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The Molecular Structure of Trimethylamine-Boron Triiodide as Studied by Gas Electron Diffraction

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The molecular structure of trimethylamine-boron triiodide $(CH_3)_3N \cdot BI_3$ has been determined from gas electron-diffraction data. The molecular parameter values and their uncertainties are r_g(B-I)$=2.245\pm0.004$ Å, r_g(N-B)$=1.663\pm0.013$ Å, r_g(C-N)$=1.497\pm0.005$ Å, r_g(C-H)$=1.103\pm0.010$ Å, $\angle$IBI$=108.6\pm0.4°$, and $\angle$CNC$=106.0\pm0.8°$. The potential barrier around the N-B bond has also been estimated to be about 3.5 kcal mol^{-1} (1 cal$=$4.184 J).

The molecular structures of the trimethylamine complexes of boron trifluoride, boron trichloride, and boron tribromide have been determined in both the gas[1–3] and solid phases,[4–6] while that of the boron triiodide complex has been done only in the solid phase.[6] These studies have given the results that the N–B bond distances of the first three complexes are significantly shorter and the B–X and C–N bond distances are longer in the solid phase than in the gas phase, and thus it is concluded that the dative bonding in trimethylamine–boron trihalides is enhanced in the solid phase.

It has also been reported that in the gas phase the fractional changes of the molecular parameters by the complex formation become larger as the atomic number of the halogen atoms involved in the complex increases,[2] correlating to the reorganization energies of boron trihalides.[7] It has also been found that the height of the rotational barrier about the N–B bond of trimethylamine–boron trihalide varies in the order $(CH_3)_3N \cdot BF_3$[1]$<(CH_3)_3N \cdot BBr_3$[2]$<(CH_3)_3N \cdot BCl_3$.[2] It is therefore interesting to determine the molecular structure of gaseous trimethylamine–boron triiodide, $(CH_3)_3N \cdot BI_3$, and the rotational barrier about the N–B bond by the electron diffraction method.

Experimental

The gas of trimethylamine that was produced by dropwise additions of an aqueous solution of sodium hydroxide to trimethylamine hydrochloride[8] was dried through soda lime and allowed to react with boron triiodide in benzene. The crude complex was dissolved in chloroform and impurities were eliminated by adding activated charcoal. The purity of the complex was checked by IR spectra.[9]

Electron diffraction photographs were taken by the use of an r^3-sector on Kodak Electron-Image plates at camera distances of 294 and 144 mm. The sample was vaporized at 483 K by means of a high temperature nozzle. An accelerating voltage was 40 kV and the wavelength was determined from the diffraction patterns of thallium(I) chloride.[10] The exposure times were about 13 and 30 s for the long and short camera distance photographs, respectively, with an electron-beam current of 0.8 μA. The pressure in the diffraction chamber was 1×10^{-5} Torr (1 Torr$=$133.322 Pa) during the experiment. Three plates were selected for each camera distance and their optical densities were measured at 0.4 mm intervals by the use of a digital microphotometer. The electron diffraction unit and the digital microphotometer used in the present study have been described elsewhere.[11]

Analysis and Results

Molecular Intensity and Radial Distribution. The scattering intensities in the range of $s=2.5$—14.8 Å^{-1} were obtained from the long camera distance plates and those in the range of $s=7.5$—34.6 Å^{-1} from the short camera distance plates. They were leveled by theoretical backgrounds, and then the intensities for each camera distance were averaged. The elastic and inelastic scattering factors were taken from the tables prepared by Schäfer *et al.*[12] and by Cromer and Mann,[13] respectively. The inelastic scattering factor for the hydrogen atom was taken from the table by Tavard *et al.*[14]

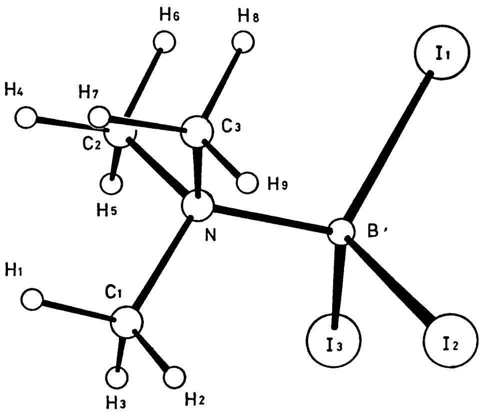

Fig. 1. Numbering of atoms in trimethylamine-boron triiodide (symmetry C_{3v}).

