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^{35}Cl NQR in 4,4′-Dichlorodiphenyl Sulfone

(NQR/Zeeman effect/sulfone)

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The ^{35}Cl NQR absorption frequencies of 4, 4′-dichlorodiphenyl sulfone have been measured as a function of temperature. This compound shows a single resonance line and a doublet, respectively, at room temperature and at 77 K, indicating the presence of at least two modifications. The phase change occurs near 152 K. The Zeeman effect of ^{35}Cl NQR line has been observed at room temperature in a single crystal. The quadrupole coupling constant and the asymmetry parameter are 68.592 and 0.098, respectively. There are two directions for the principal efg *z* axes making an angle of 100.4° which is coincident with the angle between the plane of the benzene ring. The single bond, ionic and double bond charactars are estimated, by means of the Dailey-Townes procedure, to be 0.718, 0.246 and 0.036, respectivly.

INTRODUCTION

According to the crystal structure of the compound 4,4′-dichlorodiphenyl sulfone established by X-ray[1)] and neutron diffraction[2)] studies, the crystal belongs to a monoclinic system and the space group is I2/a with four molecules in a unit cell with the dimensions $a=20.204$, $b=5.009$, $c=12.259$ Å, and $\beta=90°\ 34'$. This compound gave a single NQR line at room temperature in agreement with the results of the diffraction studies. Moreover, X-ray analysis revealed that the the chlorine atom is out of the plane of the benzene ring. It is, therefore, desirable to know how the pricipal axes of the electric field gradient (efg) tensors on the chlorine nucleus orient to the benzene ring.

The Zeeman effect of ^{35}Cl NQR lines in a single crystal was investigated to obtain information on the orientation of the principal efg axes and to clarify bond characters of the C-Cl bond. It will be revealed that the efg *y* and *z* axes lie in the plane of the benzene ring. The bond characters will be compared with those in 4,4′-dichlorodiphenyl sulfide.[3)]

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On the other hand, the title compound showed two nqr lines at 77 K. This suggests that the crystal stucture at 77 K is different from that at room temperature. In order to examine the phase change and molecular motions, temperature dependence of the resonance frequencies was measured.

EXPERIMENTAL

The ^{35}Cl nqr spectra were obtained using a Dean-type superregenerative spectrometer with frequency modulation as described previously.[4] The absorption line was observed on an oscilloscope. The resonance frequencies were determined with a VHF signal generator and a frequency counter, TR-5142G, from Takeda Riken Co., Ltd. The Zeeman effect was examined at room temperature using the zero-splitting cone method. The Zeeman field was supplied by means of a Helmholtz coil. Temperature was determined by use of a copper-constantan thermocouple.

4,4'-Dichlorodiphenyl sulfone was obtained commercially (Tokyo Chemical Industry Co., Ltd.) and was recrystallized from an ethanol solution. A single crystal was grown from the melt using the conventional Bridgman technique. The sample container was a Pyrex glass tube with 14.5 mm inner diameter.

RESULTS AND DISCUSSION

Temperature Dependence. At room temperature, a single ^{35}Cl resonance line was observed, as described above. According to diffraction studies,[1,2] the two chlorine atoms in 4,4'-dichlorodiphenyl sulfone are chemically and crystallographically equivalent. On the other hand, two resonance lines were observed at 77 K. This suggests that the chlorine atoms are situated on two nonequivalent crystal sites and that there are at least two modifications in the crystal of the title sulfone. The higher-temperature and lower-temperature phases are tentatively referred to as α-form and β-form, respectively.

Table I. NQR Parameters for 4,4'-Dichlorodipheny Sulfone

T/K	Frequency/MHz		η	e^2Qq/MHz
77	34.859	35.125		
152	34.786			
298	34.350		0.098	68.592
413	33.929			

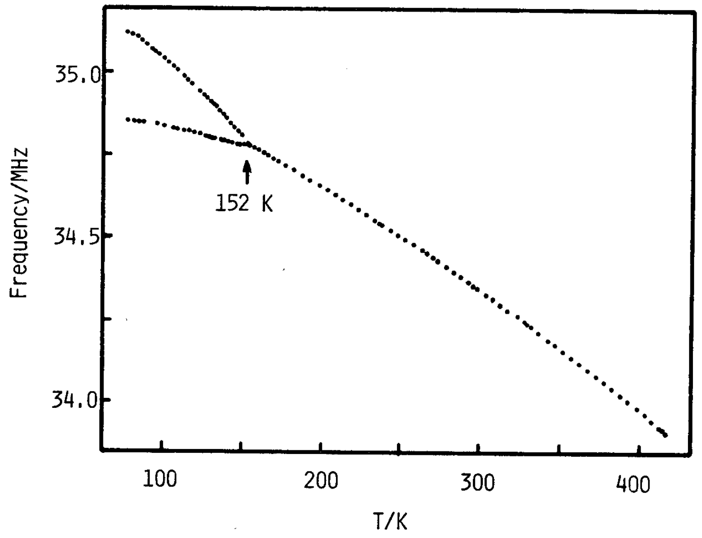

Fig. 1. Temperature dependence of the NQR frequency in 4,4'-dichlorodiphenyl sulfone.

