

## $^{35}\text{Cl}$ NQR Zeeman Study of Tetrachlorothiophene

(NQR / Zeeman effect / Tetrachlorothiophene)

Mitsuo MISHIMA

The  $^{35}\text{Cl}$  NQR of tetrachlorothiophene has been observed and the Zeeman effect on a single crystal has been examined. This compound yields four lines at room temperature. These lines are divided into two distinct groups, *i.e.*, two lower frequency lines (36.90 and 36.93 MHz) and two higher frequency ones (37.63 and 37.68 MHz). On the basis of Zeeman analysis, the lower lines are assigned to the Cl atoms at the 3- and 4-positions and the higher ones to those at the 2- and 5-positions. The angles between the C-Cl bonds have been deduced and it has been revealed that four C-Cl bonds in the molecule are nearly coplanar. From the distribution of the zero-splitting loci, it has been determined that the crystal of TCT belongs to an orthorhombic system.

---

### Introduction

NQR in tetrachlorothiophene (TCT) was first observed by Dewar and Lucken<sup>1)</sup>, who reported the NQR spectrum consisting of three lines at room temperature. We obtained crystals yielding four NQR lines at room temperature from melt. The resonance lines in these NQR spectra can be divided into lower frequency and higher frequency lines. However, these lines cannot be assigned to particular chlorine atoms without information on the bond character of the C-Cl bond. Furthermore, the frequencies for TCT are higher than those for the corresponding benzene derivatives. This can be explained in terms of a decreased  $\sigma$ -bond polarity of the C-Cl bond caused by the strongly polarized S-C bond<sup>1)</sup>. In general, decreased double bond character and/or increased single bond character of the C-Cl bond lead to an increase in frequency. It would be interesting to

determine which affects the resonance frequencies,  $\sigma$ -bonding or  $\pi$ -bonding.

Neither morphological data nor X-ray data are available for this compound. The Zeeman effect of the  $^{35}\text{Cl}$  NQR lines is investigated to obtain information regarding the crystal structure and the assignment of the resonance lines. The angles between the C-Cl bonds will be reported.

### Experimental

TCT was obtained commercially. TCT was purified by recrystallization from ethanol. A single crystal of TCT was grown from melt using the Bridgmann technique.  $^{35}\text{Cl}$  NQR spectra were observed on an oscilloscope using a Dean-type superegenerative spectrometer with frequency modulation. The Zeeman effect was observed by applying a magnetic field of about 200 G and examined by the zero-splitting cone method. The method of analysis was reported already <sup>2,3</sup>.

### Results and Discussion

In Table 1 the  $^{35}\text{Cl}$  NQR frequencies in TCT are listed. The NQR spectrum for a crystal grown from melt is different from that reported previously <sup>1)</sup> in a spectral pattern. This suggests that there may be at least two modifications in TCT. In these spectra the resonance lines are divided into two distinct groups, *i.e.*, the lower frequency lines and the higher frequency ones. The NQR lines in each group are presumed to be assigned to the chlorine atoms attached to the chemically equivalent carbon atoms of the thiophene ring. However, the assignment of the resonance lines cannot be determined unequivocally. The Zeeman effect on the chlorine resonance lines is very useful for assigning the resonance lines.

Table 1. NQR Parameters for Tetrachlorothiophene at 294 K

Line	Frequency/MHz	$\eta$	$e^2Qq h^{-1}$ /MHz	Ref.
Cl (1)	36.906			a
Cl (2)	36.931			
Cl (3)	37.740			
Cl (1)	36.904	0.084	73.721	b
Cl (2)	36.929	0.084	73.771	
Cl (3)	37.626	0.053	75.217	
Cl (4)	37.679	0.054	75.324	

a) Ref. 1.    b) This work.

