Shimane Ika Daigaku Kiyo（Bull. Shimane Med. Univ）vol.22, pp. 23-26, Dec. 1999

^{127}I Nuclear Quadrupole Resonance in 4,4'-Diiodobiphenyl

（NQR／Zeeman effect／4,4'-Diiodobiphenyl）

Mitsuo MISHIMA*

4,4'-Diiodobiphenyl（DIB）gave only one ^{127}I NQR line corresponding to the $\pm 1/2 \longleftrightarrow \pm 3/2$ transition. Zeeman effect of the ^{127}I resonance line was studied at room temperature in a single crystal of DIB. Four nonequivalent electric field gradient（efg）systems were observed. It was deduced on the basis of the orientations of the efg axes that in the crystal the benzene rings in the molecule are mutually inclined at an angle of 77.8°±0.5°and the angle between the C－I bonds is 176.1°±0.1°. Temperature dependence of the resonance frequency was interpreted in terms of torsional motions of the DIB molecules.

Introduction

Biphenyl is not planar in the gaseous phase and the benzene rings are twisted by 41.6°from each other.[1] In contrast, in the solid phase biphenyl is a perfectly planar molecule with C_{2v} symmetry in spite of the short distances between the hydrogen atoms at the ortho positions to the C－C bridge bond linking the rings.[2] 4,4'-Dihalobiphenyls in 1,1,2,2-tetrachloroethane solutions have also twisted structures similar to the gaseous molecule of biphenyl and the angles between the rings were estimated to be about 45°.[3] It has been suggested that the conjugation between the rings and the steric repulsion between the ortho-hydrogen atoms are responsible for the configuration of biphenyl.[4] On the other hand, it has been claimed that attractive van der Waals' forces between the ortho hydrogen atoms play a significant part for the non-planar configuration.[1]

The NQR frequencies of the derivatives of biphenyl were published only for 4,4'-dichlorobiphenyl (DCB)[5], 4,4'-dibromobipheyl (DBB)[6], and 4-iodobiphenyl[7]. The NQR spectra of DCB and DBB, which are very similar in spectral pattern to each other, consist of four resonance lines, suggesting that their crystal structures are somewhat complicated and there are two or four kinds of molecules in the unit cell. Although the resonance of DIB had not been observed, our preliminary observations revealed that DIB gave a single ^{127}I resonance line. This indicates that the crystal structure of DIB is comparatively simple and differs from those of DCB and DBB.

Our considerable interest is in whether 4,4'-dihalobiphenyl similar in steric repulsion to biphenyl has a planar structure in the crystalline state. The convenient means of probing the configuration of the halogenated biphenyl is the Zeeman effect on NQR which provides information about the bond direction and the orientation of the aromatic ring. DIB was chosen as a target compound because of its simple crystal structure, and the configuration of DIB was examined by the Zeeman analysis using a single crystal.

Experimental

The spectrometer used for the detection of the ^{127}I resonance lines was a super-regenerative parallel transmission line oscillator with a frequency modulation (similar to the one described by Kojima et al.[8]) The Zeeman effect was examined at room temperature using the zero-splitting cone method. A magnetic field of 100 to 200 mT was applied by means of a Helmholtz coil. The orientation of the magnetic field for the zero-splitting was determined by means of polar coordinates（Θ, 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 use of a copper-constantan thermocouple.

Commercial DIB（Tokyo Chemical Industry, E.P.）was recrystallized in benzene. A single crystal was grown from melt.

Results and Discussion

The NQR spectra of DCB and DBB consisting of four lines are similar in pattern,[5,6] suggesting that the crystals of these biphenyl derivatives are isomorphous. In contrast, the spectrum of DIB consists of a single line. The crystal structure of DIB is apparently different from those of DCB and

---

*Department of Chemistry

DBB. The two iodine atoms of DIB are crystallographically equivalent, and hence the DIB molecule is expected to have at least a twofold axis. The ν_1 resonance frequency of ^{127}I corresponding to the ±1/2←→±3/2 transition at room temperature is somewhat higher in DIB than in 4-iodobiphenyl.[7)]

The zero-splitting patterns for the ν_1 line are shown in Fig. 1. The resonance line gave four Zeeman loci. The loci of A_1 and B_1 overlap those of A_2 and B_2, respectively, over the fairly wide range, though the observed values ($\pi-\Theta, \Phi+\pi$) equivalent to the ones (Θ, Φ) are not plotted in the figure. Three twofold axes (C_2, C_{2a}, and C_{2b}) were determined from the distributions of the efg axes. These axes lie in the same plane and the angles between the C_2 and C_{2a} axes and between the C_2 and C_{2b} axes are slightly smaller than 90°. Furthermore, the C_{2a} and C_{2b} axes are exchanged for each other for the operation of rotation around the C_2 axis. Accordingly, the C_2 axis corresponds to the twofold axis of the crystal and the C_{2a} and C_{2b} axes to those of the molecules. The C_{2a} and C_{2b} axes are assigned to the molecules situated at the crystal sites, A and B, respectively (see Fig. 1). The crystal of DIB belongs to a monoclinic system,[9)] and each of the two iodine atoms in the molecule gives two Zeeman patterns.