The observed resonance frequencies are plotted against temperature in Fig. 1. The two absorption lines in the β-form approached each other gradually with increasing temperature and finally coalesced near 152 K. In the α-form the resonance frequency was decreased monotonously with increasing temperature in the range of 152 K to near melting point (147.5℃). To a fairly good approximation, the resonance frequency obeys the equation $\nu = a + BT + cT^2$ ($a = 35.127 \pm 0.001$, $b = (-1.862 \pm 0.011) \times 10^{-3}$ and $c = (-2.504 \pm 0.021) \times 10^{-6}$).

When a molecule is tosionally vibrated with mean square amplitudes ($<\theta_i^2>$) about X_i axes, the vibrationally-averaged coupling constant is related to that of the stationary molecule (e^2Qq_0) by the equation[5]

$$e^2Qq_{zz} = e^2Qq_0(1-(3/2)\Sigma<\theta_i^2>\sin\phi_i) \tag{1}$$

where ϕ_i is the angle between the efg z axis and the X_i axes. The choice of the torsional axes is shown in Fig. 2. The X_1 and X_2 axes are parallel, respectively, to the molecular twofold axis and to the straight line that passes through the two chlorine atoms, and the X_3 is perpendicular to these axes. The X-ray data on the molecular rigid body vibrations[1] show that the approximate relations $4<\theta_1^2> \simeq 3<\theta_2^2>$ and $<\theta_2^2> \simeq 2<\theta_3^2>$ hold. These relations are assumed for the molcular vibrations in the range from 152 to 413 K. If the torsional motion is approximated by a harmonic oscillator, the mean square amplitude is related to the torsional frequency (ω_i) as follows;[6]

$$2\Theta_i\omega_i<\theta_i^2> = \hbar\coth(\hbar\omega_i/2kT) \tag{2}$$

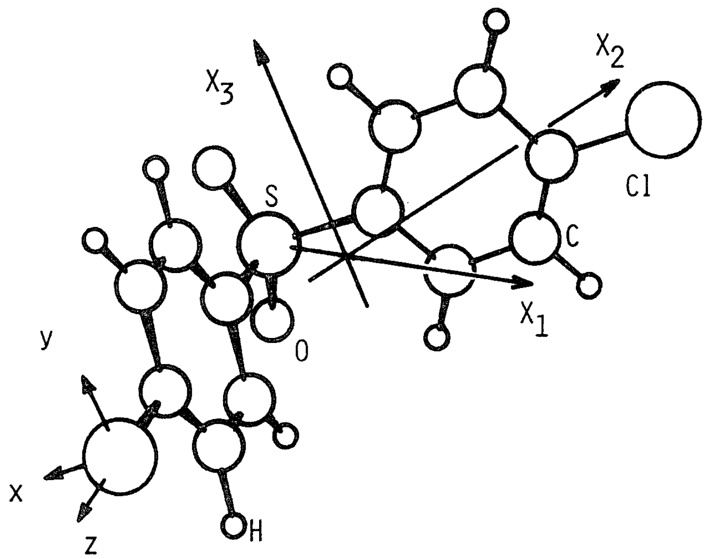

Fig. 2. Molecular geometry of 4,4′-dichlorodiphenyl sulfone and tosional axes.

where Θ_i is the moment of inertia about the X_i axis. The results obtained in this way are listed in Table Ⅱ. From the X-ray data $<\theta_1^2>$, $<\theta_2^2>$ and $<\theta_3^2>$ are calculated to be 3.71. 4.95 and 2.42×10^{-3} rad^2, respectively. These values are in good agreement with those at 153 K obtained from NQR. At room temperature, however, the calculation from the NQR data gives twice the values of the calculation from X-ray analysis. This discrepancy is attributable to the torsional motion of the benzene ring about the C-S bond.