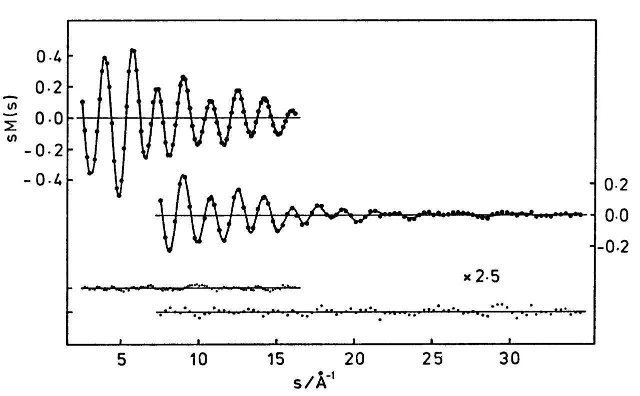

Fig. 2. Molecular intensities for trimethylamine-boron triiodide. The two upper curves are long and short camera-distance data. Dots represent observed ones, solid curves calculated ones, and their residuals are shown below.

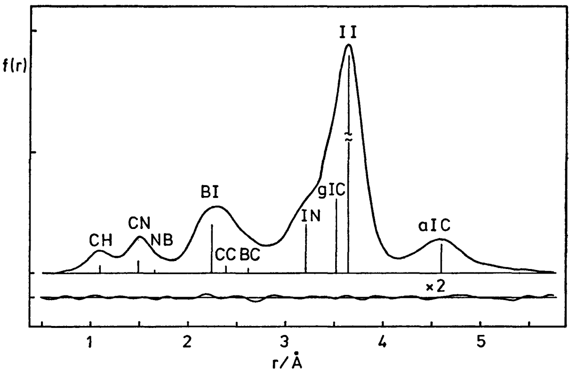

Fig. 3. Experimental radial distribution curve for trimethylamine-boron triiodide. Lower curve represents two times the difference between the experimental and the calculated curves.

The molecular intensities obtained by drawing backgrounds smoothly on the experimental intensities[15)] are shown in Fig. 2. The radial distribution function corrected for the large difference[16)] in the atomic numbers of the atoms contained in $(CH_3)_3N\cdot BI_3$ is shown in Fig. 3.

Vibrational Amplitudes and Shrinkage Corrections. Root-mean-square amplitudes of the atomic pairs in the staggered form were calculated on the basis of the Urey-Bradley force field obtained from the vibrational spectra of solid $(CH_3)_3N\cdot BI_3$.[9)] However, the calculated $l(I\cdots I)$ disagreed with the observed one in the gas phase as will be described later. The force constant $F(II)$ was adjusted to give a better agreement between the calculated and observed $l(I\cdots I)$ amplitudes, since it greatly contributes to the $l(I\cdots I)$. The corrected force constant yielded the decrease of about 50 cm^{-1} in wave numbers for the symmetric and antisymmetric deformations of BI_3. The mean amplitudes and the shrinkage corrections, $r_a - r_\alpha$,[17)] were calculated on the basis of the force constants listed in Table 1, as shown in Table 2.

Molecular Structure and Potential Barrier Height. The molecular parameters of $(CH_3)_3N\cdot BI_3$ have been determined by the least-squares analysis of molecular intensities. Both of the donor and acceptor parts in the complex molecule were assumed to have the C_{3v} symmetry. The methyl groups were also assumed to have the C_{3v} symmetry in a staggered form with respect to the C–N bonds. The geometrical parameters determined by the least-squares analysis are as follows: r(B–I), r(N–B), r(C–N), r(C–H), $r(I\cdots I)$, $r(C\cdots C)$, and ∠NCH. The mean amplitudes of some atom pairs were refined by the least-squares analysis as listed in Table 3. The mean amplitudes of other bonds and atom pairs which are independent of the rotation around the N–B bond were fixed to the values listed in Table 2. The shrinkage corrections for all the atom pairs were also fixed to the values listed in Table 2. The asymmetry parameters, κ, for the B–I, N–B, C–N, and C–H bonds were estimated to be 16, 7.9, 2.6, and 12×10^{-6} Å^3, respectively, by the diatomic approximation[18)] and those for the other atom pairs were ignored.

Table 1. Urey-bradley force field for $(CH_3)_3N\cdot BI_3$

K(NB)	1.3	H(NCH)	0.3
K(BI)	0.9	F(II)	0.2
K(CN)	2.1	F(IN)	0.7
K(CH)	4.4	F(CC)	0.3
H(IBI)	0.1	F(CB)	0.2
H(IBN)	0.05	F(HH)	0.1
H(CNC)	0.45	F(NH)	0.6
H(CNB)	0.3	Y(CN)	0.17
H(HCH)	0.4	p	−0.05

The torsional force constant, Y, and the internal tension of the methyl carbon, p, are in 10^{-18} N m, while the others are in 10^2 N m^{-1}.

