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Zeeman Effect on ^{81}Br NQR in Phosphorus Tribromide-Boron Tribromide

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The Zeeman effect on ^{81}Br NQR in a single crystal of $PBr_3 \cdot BBr_3$ was studied at room temperature. The crystal has an orthorhombic symmetry. The bond angles have been found to be 111.2±0.1° and 111.5±0.1° for Br–B–Br, and 107.0±0.1° and 109.1±0.3° for Br–P–Br. The Br atoms of BBr_3 group have relatively large values of η, 0.151 ± 0.004 and 0.120 ± 0.007, while the Br atoms of PBr_3 group have small values, 0.025 ± 0.005 and 0.020 ± 0.004. The large η values of Br atoms of BBr_3 group are ascribed to the π bonding existing in the B–Br bonds.

It is of interest to investigate the halogen nuclear quadrupole resonance (NQR) of Lewis acid-base complexes $PX_3 \cdot BY_3$ (X, Y=Cl, Br, or I), because both donors PX_3 and acceptors BY_3 contain halogen atoms. Furthermore, the strong interaction between the donors and the acceptors may shift the resonance frequency more than that expected from the crystalline field effects. The previous paper has reported the ^{79}Br and ^{127}I NQR frequencies of $PBr_3 \cdot BBr_3$, $PBr_3 \cdot BI_3$, and $PI_3 \cdot BBr_3$ at 77 K.[1] For these complex-formations, the resonance frequencies (or quadrupole coupling constants) of the donors increased significantly compared to those of the parent molecules, while those of the acceptors also increased by a small extent. The frequency increase in the donors shows that the electric charge on X atoms of PX_3 decreases through p_σ bonds on complexation. In contrast, the charge on Y atoms of BY_3 may increase through both p_σ and p_π bonds. The small increase in frequency in acceptors may be net results of the two opposite effects: frequency lowering and raising due to the increase of the number of p_σ and p_π electrons of the Y atoms, respectively.

The ground state wave function Ψ_N of the complex $PX_3 \cdot BY_3$ may be approximately expressed according to Mulliken[2] by

$$\Psi_N = a\Psi_0(PX_3, BY_3) + b\Psi_1(X_3P^+ - B^-Y_3), \qquad (1)$$

where Ψ_0 represents a no-bond structure and Ψ_1 a dative structure. (Chemical experience shows $b^2 > a^2$ in Eq. 1.) This equation shows that a decrease in B–Y π bonding will occur upon progressive increase of the dative structure. On the one hand, the asymmetry parameter η is a measure of the π character of chemical bond when only one of the p_π lone-pair orbitals of halogen atoms can interact to form a π bond.[3] Relatively large values of η, 0.104 and 0.173, were found for $-BI_3$ of $PBr_3 \cdot BI_3$.[1] Another contributions to η arise from the intermolecular bonding in which the relevant atoms participate and the asymmetric distributions of electric charges around the bonds. It is, therefore, desirable to estimate such contributions in order to discuss the bond nature. The η values of X atoms in PX_3 group will offer a clue for this. The η of I atoms in $PI_3 \cdot BBr_3$ have, however, not been obtained owing to the failure to detect these ($m = \pm 3/2 \leftrightarrow \pm 5/2$) transitions. Nor have structural studies of the $PX_3 \cdot BY_3$ been carried out. We examined the Zeeman effect on ^{81}Br NQR for $PBr_3 \cdot BBr_3$ (which is stable on melting, unlike the other complexes stated above) in order to obtain precise NQR parameters as well as information about crystal and molecular structure.

Experimental

The complex was prepared as described previously[1] using Shlenk type glasswares[4] and glove bags; the product was once purified by sublimation at *ca.* 38 °C in a closed Shlenk flask. A single crystal was obtained by the Bridgman method in the sealed glass ampoule of 15 mm diameter.

