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Molecular Shape and Phase Transitions of 4,4'-Dichlorobenzophenone Studied by Means of NQR

(dichlorobenzophenone/NQR Zeeman effect/phase transitions)

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^{35}Cl NQR frequency in 4,4'-dichlorobenzophenone was observed as a function of temperature. It was revealed that there exist three modifications in the range of 77 K to 420 K. The first-order phase changes were found to occur at 186 K and 180 K. The Zeeman effect on the ^{35}Cl resonance line in the high-temperature phase was examined at room temperature by using a single crystal. The molecular shape was deduced on the basis of the axes of the electric field gradients.

The electric field gradients (efg) which arise from electronic distributions around a nucleus in a molecule afford useful information about chemical bonding. The directions of the principal efg axes relate closely to the bond directions and the magnitudes of the field gradients to the bond nature. NQR Zeeman analysis using a single crystal serves as a tool in determining the directions of the efg axes and the magnitude of the field gradients, although the resonant nuclei are limited to those having a nuclear spin $I \geqq 1$. In addition, information about phase changes and molecular motions can be obtained from the temperature variation of the resonance frequency.

The NQR frequency for 4,4'-dichlorobenzophenone (DCBP) at 77 K was previously reported.[1] However, the resonance frequencies at other temperatures and the molecular structure of DCBP have not been studied in detail.

In the present work, it will be revealed that there are three modifications in DCBP in the range of 77 K to its melting point. Furthermore, the molecular shape of the high temperature phase will be shown to be skewed on the basis of the Zeeman effect.

Experimental

DCBP was obtained commercially (Tokyo Chemical Industry Co. Ltd.) and was recrystallized in ethanol. A single crystal was grown using Bridgeman's technique. However, some attempts to prepare a large single crystal were unsuccessful. A single crystal was always accompanied by several small single crystals. A single crystal which was cut along cleavage planes was used for the Zeeman study.

The NQR spectrometer has been described elsewhere.[2] The frequencies were determined with an accuracy of 1 kHz by a frequency counter. The Zeeman effect was examined 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 measured with a Yokogawa 7563 digital thermometer by the use of a copper-constantan thermocouple. The temperature dependence of the resonance frequency was measured from 77 K up to the melting point.

Results and Discussion

Figure 1 shows the temperature dependence of ^{35}Cl NQR frequency of DCBP. The discontinuities of the resonance frequency at 187 K and 191 K reveal that there appear successively three crystal phases I, II and III with decreasing temperature. The measurements of the resonance frquencies in the vicinity of the transition points were repeated

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several times. It is surprising that Phase II exists in the very limited temperature range. The NQR spectrum for each phase consists of a resonance line, indicating that the two chlorine atoms of the DCBP molecule in each phase are equivalent. The resonance frequency at 77 K (Phase III) is in good agreement with the literature value.[1] The temperature dependence of each phase, except Phase II, was fitted to a quadratic equation

$$\nu_T = \nu_0 + AT + 2BT^2.$$

The parameters of this equation, together with other NQR parameters, are listed in Table 1. In Phase II the temperature range is too narrow for the quadratic equation to be applied to the temperature dependence of the resonance frequency.

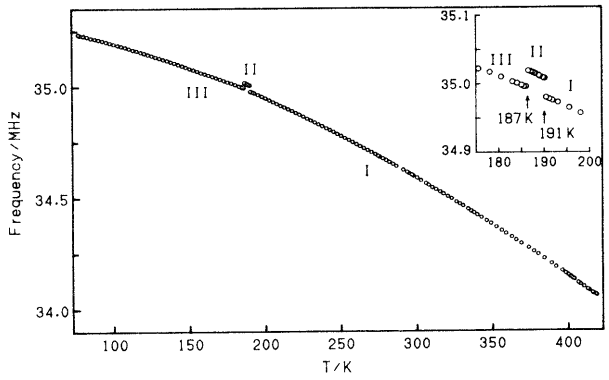

Fig. 1. Temperature dependence of ^{35}Cl NQR frequencies in 4,4'-dichlorobenzophenone.

The frequencies of torsional motions of the DCBP molecules in these phases can not be determined because of the unknown crystal structure. It is, however, possible to estimate the ratios of the torsional frequencies in the two phases from the parameters of the quadratic equation, assuming that the molecular structure is not so altered by phase change. Applying the harmonic oscillator model[3] to the torsional motion and using Brown's approximation,[4] the ratio of the average frequency in Phase I to the one in Phase III is calculated to be ca. 1.23 at 189 K. The torsional frequencies in the high-temperature phase are increased compared with those in the low-temperature phase. Unfortunately it is difficult to explain the variations in frequency at this stage, since the crystal structures of the two phases are unknown.

Table 1. ^{35}Cl NQR parameters and the temperature variations of 4,4'-dichlorobenzophenone

T/K	ν/MHz	Phase	η	e^2Qqh^{-1}/MHz	ν_0/MHz	A/kHzK^{-1}	B/HzK^{-2}
77	35.237	III			35.352	−1.16	−4.03
187	35.019	II					
191	34.980	I			35.428	−1.58	−4.02
298	34.599	I	0.116	69.045			

The Zeeman effect on the ^{35}Cl resonance line was observed at room temperature. The zero-splitting loci for Phase I is shown in Fig. 2. The resonance line gave only two patterns. Only one twofold axis was determined from the distributions of the efg axes, suggesting that the crystal of Phase I belongs to a monoclinic class.[5] The observed loci were analyzed by the method of least-squares to obtain the directions of the efg axes and asymmetry parameter (η). For ^{35}Cl nucleus the locus is described by the expression[6]

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

where θ_0 and ϕ_0 are polar and azimuthal angles, respectively, with respect to the normal coordinate system. The angles between the efg axes are listed in Table 2.

