		
	37.521(29.572)		
	37.462(29.525)		
298	37.382	0.107 ± 0.001	74.61
	37.089	0.123 ± 0.001	73.98
	36.950	0.109 ± 0.001	73.74
	36.830	0.115 ± 0.002	73.50

a) The values in parentheses are the ^{37}Cl frequencies.

b) Ref. 1. c) This work.

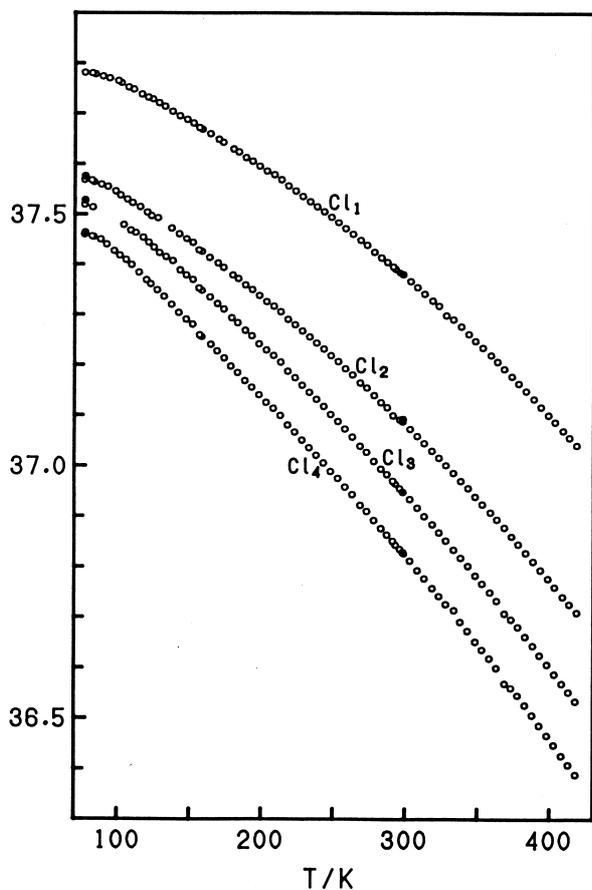


Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in dimethyl tetrachloroterephthalate. The shaded circles present the literature values at 77 and 298 K.

around 100 K could not be determined because of overlapping of the true line and the side bands of the surrounding lines. The frequencies of the quartet lines increase monotonously with a decrease in temperature. No phase transition was found between 77 K and room temperature.

The frequencies of the three higher-frequency lines of the quartet at 77 K reported by Hart et al.¹⁾ agree fairly well with those of the three lower-frequency lines in our data, as can be seen in Table 1 and in Fig. 1. No ^{35}Cl absorption line was found in the range of 29 to 37 MHz, but instead an absorption at 37.783 MHz was observed. The spectrum of an annealed sample was identical with that of a quickly cooled sample. Considering the abnormally low frequency of the unique line at 35.762 MHz and the fair agreement between three of the previous data and our corresponding data, the question is raised whether the unique line at 77 K exists.

The frequency of the unique line is lower by 1.7 MHz than those of the other lines. This implies that there are significant differences in character between the C - Cl bonds. It is difficult to imagine that one of four chemically equivalent chlorine atoms has a bond character significantly different from the others. (One of the data might have been misread.)

In any event, the spectrum obtained in this work differs from that reported previously.¹⁾ Above room temperature, all of the quartet lines also decreased monotonously with temperature, their line-widths were gradually broadened from about 380 K, and all of the lines faded out at about 420 K, suggesting that the torsional motions of the DMTCT molecules rapidly increase in amplitude from about 380 K.

Figure 2 shows the zero-splitting loci obtained from the Zeeman effect at room temperature. Each of the Cl_1 , Cl_2 , and Cl_3 lines gave a pair of loci, whereas on the Cl_4 line only one locus was found because of unfavorable orientation of the principal z axis of the electric field gradient (efg). The two-fold axis of the crystal was determined from the distributions of the Zeeman loci on the Cl_1 , Cl_2 , and Cl_3 lines. The missing locus of the Cl_4 line was deduced from the C_2 axis and the observed locus. The deduced directions of the efg axes on the missing Cl_4 line are presented by +. The angles between the efg z axes and between the efg x axes are given in Tables 2 and 3, respectively.