NQR signals were displayed on an oscilloscope using two superregenerative oscillators: One is a usual LC-oscillator for lower frequency resonances and the other is a Lecher-line oscillator for higher ones. The Zeeman effect was measured by means of a goniometer newly constructed by us. The polar angle Θ is defined by the rotation of the magnetic field which is generated by means of a Helmholtz coil. A field of 7.5×10^{-3} T is generated with a current of 1 A in the Helmholtz coil which has a diameter of 38 cm and a separation of 10 cm between a pair of coils. The azimuthal angle Φ is defined by the rotation of the Φ disk which is attached to a cylinder inserted in the Helmholtz coil. The single crystal is held in the Φ disk. All frames of the goniometer are made of brass. To attain smooth rotation, the heavy Helmholtz coil is supported on 72 pieces of 8 mm diameter brass balls in a circular groove. The scales of Θ and Φ are engraved with marking at 1° intervals. The orthogonality between the rotation axes of Θ and Φ was checked according to the method described by Dean.[5] In the preliminary investigation with a single crystal of $NaClO_3$, the accuracy of the measurement is estimated within ±0.01 in η and ±0.2° in the angle.[6] Zerosplitting cones were obtained using the magnetic field of *ca.* 2×10^{-2} T at room temperature (17—21 °C). The analysis of the data of the Zeeman effect measurement was performed by using a electronic computer HITAC M-180 from Hiroshima University. The resonance signals for $-BBr_3$ of the complex have doublet structures.[1] The measurements were done for the stronger signals of the doublets.

Results and Discussion

Figure 1 shows ^{81}Br NQR spectra of $PBr_3 \cdot BBr_3$ with those of the parent compounds at 77 K. The four resonance lines (labeled ν_1, ν_2, ν_3, and ν_4) are divided into two sets spaced widely in frequency having the signal intensity ratios $I(\nu_1) : I(\nu_2) = I(\nu_4) : I(\nu_3) \approx 1 : 2$. The sets of ν_1 and ν_2, and of ν_3 and ν_4 are ascribed to the bromine atoms of fragments BBr_3 and PBr_3 of the complex, respectively. Thus, the resonance frequencies increase significantly in the donor (*ca.* 30 MHz) but to a small extent for the acceptor (*ca.* 0.5 MHz) on

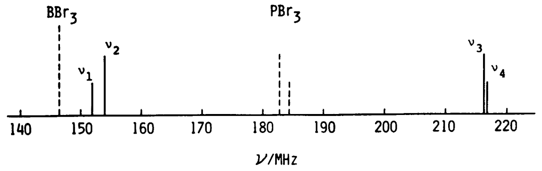

Fig. 1. ^{81}Br NQR spectra of $PBr_3 \cdot BBr_3$ at 77 K.

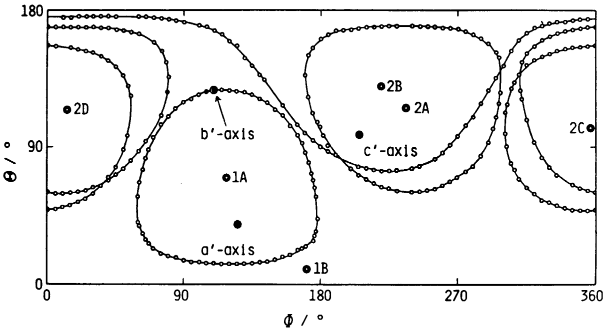

Fig. 2. Zero-splitting patterns of ^{81}Br NQR lines for $-BBr_3$ of $PBr_3 \cdot BBr_3$. 1A, 1B, *etc.*, denote the EFG z-axes of Br_{1A}, Br_{1B}, *etc.*, respectively. The zerosplitting pattern of 1B was not obtained owing to its unfavorable orientation. The direction of 1B was deduced from 1A and the crystal axes.

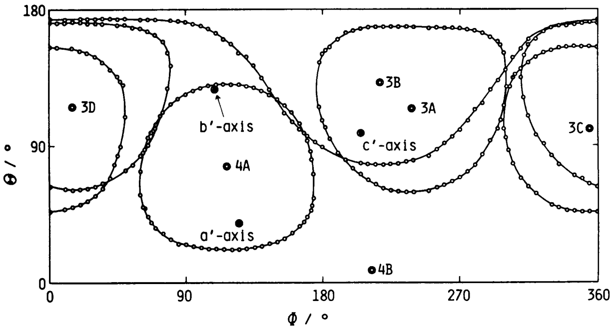

Fig. 3. Zero-splitting patterns of ^{81}Br NQR lines for $-PBr_3$ of $PBr_3 \cdot BBr_3$. 3A, 3B, *etc.*, denote the EFG z-axes of Br_{3A}, Br_{3B}, *etc.*, respectively. The zerosplitting pattern of 4B was not obtained owing to its unfavorable orientation. The direction of 4B was deduced from 4A and the crystal axes.

complexation.