Table 2. Root-mean-square amplitudes and shrinkage corrections for $(CH_3)_3N\cdot BI_3$ (in 10^{-4} Å)

Atomic pair	l	$r_a - r_\alpha$	Atomic pair	l	$r_a - r_\alpha$
B–I_1	768	21	N–C_1	551	65
B–N	657	23	$N\cdots H_1$	1036	238
$B\cdots C_1$	923	53	$C_1\cdots C_2$	824	66
$B\cdots H_1$	1136	192	C_1–H_1	784	333
$B\cdots H_2$	1763	76	$C_1\cdots H_4$	1728	102
$I_1\cdots I_2$	1233	−21	$C_1\cdots H_5$	1744	88
$I_1\cdots N$	870	8	$C_1\cdots H_6$	1067	179
$I_1\cdots C_1$	920	25	$H_1\cdots H_2$	1288	473
$I_1\cdots C_2$	1529	−16	$H_1\cdots H_4$	2532	39
$I_1\cdots H_1$	1348	98	$H_1\cdots H_5$	2732	21
$I_1\cdots H_2$	1614	54	$H_1\cdots H_6$	1862	205
$I_1\cdots H_4$	2015	54	$H_2\cdots H_5$	1828	193
$I_1\cdots H_5$	2438	−46	$H_2\cdots H_8$	1351	243
$I_1\cdots H_6$	2550	−76	$H_2\cdots H_9$	2601	26

The numbering of the atoms is shown in Fig. 1. The mean-amplitudes and shrinkage corrections were calculated for the same temperature (483 K) as in the experiment.

Table 3. Root-mean-square amplitudes for $(CH_3)_3N\cdot BI_3$

	l_{obsd}/Å[a)]	l_{calcd}/Å[b)]
B–I	0.077 (10)	0.077
C–N	0.055 (7)	0.055
C–H	0.081 (11)	0.078
$I\cdots I$	0.121 (2)	0.123
$I\cdots N$	0.086 (9)	0.087

a) Results obtained from the least-squares analysis of electron-diffraction data. Limits of error are shown in parentheses. b) Values calculated from the force constants in Table 1.

The torsional vibration around the N–B bond contributes greatly to the mean amplitude of the *gauche* $I\cdots C$ atom pair. The analysis assuming a high barrier approximation,[19)] however, could not give a reasonable value for that amplitude, so the potential barrier around the N–B bond seemed to be pretty small. Thus the molecule was treated in a low barrier approximation.[19)] The mean amplitudes of the rotation-dependent atom pairs were calculated at various torsional angles on the basis of the force field in Table

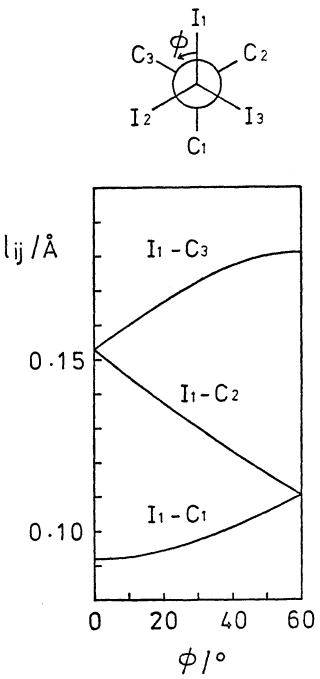

Fig. 4. Calculated mean amplitudes for the atomic pairs which are dependent on the rotation around the N-B bond. The ϕ is the rotational angle from the staggered position.

1. The dependence of these amplitudes on the torsional angle ϕ is shown in Fig. 4. They were fixed throughout the analysis. The molecular intensities were calculated at 6° intervals of the torsional angles and summed with the weights of the Boltzmann distribution. The scattering intensities in a small-angle range depend considerably on the height of the potential barrier. Therefore the potential-barrier height was determined by inspecting the shape of the backgrounds calculated from both the experimental intensities and the theoretical molecular intensities for models with various potential barriers, since the experimental backgrounds should be smooth.[20] The differences between the experimental backgrounds and the calculated backgrounds, ΔB, are shown in Fig. 5(a), and the root-mean-square values of ΔB are shown for each potential-barrier height in Fig. 5(b). These figures indicate that the potential barrier around the N–B bond is about 3.5 kcal mol^{-1}.