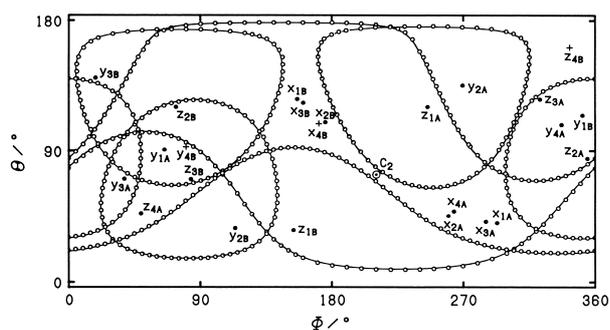


Fig. 2. Zero-splitting loci of ³⁵Cl Zeeman lines of dimethyl tetrachloroterephthalate. x_i , y_i and z_i present the directions of principal efg axes at the i th chlorine nucleus. The subscripts A and B indicate that the efg axes belong to the different sites of the crystal.

The angles between the C - Cl bonds belonging to a particular DMTCT molecule in the crystal are about 60° (or 120°) and the bond directions of the chlorine atoms are parallel to each other. Usually in an organic compound the efg z axis on the chlorine atom is parallel to the direction of the C - Cl bond and the x axis is perpendicular to the plane of the benzene ring. Therefore the directions of the x and z axes show that a pair of the Cl_1 and Cl_3 atoms apparently make one set and a pair of the Cl_2 and Cl_4 atoms another set, as can be seen in Tables 2 and 3. It can be seen from Fig. 3 that the x axes on the Cl_2 and Cl_4 atoms distribute in the neighborhood of those on the Cl_1 and Cl_3 atoms. No x-ray data are avail-

Table 2. Angles (degrees) between the efg z axes in dimethyl tetrachloroterephthalate

z-axis	Z_{1B}	Z_{2A}	Z_{2B}	Z_{3A}	Z_{3B}	Z_{4A}	Z_{4B}
Z_{1A}	115.16 (64.84) ^{a)}	108.83 (71.17)	118.73 (61.27)	63.03 (116.97)	159.95 (20.05)	162.30 (17.70)	116.51 (63.49)
Z_{1B}		118.75 (61.25)	108.76 (71.24)	160.03 (19.97)	62.94 (117.06)	63.47 (116.53)	162.26 (17.74)
Z_{2A}			83.00 (97.00)	50.38 (129.62)	87.69 (92.31)	61.77 (118.23)	76.46 (103.54)
Z_{2B}				87.66 (92.34)	50.41 (129.59)	87.70 (92.30)	61.77 (118.23)
Z_{3A}					126.16 (53.84)	111.65 (68.35)	37.20 (142.80)
Z_{3B}						37.22 (142.78)	111.68 (68.32)
Z_{4A}							123.68 (56.32)

a) The values in parentheses are supplementary angles.

Table 3. Angles (degrees) between the efg x axes in dimethyl tetrachloroterephthalate

x-axis	X_{1B}	X_{2A}	X_{2B}	X_{3A}	X_{3B}	X_{4A}	X_{4B}
X_{1A}	147.1 (32.9) ^{a)}	23.1 (156.9)	122.7 (57.3)	4.9 (175.1)	141.4 (38.6)	21.6 (158.4)	124.4 (55.6)
X_{1B}		123 (57.9)	23.5 (156.5)	141.4 (38.6)	4.7 (175.3)	124.9 (56.1)	22.0 (158.0)
X_{2A}			99.7 (80.3)	18.3 (161.7)	118.4 (61.6)	4.0 (176.0)	101.6 (78.4)
X_{2B}				117.9 (62.1)	18.8 (161.2)	101.7 (78.3)	4.2 (175.8)
X_{3A}					136.7 (43.3)	16.8 (163.2)	119.8 (60.2)
X_{3B}						120.3 (59.7)	17.5 (162.5)
X_{4A}							103.9 (76.1)

a) The values in parentheses are supplementary angles.

able for DMTCT. It is therefore necessary to examine whether the two sets of the chlorine atoms belong to one molecule or two. In the case where a group of the x axes designated by the subscript A or B are assigned to the chlorine atoms bonded to the same molecule, the DMTCT molecule has four crystallographically nonequivalent chlorine atoms. The assumed molecular shape is distorted, since the plane made up of the C - Cl₁ and C - Cl₃ bonds makes an angle of 23.1° with that made up of the C - Cl₂ and C - Cl₄ bonds. The assumed assignment of the chlorine atoms is shown in Fig. 3 (a). The angle between the C - Cl₂ and C - Cl₃ bonds is too small compared with 180°, even though the molecule is considerably distorted. The possibility of the assignment in Fig. 3 (a) is consequently rejected.

