Shimane Ika Daigaku Kiyo (Bull. Shimane Med. Univ) vol.21, pp. 41-44, Dec. 1998

Zeeman Effect of ^{35}Cl NQR on 2,4,6-Trichloroanisole

(NQR/Zeeman effect/trichloroanisole)

Mitsuo MISHIMA

In 2,4,6-trichloroanisole, three ^{35}Cl NQR lines were observed in the range of 77 K to the melting point. The Zeeman effect on each resonance line was examined at room temperature using a single crystal. The values of the asymmetry parameters for the two higher-frequency lines were ca. 0.12, whereas that for the lower-frequency line was 0.08. The angles between the C—Cl bonds were estimated to be 117.7°, 119.0°, and 123.4° on the basis of the orientations of the axes of the electric field gradients. The two higher-frequency lines were assigned to the chlorine atoms at the ortho positions and the lower frequency line to the chlorine atom at the para position on the basis of the angles between the C—Cl bond angles and the asymmetry parameters.

Introduction

Several chlorinated anisoles were studied by ^{35}Cl NQR on polycrystalline samples [1-4], though their crystal structures are unknown. The resonance frequencies of these compounds at 77 K are widespread from 34.8 MHz to 38.4 MHz. Furthermore, with an increasing number of the substituted chlorine atoms in these chlorinated anisoles the ^{35}Cl resonance frequencies are shifted to higher frequencies. These are of interest in connection with the molecular structures and the character of the C—Cl bonds. However, surprisingly the trichlorinated anisoles have not been the subject of any studies. So, we chose 2,4,6-trichloroanisole (TCA) as the subject compound. The angles between the C—Cl bonds of TCA and their bond character were studied by the Zeeman effect of ^{35}Cl NQR using a single crystal.

Experimental

TCA was a commercial product (Tokyo Kasei) and was purified by recrystallization in ethanol. A single crystal of TCA was grown using the Bridgeman method. The Zeeman effect was examined by means of the zero-splitting cones method [5]. The loci were analyzed by the least squares method.

*Department of Chemistry

The ^{35}Cl NQR spectra were recorded with a super-regenerative spectrometer [6]. The resonance frequency was determined with an accuracy of 1 kHz by a frequency counter. Temperature was determined by use of a copper-constantan thermocouple.

Results and Discussion

There exists two types of chemically different chlorine atoms, i.e., chlorine atoms at the ortho positions and the one at the para positionin TCA. Therefore the TCA is expected to give two resonance lines, if the TCA molecule is symmetric. In reality, TCA gave three resonance lines, the frequencies of which decreased monotonously with an increase in temperature. The temperature dependence of the resonance frequencies is shown in Figure 1. The resonance frequencies are listed in Table 1. The NQR spectrum at room temperature is comprised of the resonance lines that are distributed at nearly regular intervals. It is noteworthy that the ν_2 has a tendency to approach to some extent, the ν_3 line with a decrease in temperature, as seen in Fig. 1. However, the assignment of the resonance lines to particular chlorine atoms is difficult to make from the spectral pattern alone. Information on the orientations of the axes of the electric field gradient (efg) tensor and the NQR parameters is available for the assignment of the resonance lines.

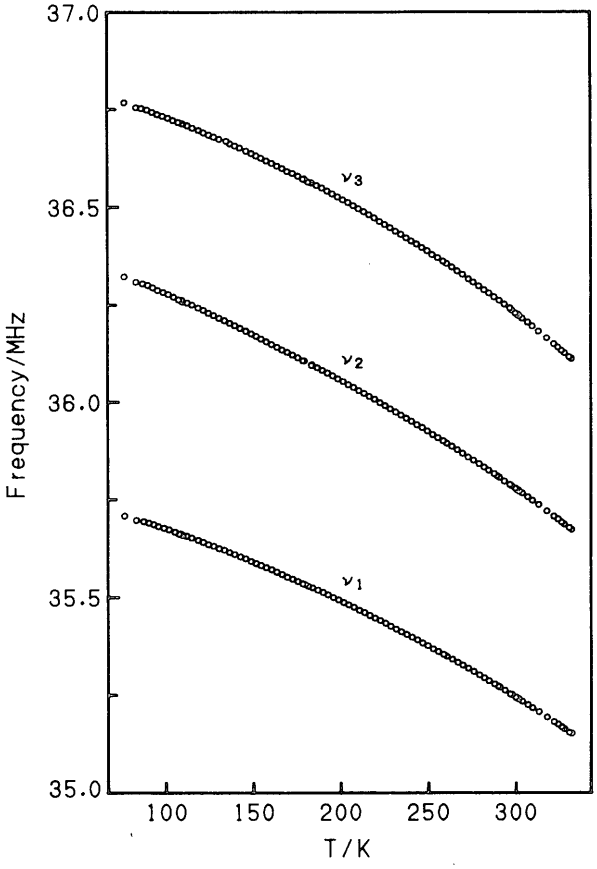

Fig. 1. Temperature dependence of ^{35}Cl resonance frequencies of 2,4,6-trichloroanisole.