Table Ⅱ. Frequencies and Mean Square Amplitudes of Torsional Motions in 4,4′-Dichlorodiphenyl Sulfone

T	$<\theta_1^2>$	$<\theta_2^2>$	$<\theta_3^2>$	ω_1	ω_2	ω_3
K		10^{-3} rad^2			cm^{-1}	
153	3.6	4.9	2.5	18.6	28.8	21.1
298	8.2	10.9	5.4	17.2	26.5	19.7
413	12.6	16.8	8.4	16.3	25.1	18.5

Orientation of the efg Axes. The Zeeman effct on a ^{35}Cl resonance line in 4,4′-dichlorodiphenyl sulfone was measured at room temperature using a single crystal. The zero-splitting patterns are shown in Fig. 3. The two loci were obtained for a resonance line, indicating that the crystal belongs to the monoclinic system in agreement with the results of X-ray analysis. The twofold axis was determined from the distribution of the zero-splitting loci. This axis coincides in direction with the crystal *b*-axis. The asymmetry parameter (η) was determined by following relation;[7)]

$$\sin^2\theta = 2/(3+\eta\cos2\phi), \qquad (3)$$

where θ and ϕ are polar and azimuthal angles, respectively. Least squares fits of the experimental data to such relationships are listed in Table I along with the other NQR paramers. The significant directions of the principal efg axes are listed in Table Ⅲ and are shown in Fig. 2.

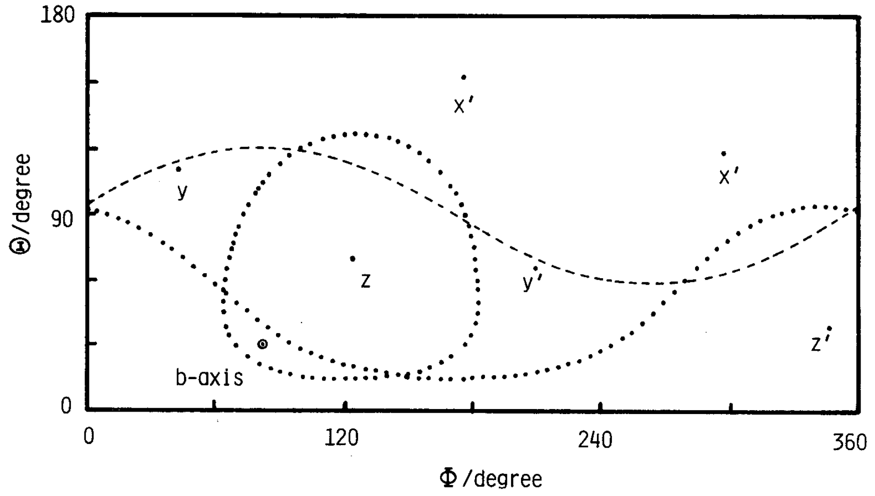

Fig. 3. Zerosplitting patterns of Zeeman lines in 4,4'-dichlorodiphenyl sulfone. The broken line indicates the *ac*-plane.

Table III. Orientation of efg Axes in 4,4-Dichlorodiphenyl Sulfone

Angle	NQR	X–ray
z–z'	100.39°	100.9°[a)]
z–b-axis	50.19	50.4 [b)]
x–x'	79.8	79.5 [c)]
y–ac-plane	2.6	3.7 [d)]

a) The angle between the C-Cl bonds. b) The angle between the b-axis and the C-Cl bond. c) The angle between the planes of the benzene rings. d) The angle between the ac-plane and the vector that lies in the plane of the benzene ring and is normal to the C-Cl bond.

According to X-ray analysis,[1)] the C-S-C bond angle and the Cl-S-Cl angle are 104.8° and 101.8° respectively. The planes of the rings orient to each other at 79.5°. The sulphur and chlorine atoms are therefore out of the ring plane. Comparison of the NQR data and the X-ray ones reveals that the efg *z* axis of the chlorine nucleus is almost parallel to this plane and the *x* axis is normal to it.

A slight deviation of the z axis from the direction of the C-Cl bond perhaps comes from π-interaction between the chlorine atom and the benzene ring and the vibration of the chlorine atom normal to the plane of the benzine ring.

