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NQR and NMR Studies of Boron Trihalide-Trimethylamine Complexes

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The character of the B–X bond (X=Cl, Br, and I) in BX_3–TMA complexes (TMA=trimethylamine) has been studied on the basis of the results of the nuclear quadrupole resonance (NQR). The ionic character of the B–X bond decreased in the order as expected from the electronegativity of the halogen atoms. The temperature dependence of the halogens on the NQR frequencies has been examined for BBr_3– and BI_3–TMA. For BBr_3–TMA, all the observed resonance lines faded out far below the melting point and this has been attributed to the hindered rotation of the BBr_3 group about the B–N bond, as with BCl_3–TMA.

The crystal structure of BX_3–TMA complexes has been recently determined by X-ray analysis[1)] and the atomic arrangement about the boron atom is shown to be approximately tetrahedral and that the B–N bond distance decreases with increasing atomic weight of the halogen atom. It is of interest to examine the character of the B–X and B–N bonds in these complexes. Furthermore, for BCl_3–TMA, the reorientation of the methyl and trimethylammonio groups is known to affect the temperature dependence of the ^{35}Cl NQR frequencies[2)] and consequently a study of the temperature dependence of the NQR frequencies for BBr_3– and BI_3–TMA will elucidate dynamic properties of the crystals.

Experimental

BCl_3 and BBr_3 were prepared by heating a mixture of potassium tetrafluoroborate with aluminum(III) chloride or bromide, respectively, up to 140—170 °C.[3)] BI_3 was prepared from sodium hydroborate and iodine according to the method of Schumb *et al.*[4)] The complexes BCl_3– and BBr_3–TMA were prepared by the dropwise addition of a dichloromethane solution of BX_3 to a dichloromethane solution of TMA under dry nitrogen. For the complex BI_3–TMA, a similar procedure was conducted using benzene as a solvent. BCl_3– and BBr_3–TMA were recrystallized from ethanol and BI_3–TMA from benzene. The compound obtained was dried in a vaccum desiccator. The elemental analyses of these complexes agreed well with theoretical values. Found: C, 20.47; H, 5.26; N, 7.75%. Calcd for $C_3H_9NBCl_3$: C, 20.44; H, 5.14; N, 7.94%. Found: C, 11.86; H, 3.01; N, 4.56%. Calcd for $C_3H_9NBBr_3$: C, 11.64; H, 2.93; N, 4.52%. Found: C, 7.96; H, 2.05; N, 3.09%. Calcd for $C_3H_9NBI_3$: C, 8.00; H, 2.01; N, 3.10%.

NQR spectra were observed on an oscilloscope using a super-regenerative oscillator with frequency modulation. NMR were observed using a broad line NMR spectrometer, JES-ME 1 from JEOL Co., Ltd.

Results and Discussion

NQR of BX_3–TMA. The NQR frequencies of boron trihalides and their complexes are listed in Table 1. Each NQR line for BBr_3, BI_3, and their complexes was split into a doublet by the boron isotope, ^{10}B and ^{11}B.[6)] However, the frequencies are listed only for the halogen atoms linked to the ^{11}B atom. Each complex has two resonance lines with an intensity ratio of 1 to 2 and this is consistent with the X-ray analysis.[1)] The weaker resonance line in each complex is due to the halogen atom on the symmetry plane and the stronger to the two halogen atoms symmetrically located with respect to this plane.

It has been established that the B–X bond in BX_3 has a considerably large double bond character.[5,6)] When BX_3 forms a complex with TMA, the BX_3 molecule is deformed from a planar to a pyramidal configuration. As a direct consequence most of the double bond character of the B–X bond is lost *i.e.*, the asymmetry parameter of the halogen atoms becomes very small as shown in BI_3–TMA. For ^{35}Cl and ^{81}Br atoms, the quadrupole coupling constant, e^2Qq/h, is obtained from the equation,

$$\nu = (1/2)(e^2Qq/h)(1+\eta^2/3)^{1/2}, \qquad (1)$$

where ν is the resonance frequency and η the asymmetry parameter. For BCl_3– and BBr_3–TMA, the asymmetry parameter has been assumed to be zero. For ^{127}I atom,