Table 1. ^{35}Cl NQR parameters for 2,4,6-trichloroanisole at 297 K.

Line	Frequency/MHz[a)]	η	e^2Qqh^{-1}/MHz
ν_1	35.252	0.083±0.001	70.424±0.002
ν_2	35.778	0.116±0.001	71.425±0.003
ν_3	36.241	0.119±0.003	72.313±0.005

a) The corresponding resonance frequencies at 77 K are 35.708, 36.322, and 36.766 MHz for ν_1, ν_2 and ν_3, respectively.

Figure 2 shows the zero-splitting patterns obtained from the Zeeman effect of the resonance lines of TCA at room temperature. The directions of the efg axes are represented by x_i, y_i, and z_i at the ^{35}Cl nucleus contributing to the ν_i line. Each resonance line gave a pair of loci. These are related to each other by the twofold axis (C_2) which is determined from the distribution of the efg axes, suggesting that the crystal of TCA is monoclinic [7]. The directions of the efg axes and the asymmetry

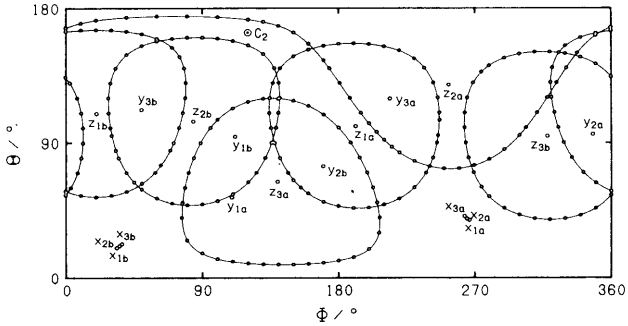

Fig. 2. Zero-splitting patterns of ^{35}Cl NQR lines in 2,4,6-trichloroanisole. x_i, y_i, and z_i indicate the directions of the principal efg axes at the halogen nucleus giving a ν_i line.

parameter (η) were determined using the following relation;

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

where θ_0 and ϕ_0 are polar and azimuthal angles, respectively. The quadrupole coupling constants (e^2Qqh^{-1}) were calculated from the following relation;

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

The values of the asymmetry parameters and the coupling constants are listed in Table 1 along with the resonance frequencies. It is noteworthy that the value of the asymmetry parameter for the ν_2 line is almost the same as that for the ν_3 line and is 1.5 times that for the ν_1 line. The chlorine atoms that the ν_2 and ν_3 lines should be assigned to appears to be chemically equivalent, since the asymmetry parameter is closely related to the bond character.

The angles between the efg axes are given in Table 2. In halegenated organic compounds the efg z and x axes at the halogen atoms are related to the directions of the sigma and pi orbitals, respectively. The three C—Cl bonds in a molecule are inclined at an approximate angle of 120° to one another. Therefore, the angles between the C—Cl bonds in the molecule situated at a particular crystal site can be estimated on the basis of the efg axes. The results are shown in Fig. 3. The ν_2 and ν_3 lines were assigned to the chlorine atoms at the ortho positions and the remaining ν_1 line to the chlorine atom at the para position. These assignments are based on the asymmetry parameters and

Table 2. Angles (degrees) between the efg principal axes in 2,4,6-trichloroanisole.

a) Angles between the z axes

Axis	Z_{1b}	Z_{2a}	Z_{2b}	Z_{3a}	Z_{3b}	C_2
Z_{1a}	32.23	118.91	103.36	117.69	124.54	73.86
Z_{1b}		103.32	119.00	128.97	117.62	73.93
Z_{2a}			54.31	123.39	112.43	62.87
Z_{2b}				112.39	123.37	62.82
Z_{3a}					21.33	79.35
Z_{3b}						79.32

b) Angles between the x axes

Axis	X_{1b}	X_{2a}	X_{2b}	X_{3a}	X_{3b}	C_2
X_{1a}	52.75	1.37	54.16	3.36	55.68	26.27
X_{1b}		53.93	1.43	55.93	3.00	26.48
X_{2a}			55.33	2.04	56.87	27.66
X_{2b}				57.35	1.56	27.68
X_{3a}					58.88	29.67
X_{3b}						29.21

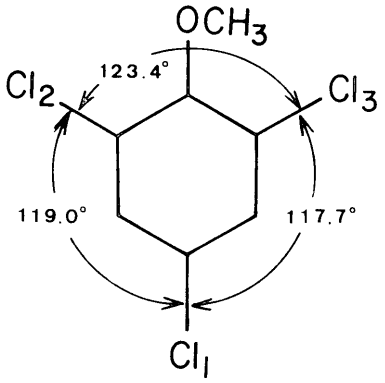

Fig. 3. Angles between the C−Cl bonds in 2,4,6-trichloroanisole.

the angles between the C—Cl bonds.