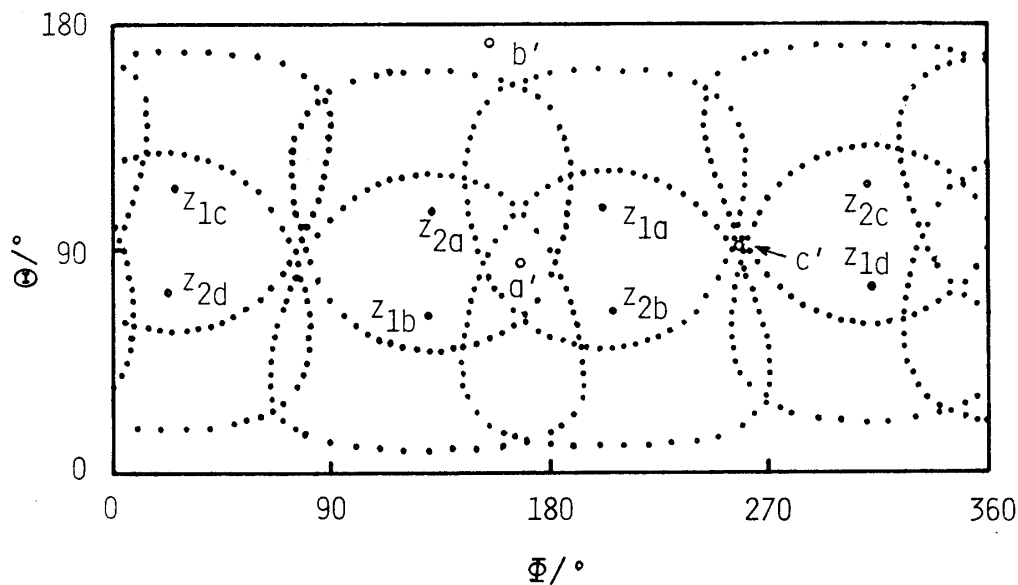


Fig. 1. Zero-splitting patterns for lower frequency lines in tetrachlorothiophene.

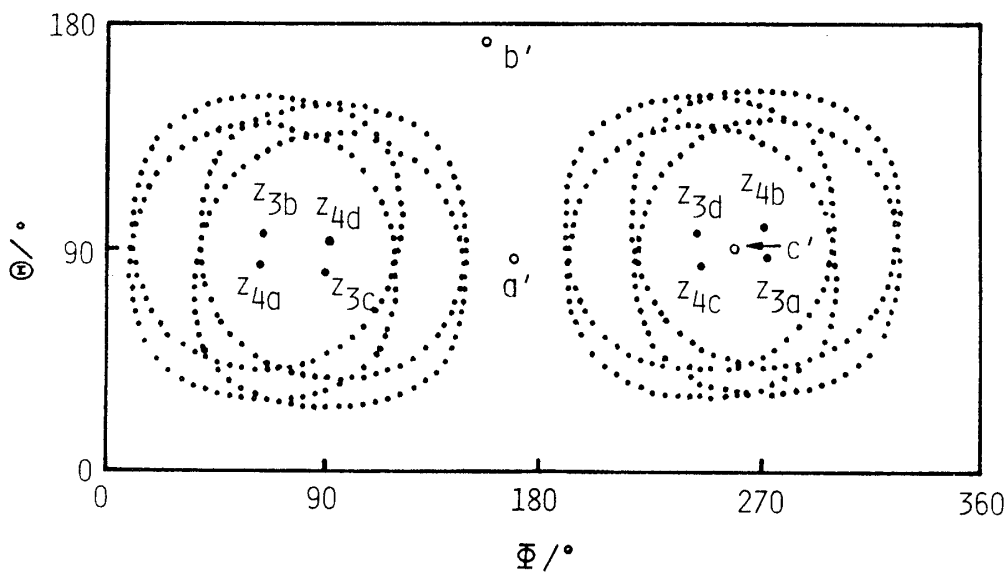


Fig. 2. Zero-splitting patterns for higher frequency lines in tetrachlorothiophene.

*Molecular Shape and Molecular Plane.* Figures 1 and 2 show the zero-splitting patterns of TCT at room temperature. All the resonance lines were considerably broad and the higher frequency lines gave partly overlapped Zeeman patterns. Accordingly, the directions of the efg principal axes and the values of the asymmetry parameters are not completely accurate. Each line gave four loci. Three mutually perpendicular twofold axes were determined from the distribution of these loci. These axes are arbitrarily termed a',

b', and c'. None of the efg z axes is perpendicular or parallel to these twofold axes, suggesting that the crystal of TCT grown from melt belongs to an orthorhombic system<sup>4)</sup>.