Table 1. NQR parameters at 77 K

Compound	Nucleus	Frequency(MHz)	Intensity ratio	η	e^2Qq/h (MHz)
BCl_3[a)]	^{35}Cl	21.582		0.54	41.208
BCl_3–TMA[b)]	^{35}Cl	21.532	1		43.064
		21.779	2		43.558
BBr_3[c)]	^{81}Br	146.43		0.45	283.45
BBr_3–TMA	^{81}Br	144.28	1		288.56
		147.20	2		294.40
BI_3	^{127}I	ν_1 214.00 ν_2 342.95		0.453	1186.3
BI_3–TMA	^{127}I	ν_1 186.65 ν_2 371.19	2	0.066	1238.4
		ν_1 190.48 ν_2 378.84	1	0.066	1263.9

a) Ref. 5. b) Ref. 2. c) Ref. 6.

the quadrupole coupling constant and asymmetry parameter can be derived from the frequency ratio, ν_1/ν_2 (ν_1 and ν_2 are the frequencies corresponding to the $\pm 1/2 \leftrightarrow \pm 3/2$ and $\pm 3/2 \leftrightarrow \pm 5/2$ transitions, respectively). The quadrupole coupling constants thus obtained are listed in Table 1.

The Character of the B–X Bond. The amount of the unbalanced p-electron, U_p, is given by[7]

$$U_p = |e^2Qq/e^2Qq_0|, \qquad (2)$$

where e^2Qq_0/h is the quadrupole coupling constant for the free halogen atom (−109.746, 643.032, and −2292.712 MHz for ^{35}Cl, ^{81}Br, and ^{127}I, respectively). Assuming that the B–X bond is represented by the resonance between B–X, $B^-{=}X^+$, and B^+X^-, U_p is then related to the ionic character, i, and the double bond character, f, expressed by[6,8]

$$U_p = (1-i)(1-s) - (f/2)\{1-(1-2s)\varepsilon\}, \qquad (3)$$

where s is the fractional s character of the B–X bond and ε the correction for the increase in field gradient attributed to the positive fractional charge at the halogen atom.[8] In addition, the double bond character is related to the asymmetry parameter expressed by

$$\eta = (3/2)f(1+\varepsilon)/U_p. \qquad (4)$$

Thus, U_p, i, and f can be deduced from Eqs. 2—4, by selecting $s=0.15$ and ε to be 0.14, 0.13, and 0.12 for Cl, Br, and I, respectively,[9] the results of which are listed in Table 2.

Table 2. The nature of the B–X bond

Compound	U_p	i(%)	f(%)
BCl_3	0.376	50	12
BCl_3–TMA[a]	0.395	54	0
BBr_3	0.441	42	12
BBr_3–TMA[a]	0.455	47	0
BI_3	0.517	32	14
BI_3–TMA[a]	0.544	35	2

a) For each complex, the weighted-mean value of the two resonance lines is listed.

In each complex, U_p is greater than that of the halogens in BX_3 caused largely by the loss of double bond character upon complex formation. In addition, the ionic character of the complexes decreases in the order, chloride>bromide>iodide which is consistent considering the electronegativity of the halogen atoms.

Attempts to obtain the quadrupole coupling constant of the ^{11}B atom at 13 MHz in each complex gave neither first-order nor second-order splitting. The quadrupole coupling constant of the ^{11}B atom in each complex was however estimated to be less than 500 kHz from the line-width of the polycrystalline sample. This value was far less than *ca.* 2.5 MHz for BX_3.[10] Consequently, in the complex, the B–N bond and the three B–X bonds are arranged almost tetrahedrally and thus each bond may be regarded as equivalent.

The Temperature Dependence of the NQR Frequencies. For BCl_3–TMA, it has been established that the reorientation of the methyl and trimethylammonio groups affects the ^{35}Cl NQR line, *i.e.*, the temperature coefficient of the NQR frequency varied at 100 and 204 K, respectively.[2] A similar phenomenon was however not observed for both BBr_3– and BI_3–TMA.