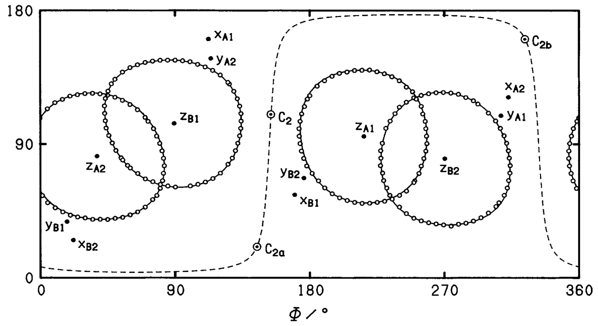

Fig. 1. Zero-splitting patterns of a ^{127}I NQR line in 4,4'-diiodobiphenyl. x_i, y_i and z_i indicate the principal efg axes at the iodine nuclei. The broken line presents the plane including the twofold axes (C_2, C_{2a}, and C_{2b}). The subscripts, A and B indicate that the iodine atoms belong to the molecule situated at the different crystal sites.

The Zeeman locus is expressed for I=5/2 as follows:10)

$$\sin^2\theta_0 = A/(B - C\cos 2\phi_0) \qquad (1)$$

where θ_0 and ϕ_0 are polar and azimuthal angles of the zero-splitting cone, respectively. A, B and C are the constants depending on the asymmetry parameter (η) and the transition state. The η-value was determined from the values of θ_0(max) and θ_0(min). The coupling constant $(e^2Q\ q^{-1})h$ was determined by solving the secular equation for the pure quadrupole interaction,[10)] using the experimentally determined η-value and the resonance frequency. The NQR parameters thus obtained are listed in Table 1 along with the resonance frequencies.

The ν_2 frequencies corresponding to the ±3/2←→±5/2 transition was measured only at room temperature because of a weak resonance. The η-value was also determined from the frequency ratio of ν_2/ν_1. The value determined from the Zeeman effect is somewhat smaller than that from the frequency ratio. This presumably results from overlapping of the Zeeman patterns.

The angles between the efg axes and the symmetry axes are listed in Table 2. Fortunately, the overlapping of the loci

Table 1. ^{127}I NQR parameters for 4,4'-diiodobiphenyl

Line	Frequency/MHz 77 K	Frequency/MHz 298 K	η	$e^2Q\ q^{-1}h$/MHz
ν_1	280.889	277.19	0.045	1843.9
ν_2		555.48	(0.051)[a)]	(1842.6)[a)]

a) The values in the parentheses were determined from the frequency ratio of ν_2/ν_1.

Table 2. Angles (degrees) between the efg axes and the twofold axes

a) Angles between the x axes

Axis	x_{A2}	x_{B1}	x_{B2}	C_{2a}	C_{2b}	C_2
x_{A1}	77.2	67.6	31.3	38.6	37.3	56.3
x_{A2}		31.3	70.3	38.6	39.9	56.1
x_{B1}			78.0	37.7	39.0	56.1
x_{B2}				40.3	39.0	54.6

b) Angles between the y axes

Axis	y_{A2}	y_{B1}	y_{B2}	C_{2a}	C_{2b}	C_2
y_{A1}	77.1	86.7	44.9	51.5	52.7	46.5
y_{A2}		45.2	84.4	51.5	50.2	47.6
y_{B1}			77.9	52.3	51.1	46.8
y_{B2}				49.8	51.0	48.0

c) Angles between the z axes and the twofold axes

Axis	z_{A2}	z_{B1}	z_{B2}	C_{2a}	C_{2b}	C_2
z_{A1}	176.16	124.14	55.74	88.09	88.75	62.13
z_{A2}		55.99	124.43	88.06	87.40	62.15
z_{B1}			176.12	88.66	87.98	62.01
z_{B2}				87.47	88.14	62.28
C_{2a}					178.6	89.4
C_{2b}						89.2

does not exert significant influence on the orientations of the efg axes, because the C_2 axis determined from the z axes is almost coincident with that from the x or y axes.