Table 2. Angles between the efg z Axes and Crystal Axes in Tetrachlorothiophene

axis	group	Crystal axes		
		a'	b'	c'
z <sub>1</sub>	a	139.00°	110.00	124.05
	b	41.07	110.00	124.12
	c	139.00	70.01	124.06
	d	41.03	69.97	124.06
z <sub>2</sub>	a	41.23	69.34	56.17
	b	138.73	69.27	56.18
	c	41.23	110.66	56.17
	d	138.79	110.63	56.18
z <sub>3</sub>	a	76.24	84.39	14.90
	b	103.89	84.39	15.02
	c	76.25	95.55	14.87
	d	103.91	95.54	15.02
z <sub>4</sub>	a	103.62	96.34	164.93
	b	76.36	96.25	164.95
	c	103.59	83.69	164.96
	d	76.34	83.74	164.92

The angles between the efg z axes and the crystal axes are summarized in Table 2, where the crystal is assumed to possess the symmetry D<sub>2</sub>. The resonance lines are designated Cl (1), Cl (2), Cl (3), and Cl (4) in the order of increasing frequency. The z<sub>i</sub> indicates the directions of the efg tensor at the <sup>35</sup>Cl nucleus which yields a Cl (i) line. The calculated asymmetry parameters (η) and the coupling constants (e<sup>2</sup>Qqh<sup>-1</sup>) are listed in Table 1. These parameters were determined by using the following relation;<sup>5)</sup>

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

The NQR lines can be assigned by comparing the efg z axes with the C-Cl bond directions in a crystal. Unfortunately, no X-ray data are available for TCT. It was assumed that each molecule of a unit cell had to be represented by four of the C-Cl bond directions, one from each of the four NQR lines. On the further assumption that the angles between the C-Cl bonds should be the order of 60° to 70° and the four C-Cl bonds should be coplanar, two reasonable pictures of the molecule emerged. The reason is

that any of the  $z_1$  axes is nearly parallel (or antiparallel) to one of the  $z_2$  axes and any of the  $z_3$  to one of the  $z_4$ , as can be seen in Table 2. The angles between the C-Cl bonds were calculated, assuming that the efg  $z$  axis is parallel to the C-Cl bond. These angles are listed in Table 3 and the arrangement of the chlorine atoms around the thiophene ring are shown in Fig. 3 together with the significant angles.

Table 3. Angles between the C-Cl Bonds in the Molecule of Tetrachlorothiophene

(1) Case-1			
Bond	C—Cl (1)	C—Cl (2)	C—Cl (3)
C—Cl (1)	$67.90 \pm 0.02^\circ$		
C—Cl (2)	$139.00 \pm 0.07^\circ$	$71.11 \pm 0.05^\circ$	
C—Cl (3)	$77.99 \pm 0.03^\circ$	$138.88 \pm 0.01^\circ$	$150.00 \pm 0.08^\circ$
(2) Case-2			
Bond	C—Cl (1)	C—Cl (2)	C—Cl (3)
C—Cl (2)	$67.90 \pm 0.02^\circ$		
C—Cl (3)	$70.87 \pm 0.07^\circ$	$138.75 \pm 0.05^\circ$	
C—Cl (4)	$139.13 \pm 0.02^\circ$	$71.23 \pm 0.01^\circ$	$150.00 \pm 0.08^\circ$