The quadrupole coupling constant (e^2Qqh^{-1}) are determined from the following relation

$$\nu = (e^2Qqh^{-1}/2)\ (1 + \eta^2/3)^{1/2},$$

where ν is the resonance frequency. The calculated parameters are listed in Table 1.

The twofold axis of the crystal is coincident with that of the DCBP molecule, *i.e.*, the direction of the C=O bond. The distributions of

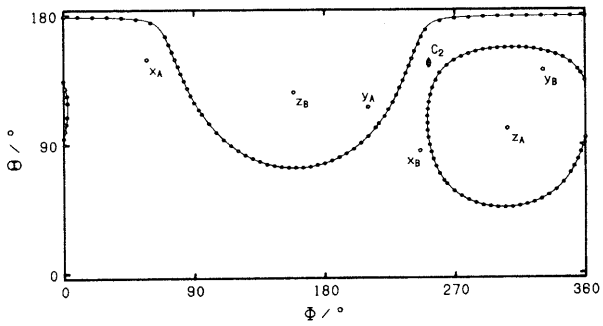

Fig. 2. Zero-splitting patterns of a ^{35}Cl NQR line in Phase I of 4,4'-dichlorobenzophenone. x_i, y_i and z_i indicate the directions of principal efg axes at the ith chlorine nucleus.

Table 2. Angles (degrees) between the efg axes

Axis	X_B	Y_B	Z_B	C_2	$Z_AZ_B$plane
X_A	123.33	45.14	63.40	62.45	58.09
Y_A	46.36	85.35	44.02	42.03	31.09
Z_A	61.90	45.25	122.10	61.05	0.00
X_B				60.89	56.22
Y_B				43.34	33.78
Z_B				61.05	0.00

the efg axes indicate that the DCBP molecule has no plane of symmetry. Therefore the molecule of Phase I has C_2 symmetry. The angle between the two C-Cl bonds is calculated to be 122.1°, assuming that the efg z axis is parallel to the bond direction. This value is very close to that expected from the hybrid orbitals on the carbon atom of the carbonyl group. The molecular shape of DCBP deduced on the basis of the Zeeman analysis is shown in Fig. 3.

It is generally assumed that the x axis is perpendicular to the aromatic ring and the y and z axes lie in the ring plane, since the x axis is normally parallel to the direction of the π bond. Following this convention the angles between the benzene rings and the plane containing the two C-Cl bonds are estimated to be *ca.* 33° and the ring planes are inclined at an angle of *ca.* 57° (or 123°) to each other, as can be seen from Table 2. Accordingly the DCBP molecule in Phase I is skewed. The mirror image of the molecular configuration shown in Fig. 3 is not superimposable on the original configuration. This suggests that in Phase I there are probably two kinds of crystals which are enantiomorphous. This may be related to the fact that plural single crystals were always obtained from melt.

The η-value for DCBP is somewhat large compared with those for the para substitution products of chlorobenzene that have been examined by the Zeeman study. The reported η-values are 0.067 for p-dichlorobenzene,[7] 0.049[8] or 0.06[9] for p-chloroaniline, 0.07 for p-chlorobenzyl chloride,[8] and 0.058 and 0.223 for p-chlorophenol.[10] (In chlorophenol there are two chemically different molecules and one of them has the hydrogen-bonded chlorine atom having a very large asymmetry parameter.) The angle between the ring plane and the C=O bond of the carbonyl group is calculated to be approximately 45° from the Zeeman data. This indicates that the π orbital of the benzene ring interacts appreciably with the σ and π orbitals of the carbonyl group. This interaction is probably a main cause of the comparatively large asymmetry parameter.

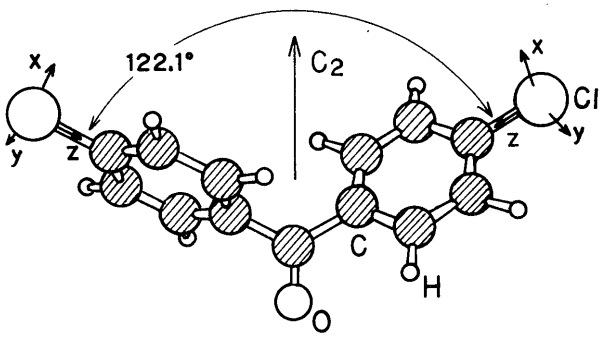

Fig. 3. Molecular shape of 4,4'-dichlobobenzophenone in Phase I and the efg axes.

From the quadrupole coupling constant and the η-value, the bond parameters were calculated using the atomic coupling constant for chlorine of 109.74 MHz.[11] Following the valence bond description,[12] the bond is described as a combination of ionic, singly and doubly bonded structures. The ionic, single bond and double bond characters of the C-Cl bond are in the ratio 23.2:72.1:4.7.

References

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