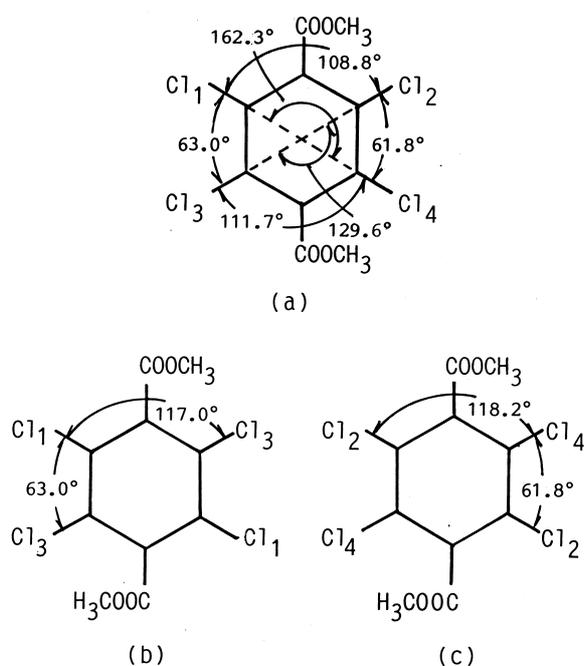


Fig. 3 Assumed molecular shapes of dimethyl tetrachloroterephthalate.

A set of the Cl₁ and Cl₃ atoms and another set of the Cl₂ and Cl₄ atoms should therefore be assigned to two separate molecules. In this case, there are two crystallographically nonequivalent molecules in the crystal and each of them has two pairs of crystallographically nonequivalent chlorine atoms which are coplanar. Each molecule has an inversion center lying in the benzene ring or a two-fold axis perpendicular to the ring. The shapes of these molecules are shown in Fig. 3 (b) and (c).

The angles between the adjacent C - Cl bonds in the two

nonequivalent molecules ($62.99 \pm 0.05^\circ$ and $61.77 \pm 0.05^\circ$) are somewhat greater than 60° and are almost the same as those in 1,2,4,5-tetrachlorobenzene (TCB) ($63 \pm 1^\circ$).⁴⁾ These enlarged angles are considered to result from repulsive van der Waals' forces between the adjacent chlorine atoms. The distance between the adjacent chlorine atoms in DMTCT is roughly estimated to be 0.31 nm. In the case where the methoxycarbonyl group and the benzene ring are coplanar, the roughly estimated distance between the double-bonded oxygen atom of the methoxycarbonyl group and the close-neighboring chlorine atom is shorter than 0.21 nm and the corresponding distance relating to another oxygen atom is similarly shorter than 0.21 nm. These values are much smaller than the sum of van der Waals radii of the oxygen and chlorine atoms (0.32 nm).^{5,6)} The sum of van der Waals radii of the chlorine atoms is 0.35 nm. Taking the angles between the C - Cl bonds into consideration, it is presumed that the methoxycarbonyl groups do not lie in the benzene ring and may be twisted around the C - C bonds. The conjugation of the methoxycarbonyl groups with the ring appears not to be significant.

The asymmetry parameter (η) can be estimated by transforming the zero-splitting locus in the coordinate system fixed to the crystal into the principal axis system, in which the locus is expressed for nuclear spin 3/2 as follows:⁷⁾

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

where θ_0 and ϕ_0 are polar and azimuthal angles, respectively. The quadrupole coupling constant ($e^2Qq_z h^{-1}$) is obtained from the NQR frequency (ν) and the asymmetry parameter according to the following relation:

$$\nu = (1/2)e^2Qq_z h^{-1}(1 + \eta^2/3)^{1/2}. \quad (2)$$

The calculated parameters are listed in Table 1.

Neglecting the intermolecular contribution to the asymmetry parameter, the partial double bond character (δ) can be worked out in terms of the values of ν and $e^2Qq_z h^{-1}$ as follows:⁸⁾

$$\delta = (2/3) |e^2Qq_z h^{-1} / e^2Qq_{ab} h^{-1}|, \quad (3)$$

where $e^2Qq_{ab} h^{-1}$ is the atomic coupling constant which is 109.746 MHz for ³⁵Cl.⁹⁾ The double bond characters of the chlorine atoms which are calculated to be 0.050 on the average are equal in magnitude to those in TCB (0.051),¹⁰⁾ though the resonance frequencies of the latter are lower by 0.7 MHz than those of DMTCT.⁴⁾ This also suggests that the conjugation between the methoxycarbonyl group and the benzene ring is insignificant.

The average ionic characters of the chlorine atoms of DMTCT and TCB are calculated to be 0.17 and 0.19, respectively. That is, the chlorine atoms of DMTCT are less negatively charged than those of TCB. It has been shown that in a series of compounds RCH₂Cl the NQR frequency increases linearly with the Taft constant σ^* relating to the inductive effect of the substituent R.¹⁰ The Taft constant for the methoxycarbonyl group is larger by 1.51 units than that for the hydrogen atom.¹⁰ Therefore, the difference in average frequency between DMTCT and TCB is attributed mainly to that in inductive power between the substituents.

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