It is usually assumed that on the halogen atom bonded to the aromatic ring the z axis is parallel to the bond direction and the x and y axes are perpendicular and parallel to the ring plane, respectively. The z axes belonging to a particular molecule can be easily assigned, since the two C—I bonds are nearly on the straight line. The angle between the C—I bonds in the molecule is estimated to be $176.14^\circ \pm 0.06^\circ$, suggesting that the DIB molecule is slightly bent in the crystal. The angles between the x axes and between the y axes indicate that the rings of DIB are mutually inclined at an angle of $77.8^\circ \pm 0.5^\circ$ in contrast to the crystal of biphenyl. This suggests that there is no conjugation between the rings and the DIB molecule in the crystal is completely free from intramolecular steric repulsion. Figure 2 shows the configuration of the DIB molecule in the crystal deduced from the Zeeman study.

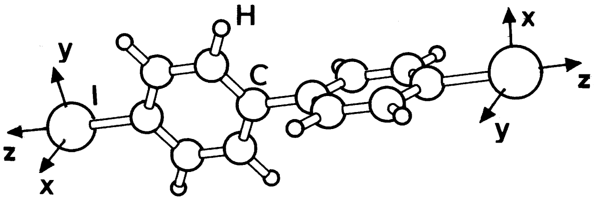

Fig. 2. Configuration of 4,4'-diiodobiphenyl and the orientations of the efg axes on the iodine atoms.

It has been suggested on the basis of the X-ray data that in biphenyl intermolecular forces play a significant part for the planar structure.[2] It has also been suggested that in addition to repulsive van der Waals' forces attractive van der Waals' forces of the London type between the ortho hydrogen atoms are responsible for the non-planar structure of biphenyl in the gaseous phase.[1] DIB and biphenyl are quite similar in interaction between the ortho hydrogen atoms. The bridge bond in biphenyl is lengthened by the repulsion between the ortho hydrogen atoms and is longer by 0.017 nm in the solid phase than in the gaseous phase.[2] Even in the gaseous molecule, the length of the bridge bond (0.149 nm) is not shorter than the sp^2-sp^2 single bond length (0.147 nm).[1] It appears that the conjugation is not so important for determining the angle between the rings, especially in the crystal. In the solid phase, intermolecular forces probably play the most important role in determining the molecular configuration, considering the approximately orthogonal structure of DIB which is in a marked contrast to the planar structure of biphenyl.

The resonance frequency of the ν_1 line of ^{127}I is plotted against temperature in Fig. 3. The frequency decreases with an increase in temperature and a phase transition is not found. The data for the frequency variation with temperature can be expressed by the following quadratic equation,

$$\nu = a_0 + a_1T + a_2T^2, \qquad (2)$$

$$a_0 = 281728.6 \pm 0.7 \text{ kHz},$$

$$a_1 = -9.525 \pm 0.065 \text{ kHzK}^{-1},$$

$$a_2 = -(1.916 \pm 0.013) \times 10^{-2} \text{ kHzK}^{-2}.$$

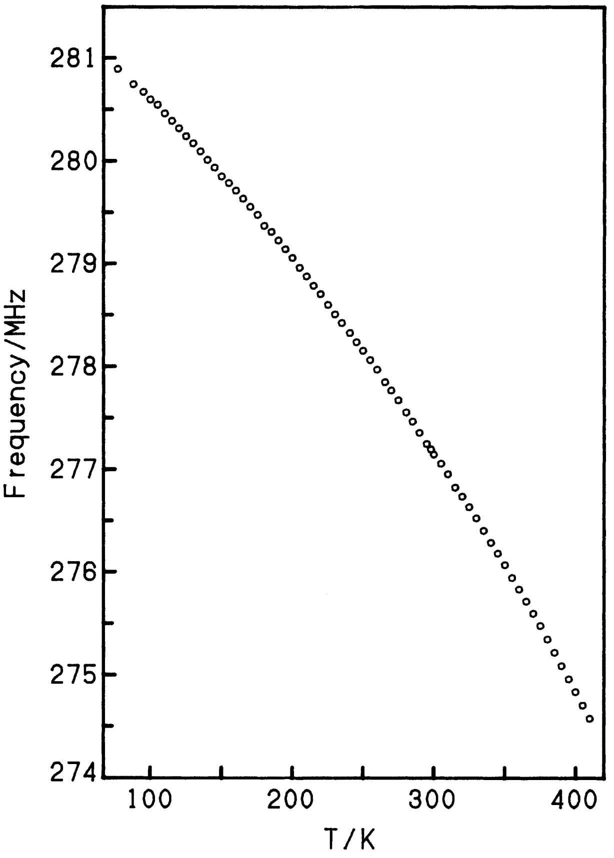

Fig. 3. Temperature dependence of the ^{127}I NQR frequency, ν_1, in 4,4'-diiodobiphenyl.