The zero-splitting patterns obtained from the Zeeman effect of the resonance lines for $-BBr_3$ and $-PBr_3$ of the complex are shown in Figs. 2 and 3. The existence of four loci for ν_2 and ν_3, and of two loci for ν_1 and ν_4 was confirmed, but one of the two loci for each of ν_1 and ν_4 could not be determined owing to its unfavorable orientation. The number of the loci shows that the crystal belongs to orthorhombic symmetry. The directions of z-axes of electric field gradients (EFG) obtained from the zero-splitting loci and the crystal axes (tentatively named a′, b′, and c′) which are found from the symmetrical distributions of the z-axes are shown in Figs. 2 and 3. The z-axes of the missing loci 1B and 4B are also shown.

The angles between the z-axes of EFG tensors are listed in Table 1. The bond angle Br–P–Br in gaseous PBr_3 has been found to be 101.0°.[7] In a recent X-ray analysis of solid PBr_3 at 193 K, Enjalbert and Galy[8] have found the bond angles of 101.3° and 99.0°. On the other hand, all the Br–B–Br angles in the few know complexes of the present type $(CH_3)_3N \cdot BX_3$,[9,10] $(CH_3)_3P \cdot BX_3$,[11,12] and $CH_3CN \cdot BX_3$[13] are close to 111° in both gaseous and crystalline states. Taking these angles into consideration and assuming that the z-axes are parallel to the directions of bond axes, the angles Br–M–Br (M=P and B) can be deduced from the angles in Table 1 (and their supplementary angles). These values are listed in Table 2. Further, assuming that the complex molecule has a staggered conformation, (Br_{1A}, Br_{2B}, Br_{2D}, Br_{3B}, Br_{3D}, and Br_{4A}) and (Br_{1B}, Br_{2A}, Br_{2C}, Br_{3A}, Br_{3C}, and Br_{4B}) belong to each molecule which orients in two different directions. The angles Br–B–Br and Br–P–Br in $PBr_3 \cdot BBr_3$ are a little larger than the Br–B–Br and C–M–C (M=P, N) in solid $(CH_3)_3P \cdot BBr_3$[12] and solid $(CH_3)_3N \cdot BBr_3$,[10] respectively. On complexing, the Br–B–Br angles decrease by 7% from the value of a free molecule of BBr_3[14] (Br–B–Br=120°), while the Br–P–Br angles increase by 7% from the value of a free molecule of PBr_3[7] (Br–P–Br=101.0°).

The angles between EFG axes and the crystal axes are listed in Table 3. The B–Br_1 and P–Br_4 bonds exist in the a′b′-plane within experimental errors. For further investigation, the direction of the vector P–Br(G_p) which is directed to the center of mass of three Br atoms in $-PBr_3$, and that of the corresponding vector B–Br(G_B) in $-BBr_3$ were obtained on the assumption that all P–Br or B–Br bonds had equal bond lengths. The angle between the P–Br(G_p) and the B–Br(G_B) in one molecule is 1.4±0.1°. The small angle indicates that the molecule

Table 1. Angles between z-axes of EFG (in degrees)

	B–Br_{1A}	B–Br_{1B}	B–Br_{2A}	B–Br_{2B}	B–Br_{2C}	B–Br_{2D}	P–Br_{3A}	P–Br_{3B}	P–Br_{3C}	P–Br_{3D}	P–Br_{4A}
B–Br_{1B}	115.48										
B–Br_{2A}	56.87	111.02									
B–Br_{2B}	68.59	122.86	19.71								
B–Br_{2C}	56.94	111.15	111.43	115.14							
B–Br_{2D}	68.69	122.87	115.24	111.66	19.62						
P–Br_{3A}	54.92	110.10	2.51	22.09	110.01	114.64					
P–Br_{3B}	69.78	124.74	22.28	2.63	114.77	110.39	24.63				
P–Br_{3C}	55.18	109.87	110.26	114.87	2.59	22.17	108.75	114.63			
P–Br_{3D}	69.77	124.43	115.01	110.64	21.84	2.25	114.51	109.28	24.37		
P–Br_{4A}	6.16	109.32	58.08	71.51	58.18	71.62	55.95	72.93	56.19	72.89	
P–Br_{4B}	109.31	6.16	108.07	121.60	108.19	121.59	106.92	123.70	106.70	123.35	103.15