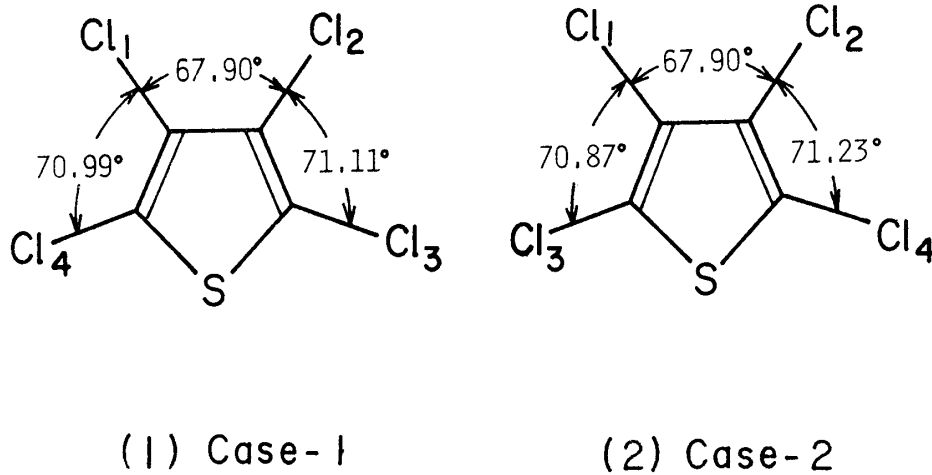


Fig. 3. Arrangement of the chlorine atoms in tetrachlorothiophene.

In case-1 of Fig. 3 the deviations of the  $z_3$  and  $z_4$  axes from the  $z_1 z_2$  plane are, respectively,  $0.14 \pm 0.05^\circ$  and  $0.50 \pm 0.06^\circ$ , whereas in case-2 the corresponding deviations are  $1.22 \pm 0.05^\circ$  and  $-0.58 \pm 0.05^\circ$ . The molecular shape in case-1 therefore surpasses that in case-2 in planarity. In any case, the lower frequency lines are assigned to the Cl atoms at the 3- and 4-positions and the higher

frequency ones to those at the 2- and 5-positions. Furthermore, the angle between the C-Cl bonds at the 2- and 3-position is calculated to be  $70.1 \pm 0.1^\circ$ . The molecular plane makes angles of  $24.8^\circ$ ,  $65.2^\circ$ , and  $0.6^\circ$ , respectively, to the  $a'$ ,  $b'$  and  $c'$  axes, assuming that the plane containing the C-Cl (1) and C-Cl (2) bonds is parallel to the molecular plane. The molecular plane is nearly parallel to one of the crystal axes.

*Bond Character.* The values of the asymmetry parameters in TCT are comparable to those in 2,5-dichloroaniline (DCA) ( $e^2Qqh^{-1} = 67.72$  MHz ;  $\eta = 0.079$  and  $e^2Qqh^{-1} = 67.98$  MHz ;  $\eta = 0.059$ )<sup>6)</sup> and p-dichlorobenzene (DCB) ( $e^2Qqh^{-1} = 68.45$  MHz ;  $\eta = 0.067$ )<sup>6, 7)</sup>. This is suggestive of a resemblance of  $\pi$ -bonding between benzene and thiophene. The occupation number of the  $p_x$  orbital ( $N_x$ ) can be estimated according to the following relation ;<sup>8)</sup>

$$N_y - N_x = \frac{2}{3} \eta \left| \frac{e^2Qq}{e^2Qq_0} \right| \quad (2)$$

where  $e^2Qq_0h^{-1}$  is the atomic quadruple coupling constant, which is 109.74 MHz for  $^{35}\text{Cl}$ . The quadrupole coupling constant can be related to the populations on the p orbitals as follows ;

$$e^2Qq = e^2Qq_0 [(N_x + N_y)/2 - N_z], \quad (3)$$

where  $N_y$  was assumed to be 2. The calculated orbital populations are listed in Table 4.

The values of  $N_x$  for DCA and DCB are calculated to be 1.963 to 1.975<sup>6)</sup>. The differences between the benzene derivatives and chlorothiophene in  $\pi$ -electron distribution at the chlorine atom is very small and the  $\sigma$  bond populations of the chlorine atoms in TCT are about 0.06 less than those in DCA and DCB<sup>6)</sup>. This supports the view of Dewar and Lucken that the increased NQR frequencies result not from decreased  $\pi$  character but from decreased polarity of the C-Cl  $\sigma$  bond<sup>1)</sup>.