The geometrical parameters obtained by the least-squares calculation, in which the potential-barrier height was assumed to be 3.5 kcal mol^{-1}, are listed in Table 4 with the limits of error. The random errors were 2.6 times as large as the errors estimated by the least-squares calculations. The systematic errors were estimated from the errors in both the measurements of camera distance (0.04%) and wavelength (0.09%). The best-fit theoretical molecular intensities are shown in Fig. 2. The experimental intensities, the experimental smooth backgrounds, and the correlation matrix for the molecular parameters are deposited in Document No. 8328 at the Office of the Editor of the Bulletin of the Chemical Society of Japan. The calculations of the mean-amplitudes and the shrinkage corrections and the least-squares analysis were carried out on a HITAC M-200H computer in the Computer Center of the University of Tokyo.

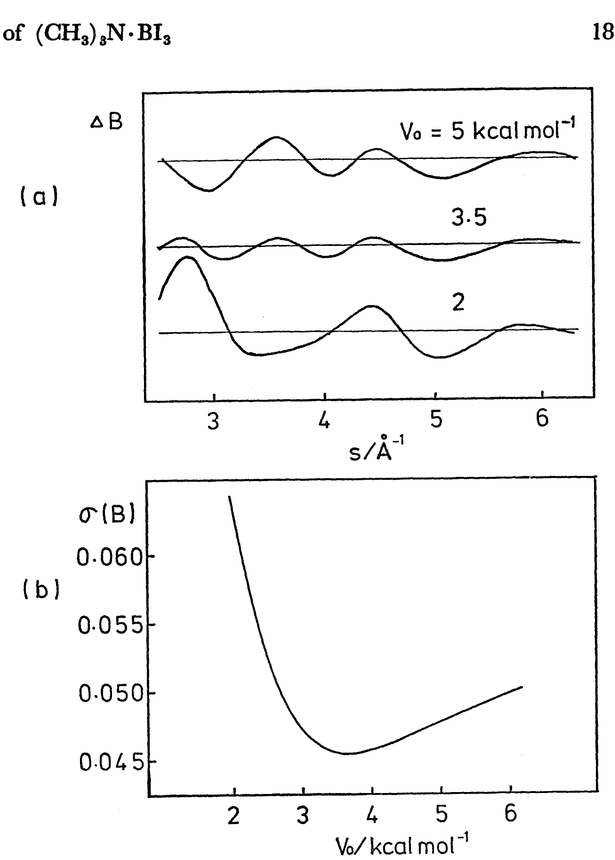

Fig. 5. (a) The difference curves between the smooth and the calculated backgrounds in the small angle range. The V_0 is the assumed potential-barrier height around the N-B bond. (b) The root-mean-square value of ΔB versus the assumed potential-barrier height around the N-B bond.

Table 4. Molecular parameters obtained from least-squares analysis for $(CH_3)_3N{\cdot}BI_3$

	r_α[a]	r_g[a]	ε[b]
B-I	2.240	2.245	0.004
N-B	1.658	1.663	0.013
C-N	1.488	1.497	0.005
C-H	1.064	1.103	0.010
I···I	3.644	3.646	0.004
C···C	2.381	2.390	0.014
∠NCH	110.3		1.7
∠IBI[c]	108.9	108.6	0.4
∠CNC[c]	106.2	106.0	0.8

Bond distance: Å unit; bond angle: degree unit. a) Ref. 17. b) Limits of error. c) Calculated from independent parameters.

Discussion

The molecular parameters for the trimethylamine-boron trihalide complexes in the gas phase are listed in Table 5, together with those in the solid phase[4–6] and those for the component molecules.[21–25] As seen for all of trimethylamine–boron trihalide complexes, the distances of B–X and C–N bonds increase and the angles of XBX and CNC decrease on the complex

TABLE 5. COMPARISON OF MOLECULAR PARAMETERS

		r(N-B)/Å	r(B-X)/Å	r(C-N)/Å	∠XBX/°	∠CNC/°
$(CH_3)_3N\cdot BF_3$	(gas)[a]	1.674 (4)	1.374 (2)	1.485 (2)	112.6 (3)	109.2 (4)
	(solid)[b]	1.585	1.39	1.50	107	114
$(CH_3)_3N\cdot BCl_3$	(gas)[c]	1.652 (9)	1.836 (2)	1.497 (3)	110.9 (2)	108.1 (3)
	(solid)[d]	1.609 (6)	1.864 (4)	1.52 (1)	109.5 (2)	108.6 (14)
$(CH_3)_3N\cdot BBr_3$	(gas)[c]	1.663 (13)	2.001 (3)	1.500 (5)	110.3 (3)	107.8 (5)
	(solid)[d]	1.60 (2)	2.04 (2)	1.52 (1)	108.3 (7)	107.7 (10)
$(CH_3)_3N\cdot BI_3$	(gas)[e]	1.663 (13)	2.245 (4)	1.497 (5)	108.6 (4)	106.0 (8)
	(solid)[d]	1.58 (3)	2.28 (2)	1.52 (1)	108.3 (7)	105.1 (16)
$(CH_3)_3N$[f]				1.461 (2)		110.6 (6)
BF_3[g]			1.313 (1)		120	
BCl_3[h]			1.742 (4)		120	
BBr_3[i]			1.893 (5)		120	
BI_3[j]			2.118 (5)		120	