Table 2. Bond angles

Compound	Bond angle	$\theta/°$
$PBr_3 \cdot BBr_3$	Br_1–B–Br_2	111.2±0.1
(solid)	Br_2–B–Br_2	111.5±0.1
	Br_3–P–Br_3	107.0±0.1
	Br_3–P–Br_4	109.1±0.3
$(CH_3)_3P \cdot BBr_3$[a]	Br–B–Br	110.4[c]
(solid)	C–P–C	107.2[c]
$(CH_3)_3N \cdot BBr_3$[b]	Br–B–Br	108.4[c]
(solid)	C–N–C	107.5[c]

a) Ref. 12. b) Ref. 10. c) Averaged value.

Table 3. Angles between principal axes of EFG and crystal axes (in degrees)

EFG	axis	a′-axis	b′-axis	c′-axis
Br_1	z	32.3±0.4	57.7±0.1	90.0±0.1
	x	58.1±0.1	147.7±0.1	89.2±0.3
	y	89.5±0.3	90.7±0.4	179.2±0.5
Br_2	z	57.6±0.1	80.2±0.2	34.2±0.1
	x	91.0±0.4	167.7±0.3	77.7±0.3
	y	32.4±0.1	97.4±0.6	121.4±0.2
Br_3	z	57.3±0.1	77.8±0.3	35.5±0.1
Br_4	z	38.4±0.4	51.6±0.1	90.0±0.1

Table 4. ^{81}Br NQR parameters at room temperature

Compound		Frequency[a] / MHz	$e^2q_{zz}Q/h$ / MHz	η	f	Assignment
$PBr_3 \cdot BBr_3$	ν_1	150.31	299.48	0.151±0.004	0.05	BBr_3
	ν_2	151.68	302.63	0.120±0.007	0.04	
	ν_3	212.53	425.01	0.025±0.005		PBr_3
	ν_4	213.22	426.41	0.020±0.004		
BBr_3[b]		146.41	283.80	0.45	0.12	

a) At 293 K. b) Ref. 18; at 77 K.

has effective $3m$ symmetry. The angle between the respective P–Br(G_p) (or B–Br(G_B)) vectors of the two molecules in different orientations is 30.4±1.4°, which is considered as almost coinciding with the angles between the P–B bonds in different orientations.

The asymmetry parameter can be deduced by transforming the zero-splitting locus in the EFG principal axis system,[15] in which the locus is expressed for $I=3/2$ as follows:[16]

$$\sin^2\theta = 2/(3-\eta\cos 2\phi), \tag{2}$$

where θ and ϕ are polar and azimuthal angles, respectively. Thus, the quadrupole coupling constant $e^2q_{zz}Q/h$ is obtained using the resonance frequency ν and η according to the following equation:

$$\nu = (1/2)(e^2q_{zz}Q/h)[1+(1/3)\eta^2]^{1/2}. \tag{3}$$

The $e^2q_{zz}Q/h$ and η at room temperature are listed in Table 4. It is noted that η values are relatively large for the Br atoms of $-BBr_3$ but very small for the Br atoms of $-PBr_3$ in the complex. This finding may show that the intermolecular contributions to η are very small in the crystal and that the large η of the Br atoms of $-BBr_3$ originate mostly in the π-bonding existing in the B–Br bonds. Neglecting the intermolecular contributions to η, we can estimate the π bonding character of B–Br bonds of $PBr_3 \cdot BBr_3$ according to the following equation:[2]

$$f = (2/3)\eta(e^2q_{zz}Q/h)/(e^2q_{at}Q/h), \tag{4}$$

where f denotes the degree of π character and $e^2q_{at}Q/h$ denotes the atomic quadrupole coupling constant, which is 643.03 MHz for ^{81}Br atom.[17] The values of f are listed in Table 4. On complex-formation, the π character of B–Br bonds reduces from *ca.* 12% to 5%. It is found from Table 3 that the x-axis of the Br_1 atom exists in the mirror plane in which the B–Br_1 bond lies. Furthermore the x-axis of the Br_2 atom makes only a small angle, 5.3±0.3°, with the plane which contains the B–Br_2 bond and the B–Br(G_B) vector in a molecule. This is consistent with the existence of the π bonding in the B–Br bonds of the complex.

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