As described above, the asymmetry parameters for the ν_2 and ν_3 lines are very similar in magnitude and are fairly greater than that for the ν_1 line. Furthermore, the angle between the C−Cl_2 and C−Cl_3 bonds is considerably greater than the other corresponding angles. In the TCA molecule the methoxy group lies between the two ortho chlorine atoms. It is therefore presumed that the steric repulsion between this group and the two chlorine atoms pushes the two chlorine atoms toward both sides. In the related compounds such enlarged angles were observed; for example, 122.1° in 2,4,6-trichloronitrobenzene [8], 125.1° in 2,6 dichlorobenzyl -bromide [9], 125.1° in 2,6-dichlorobenzyl chloride [10], and 129.0° in 2,6-dichlorobenzaldehyde [11].

The three C—Cl bonds are somewhat out-of-plane. It is of interest to know which bond deviates from the ring plane. Unfortunately the exact plane cannot be defined from the Zeeman experiment except that all the efg z axes in a molecule are completely coplanar. Referring to the plane made up of the C—Cl_1 and C—Cl_2 bonds, the deviation of the C—Cl_3 bond from this plane are calculated to be 0.78° ±0.02°. This discrepancy may result from the repulsion between the methoxy group and the ortho chlorine atoms, as not fully understood.

The populations of the p orbitals, N_i, on the chlorine atom are related to the coupling constant and the asymmetry parameter as follows:

$$e^2Qqh^{-1} = e^2Qq_0h^{-1}[(N_x + N_y)/2 - N_z], \quad (3)$$

and

$$\eta e^2Qqh^{-1} = (3/2)e^2Qq_0h^{-1}[N_y - N_x], \quad (4)$$

where the atomic quadrupole coupling constant, $e^2Qq_0h^{-1}$, is 109.74 MHz for ^{35}Cl[12]. The calculated populations thus obtained are given in Table 3. The values of N_x for the Cl_2 and Cl_3 atoms are very similar in magnitude and are less than that for the Cl_1 atom. This supports the above assignments of the resonance lines. The Cl_2 and Cl_3 atoms differ in the N_z value from one another, suggesting that an increase in the ionic character of the C—Cl_2 bond lowers the resonance frequencies of the Cl_2 atom.

Table 3. Orbital populations in 2,4,6-trichloroanisole.

Atom	N_x	N_y [a]	N_z
Cl_1	1.964	(2)	1.337
Cl_2	1.950	(2)	1.324
Cl_3	1.948	(2)	1.315

a) Assumed to be 2.

References

[1] H.C.Meal, *J. Amer. Chem. Soc.*, **74**, 6121 (1952).

[2] P.C.Bray and R.G.Barnes, *J. Chem. Phys.*, **27**, 551 (1957).

[3] P. C. Casabella, P. J. Bray, S. L. Segel and R.G.

Barnes, *J. Chem. Phys.*, **25**, 1280 (1956).

[4] V. S. Grechishkin and I. A. Kyuntsel, *Trudy Estestvennonauchnog Instituta Permskogo Gosudarstvennogo Universiteta*, **12**, 15 (1966). I.P. Biryukov, M.G. Voronkov, and I.A. Safin, "Tables of Nuclear Quadrupole Resonance Frequencies", Israel Program for Scientific Translations, Jerusalem (1969).

[5] C.Dean, *Phys. Rev.*, **96**, 1053 (1954).

[6] M.Mishima and T.Okuda, *J. Mol. Chem.*, **412**, 205 (1997).

[7] K.Shimorura, *J. Phys. Soc. Jpn.*, **12**, 652 (1957).

[8] M. Mishima, *Bull. Shimane Med. Univ.*, **19**, 49 (1996).

[9] M. Mishima, *Bull. Shimane Med. Univ.*, **14**, 21 (1991).

[10] M. Mishima, *Bull. Shimane Med. Univ.*, **16**, 41 (1993).

[11] M. Mishima, *Bull. Shimane Med. Univ.*, **15**, 77 (1992).

[12] V. Jaccarino and I.G.King, *Phys. Rev.*, **43**, 471 (1951).

(Received October 2, 1998)