Bond Character of C-Cl bond. The quadrupole coupling constant (e^2Qq_{zz}) can be related to the resonance frequecy (ν) and the asymmerty parameter by the following equation;

$$2\nu = |e^2Qq_{zz}/h| \, (1+\eta^2/3)^{1/2}. \tag{4}$$

The number of the unbalanced p-electron (U_p) is given by

$$U_p = |e^2Qq_{zz}| / |e^2Qq_{atom}|, \tag{5}$$

where e^2Qq_{atom} is the quadrupole coupling constant for the free chlorine atom. Using the value of $e^2Qq_{atom} = 109.74$ MHz, U_p was estimated to be 0.6250 from the experimental coulping constant. Assuming that the C-Cl bond is represented as a resonance of C-Cl $\longleftrightarrow$ C^+Cl^- $\longleftrightarrow$ C=Cl. U_p can be related to the single bond character (σ), the ionic charater (i) and the double bond character (f) as follows;[8]

$$U_p = \sigma(1-s) - (f/2)(1-2s)(1+\varepsilon). \tag{6}$$

Here ε is the correction parameter for the ionization and s is the fractional s character of the bonding orbital of the chlorine atom. The values of $\varepsilon = 0.15$ and $s = 0.15$ were assumed for the chlorine atom in accordance with Dailey and Townes.[9] The double bond character can be deduced from the equation[10]

$$\eta = 3f(1+\varepsilon)/(2U_p). \tag{7}$$

σ, f and i were estimated to be 0.718, 0.036, and 0.246, respectively. These values are comparable with those for 4, 4′-dichlorodiphenyl sulfide ($\sigma : f : i = 0.720 : 0.032 : 0.248$),[3] although at room temperature the resonance frequency in the sulfide is 0.33 MHz higher than that in the sulfone.[3] No significant difference in electronic distribution between the sulfone and the sulfide could be perceived by means of NQR.

In order to examine the contribution of the two oxygen atoms of the sulfone to the electronic charge distribution in the aromatic ring, MO calculations of MNDO[11-13] were carried out. For the molecular geometry of 4, 4′-dichlorodiphenyl sulfone the atomic coordinates obtained from the X-ray diffraction study[1] were used. On the other hand, no data on the configuration of 4,4′-dichlorodiphenyl sulfide are available. For the sulfide the geometry of the sulfine, exclusive of the oxygen atoms, was assumed, although the angles between the C-Cl bonds in the sulfide was reported to be 72° (or 98°) from the NQR Zeeman study on a single crytal.[3] The results are listed in Table Ⅳ.

The double bond characters of the chlorine atoms in the sulfone and the sulfide were estimated to be about 0.02 from the MO calcuations. These values are almost the same as those obtained from NQR. However, it is seen from the calculated *s* electron density that fractional *s* character of the chlorine atom was considerably overestimated. The value of 0.02 seems more suitable. Using this value, the bond characters σ, f and i are calculated to be in the ratio 61.8 : 3.6 : 34.6.

As compared with the orbital populations on the sulfide, the oxygen atoms of the sulfone enlarge undulation in the ***pi*** density. Although the density on the carbon atom at the 4-position is increased by about 0.04, the double bond character of the chlorine atom is little affected. As for the ***sigma*** electrons, as expected, the population on the carbon atom shows the greatest decrease at the 1-position. In spite of little variation in density on the carbon atoms at the 2- and

Table Ⅳ. Electronic Distribution of Choline Atoms and Other Significant Atoms in 4,4′-Dichlorodiphenyl Sulfone and 4,4′-Dichlorodiphenyl sulfide

	N_s	N_{px} [a]	N_{py}	N_{pz}	Net charge
sulfone					
Cl	1.981	1.970	1.994	1.141	−0.086
C(1) [b]	1.256	1.154	0.966	0.967	−0.344
C(2)	1.194	0.925	0.888	0.962	+0.031
C(3)	1.199	1.007	0.894	0.958	−0.058
C(4)	1.200	1.002	0.941	0.815	+0.044
sulfide					
Cl	1.981	1.973	1.994	1.151	−0.098
C(1)	1.219	1.052	0.934	0.901	−0.106
C(2)	1.195	0.969	0.902	0.951	−0.017
C(3)	1.198	0.999	0.901	0.956	−0.049
C(4)	1.198	1.038	0.807	0.941	+0.017

a) The value of N_{px} is nearly equal to the pi density.
b) The figures in the parentheses represent the positions of the carbon atoms.

4-positions, the oxygen atoms increase the ***sigma*** populations on the carbon atom at the 4-positions and the chlorine atom by 0.01. In solid, however, the variation in the ionic character atom of the order of 1% is masked by crystal-field effects. Judging from the electronic distributions in the sulfide and the sulfone, it is presumed that the bond character of the chlorine atom in dichlorodiphenyl sulfone is little different from the sulfide with the identical chlorophenyl groups, even though the chlorine atoms are bonded to the other positions of the benzene ring.

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