The  $^{35}\text{Cl}$  NQR frequencies of TCT were combined with the MNDO theory<sup>9-12)</sup> and the INDO/S molecular orbital theory<sup>13, 14)</sup>, in order to make sure that the resonance lines were correctly assigned. In these calculations the ring geometry of tetrahydrothiophene<sup>15)</sup> with  $C_{2v}$  symmetry was adopted as that of TCT. All the C-Cl bond distances were assumed to be 173 pm and the Cl-C-C angles were estimated from the results of Zeeman analysis. The results are listed in Table 4.

Table 4. Orbital Occupations of Chlorine Atoms in Tetrachlorothiophene

Atom	Parameter	Method of calculation		
		INDO/S	MNDO	Experimental
Cl (1, 2)	<i>N<sub>x</sub></i> (electrons)	1.978	1.969	1.962
	<i>N<sub>y</sub></i> (electrons)	1.997	1.989	(2.000) <sup>a)</sup>
	<i>N<sub>z</sub></i> (electrons)	1.315	1.083	1.388
	Frequency/MHz	36.9	49.2	36.9
	$\eta$	0.042	0.034	0.084
Cl (3, 4)	<i>N<sub>x</sub></i> (electrons)	1.975	1.967	1.976
	<i>N<sub>y</sub></i> (electrons)	1.997	1.984	(2.000) <sup>a)</sup>
	<i>N<sub>z</sub></i> (electrons)	1.305	1.068	1.396
	Frequency/MHz	37.4	49.8	37.7
	$\eta$	0.050	0.028	0.053

a) Assumed to be 2.

The INDO/S theory gives fairly good predictions of the NQR frequencies and the orbital populations, while the asymmetry parameters are unsatisfactorily predicted. Although it has been shown that the MNDO values for heats of formation, dipole moments, molecular geometries, and ionization potentials<sup>16)</sup>, the MNDO theory gives no quantitative agreement between the experimental parameters and the calculated ones. The calculated resonance frequencies are too high because of the overestimated single bond character of the C-Cl bond. However, the relationship between the NQR parameters and the chlorine position is reproduced qualitatively. The molecular orbital calculations show that the chlorine atom at the 2- or 5-position gives higher resonance frequency than that for the chlorine atom at the 3- or 4-position. This is consistent with the results of the Zeeman study.

### References

- 1) M.J.S. and E.A.C. Lucken, *J. Chem. Soc.*, **1959**, 426.
- 2) K. Shimomura, *J. Phys. Soc. Jpn.*, **12**, 657 (1957).
- 3) M. Mishima and T. Okuda, *Bull. Chem. Soc. Jpn.*, **62**, 2263 (1989).
- 4) K. Shimomura, *J. Phys. Soc. Jpn.*, **12**, 652 (1957).
- 5) C. Dean, *Phys. Rev.*, **96**, 1053 (1954).
- 6) E.A.C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London and New York (1969), Chap. 10.
- 7) R. Bersohn, *J. Chem. Phys.*, **27**, 2078 (1954).
- 8) P. Bucci, P. Cecchi, and E. Scrocco, *Ric. Sci.*, **34**, 129 (1964).
- 9) M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4899 (1977).
- 10) M.J.S. Dewar, M.L. McKee, and H.S. Rzepa, *J. Am. Chem. Soc.*, **100**, 3607 (1978).
- 11) M.J.S. Dewar and J. McKee, *J. Comput. Chem.*, **4**, 84 (1983).
- 12) M.J.S. Dewar and H.S. Rzepa, *J. Comput. Chem.*, **4**, 158 (1983).
- 13) J. Ridley and M.C. Zerner, *Theoret. Chim. Acta*, **32**, 111 (1973).
- 14) A.D. Bacon and M.C. Zerner, *Theoret. Chim. Acta*, **53**, 21 (1979).

- 15) B. Bak, D. Christensen, L. Hansen-Hygaard, and J. Rastrup-Anderson, *J. Mol. Spectrosc.*, **7**, 58 (1961).
- 16) M.J.S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **99**, 4907 (1977).