The asymmetry parameter for the iodine atom in DIB is negligibly small. When $\eta=0$, the quadrupole coupling constant is related to the mean square amplitudes around the efg x and y axes, $<\theta_x^2>$ and $<\theta_y^2>$, as follows:

$$e^2Qqh^{-1} = e^2Q_0qh^{-1}[1-3(<\theta_x^2>+<\theta_y^2>)/2], \qquad (3)$$

where $e^2Q_0qh^{-1}$ is the coupling constant in the stationary molecule. The molecular dimensions of biphenyl and the inter planar angle determined from the Zeeman effect were applied to the geometry of DIB since the moments of inertia cannot be accurately evaluated because of the unknown crystal structure of DIB. The moments of inertia of the DIB molecule around the x and y axes are nearly equal since the rings are nearly at right angles to each other. They are roughly estimated to be 1.47×10^{-43} kgm^2.

Considering the moments of inertia, it was assumed that $<\theta_x{}^2> = <\theta_y{}^2>$. Applying the Brown's approximation11), a_1 and a_2 are expressed as follows:

$$a_1 = -3k\,a_0/(\omega_0{}^2\Theta), \qquad (4)$$

$$a_2 = 2a_1 g\ ,$$

where ω_0, Θ and k are the torsional oscillation frequency at 0 K, the moment of inertia, and the Boltzmann constant, respectively. In a quasi-harmonic approximation, the temperature dependence of the torsional frequency is expressed empirically by

$$\omega_T = \omega_0(1 - gT), \qquad (5)$$

where g is a positive constant.12)

Using Eqs. (3), (4), and (5), the values of $g = 1.01\times10^{-3}$ K^{-1} and $\omega_0 = 153$ cm^{-1} are obtained for the assumed moment of inertia. The torsional frequency at 300 K is calculated to be 107 cm^{-1}. One of the Raman lines of lattice modes is presumed to exist near 110 cm^{-1} at room temperature.

From the values of the asymmetry parameter and the coupling constant, the ionic and double bond characters are calculated to be 2.3 and 2.6 percent, respectively, using the quadrupole coupling constant (2292.712 MHz) for the free iodine atom13). The iodine atoms of DIB are little charged, since negative and positive charges on the iodine atom are canceled out.

References

1) O.Bastiansen and M.Traetteberg, *Tetrahedron*, **17**, 147 (1962).

2) A.Hargreaves and S.H.Rizvi, *Acta Crystallogr.*, **15**, 365 (1962).

3) R.J.Kurland and W.B.Wise, *J. Amer. Chem. Soc.*, **86**, 1877 (1964).

4) I.Fischer-Hjalmars, *Tetrahedron*, **19**, 1805 (1960).

5) G.K.Semin, T.A.Babrushkina, and V.I.Robas, *Zh. Fiz. Khim.*, **11**, 2564 (1964); I.P.Biryukov, M.G.Voronkov, and I.A.Semin, "Tables of Nuclear Quadrupole Resonance Frequencies," IPST Press, Jerusalem (1969).

6) P.J.Bray and R.G.Barnes, *J. Chem. Phys.*, **22**, 2023 (1954); H.Hatton, and R.V.Rollin, *Trans. Faraday Soc.*, **50**, 358 (1954).

7) G.W.Lutwig, *J. Chem. Phys.*, **25**, 159 (1956).

8) S.Kojima, K.Tsukada, and A.Shimauchi, *J. Phys. Soc. Jpn.*, **9**, 795 (1954).

9) K.Shimomura, *J. Phys. Soc. Jpn.*, **12**, 657 (1957).

10) T.P.Das and E.L.Hahn, "Nuclear Quadrupole Resonance Spectroscopy," Solid State Physics, Suppl. 1, Academic Press New York (1957) Chap. 1.

11) R.J.Brown, *J. Chem. Phys.*, 2, 199 (1960).

12) I.Ichishima, *Nippon Kagaku Zasshi*, **71**, 607 (1960); A.A.Maradudin and R.F.Waller, *Phys. Rev.*, **125**, 1277 (1962).

13) V.Jaccarino, J.G.king, R.H.Satten, and H.H.Stroke, *Phys. Rev.*, **94**, 1978 (1954).

(Received October 29, 1999)