For BBr_3–TMA, the resonance lines faded out in the noise level at about 285 K, which far below the melting point, 511 K, as seen for BCl_3–TMA. The resonance lines became increasingly broad from 260 K, although the accurate evaluation of line-widths could not be made, since each NQR line was a doublet. The disappearance of the NQR line may be caused by the hindered rotation of the BBr_3 group. It is known that the activation energies of the reorientation of trimethylammonio group in BCl_3– and BBr_3–TMA are greater than those of BH_3– and BF_3–TMA.[11] This suggests that in BCl_3– and BBr_3–TMA, the molecule rotates as a whole, that is, the triemethylammonio and BX_3 groups do not rotate independently. For BBr_3–TMA, the frequency of this motion or the rotation of the BBr_3 group reaches 10^4—10^5 Hz in the vicinity of 285 K and approaches the NQR frequency.[12] Therefore, rotation of the BBr_3 group or the whole molecule is thought to induce broadening of NQR lines. Moreover, at a particular rate of rotation, averaging of the field gradient will occur along the axis of rotation reducing the NQR frequency to[13]

$$\nu_T = \nu_Q(3\cos^2\theta - 1)/2, \qquad (5)$$

where ν_T is the averaged NQR frequency, ν_Q the NQR frequency of the stationary molecule, and θ the angle between the B–Br bond and the axis of rotation. An attempt to observe the resonance lines above room temperature however was unsuccessful.

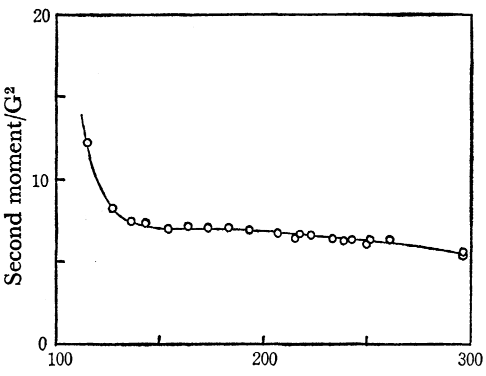

Fig. 1. Temperature dependence of the second moment of ^{1}H NMR spectrum for BI_3–TMA.

Table 3. Calculated second moments for BI_3–TMA

Group		Second moment (G²)
CH_3	$N(CH_3)_3$	
Static	Static	28.6
Rotating	Static	9.7
Rotating	Rotating	1.6

For BI_3–TMA, the resonance lines could be observed up to 353 K at which time the sample began to turn brown. For this complex, the second moment of ^{1}H NMR spectrum was approx. 7.5 G² from 113 to 300 K as shown in Fig. 1. The theoretical second moment was calculated on the basis of the crystal structure[1] based on the same assumptions for the hydrogen position as for Ref. 11, the results of which are listed in Table 3. The reorientation of the trimethylammonio group is not expected in this temperature range, from a comparison of the observed with the calculated values.

References

1) P. H. Clippard, J. C. Hanson, and R. C. Taylor, *J. Cryst. Mol. Struct.*, **1**, 363 (1971).

2) D. F. R. Gilson and R. M. Hart, *Can. J. Chem.*, **48**, 1976 (1970).

3) E. L. Gamble, *Inorg. Synth.*, **3**, 27 (1950).

4) W. C. Schumb, E. L. Gamble, and M. D. Banus, *J. Am. Chem. Soc.*, **71**, 3225 (1949).

5) J. A. S. Smith and D. A. Tong, *J. Chem. Soc., A*, **1971**, 173.

6) T. Chiba, *J. Phys. Soc. Jpn.*, **13**, 860 (1958).

7) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York (1955), Chap. 9.

8) E. A. C. Lucken, "Nuclear Quadrupole Coupling Constants," Academic Press, London and New York (1969), Chap. 7.

9) B. P. Dailey and C. H. Townes, *J. Chem. Phys.*, **23**, 118 (1956).

10) P. A. Casabella and T. Oja, *J. Chem. Phys.*, **50**, 4814 (1969).

11) C. T. Yim and D. F. R. Gilson, *Can. J. Chem.*, **48**, 515 (1970).

12) T. T. Ang and B. A. Dunell, *Can. J. Chem.*, **52**, 1840 (1974).

13) R. Sh. Lotfullin and G. K. Semin, "Advances in Nuclear Quadrupole Resonance," ed by J. A. S. Smith, Heyden, London (1977), Vol. 2, p. 1.