The values for the gas phase represent r_g parameters. a) Ref. 1. b) Ref. 4. c) Ref. 2. d) Ref. 6. e) Present study. f) Ref. 21. g) Ref. 22. h) Ref. 23. i) Ref. 24. j) Ref. 25.

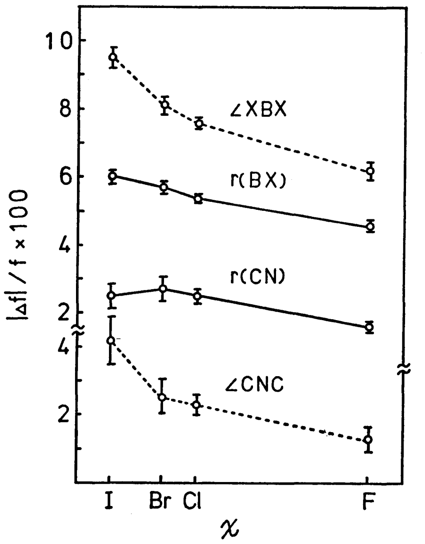

Fig. 6. Parameter changes on complex formation. The abscissa shows the magnitude of the electronegativity χ of the halogen atoms in the acceptor molecules. Solid curves represent positive Δf and dashed curves negative Δf.

formation and the magnitudes of the structural changes of the acceptor molecules are larger than those of the donor molecules. The fractional differences of the parameters, $\Delta f/f$, between the complex and the corresponding free molecules are plotted in Fig. 6 *versus* the electronegativity values of the halogen atoms[26] in the complexes. The differences are in the order $(CH_3)_3N\cdot BF_3 < (CH_3)_3N\cdot BCl_3 < (CH_3)_3N\cdot BBr_3 < (CH_3)_3N\cdot BI_3$, while the N–B bond distances in the trimethylamine complexes are nearly constant in the gas phase as well as in the solid phase with no systematic change by the halogen atoms. This order agrees with the order of heat of reaction of boron trihalides with pyridine from the calorimetric measurements,[27] and also with the order of the relative acceptor power of boron trihalides from the gas-phase displacement reactions,[28,29] though there have been no data for the $(CH_3)_3N\cdot BI_3$ complex. Thus it may be concluded that a complex formed with larger heat of reaction is subject to greater distortion and that a stable complex is not necessarily accompanied by the dative bond with a short distance. However, it is noted that these structural changes found in trimethylamine–boron trihalides are in contrast with those in the complexes of trimethylphosphine–boron trihalides;[30] on the complex formation of trimethylphosphine–boron trihalide the change of the molecular parameters for the complex with larger halogen atom is smaller in spite of the larger heat of reaction.[31,32] This situation cannot be reasonably explained at the present stage.

In the solid phase the B–I and C–N distances are larger and the IBI and CNC angles are smaller than in the gas phase. The structural changes on the complex formation seem to be magnified in the solid phase. The N–B bond distance of $(CH_3)_3N\cdot BI_3$ is smaller than in the gas phase by 0.08 Å. The same trends are seen in other trimethylamine–boron trihalide complexes. Thus it will be concluded that in all trimethylamine–boron trihalides the donor–acceptor bondings are enhanced in the solid phase.

The rotational barrier around the N–B bond in $(CH_3)_3N\cdot BI_3$ is about 3.5 kcal mol^{-1}. In the series of the trimethylamine–boron trihalide complexes, the rotational barriers decrease in the sequence of $(CH_3)_3N\cdot BCl_3$ (>18 kcal mol^{-1}),[2] $(CH_3)_3N\cdot BBr_3$ (10 kcal mol^{-1}),[2] and $(CH_3)_3N\cdot BI_3$. However, the rotational barrier height of $(CH_3)_3N\cdot BF_3$ was found to be 4.3 kcal mol^{-1},[1] which is nearly equal to that of the $(CH_3)_3N\cdot BI_3$ complex. These results are consistent with the results from NMR measurements.[33] The rotation around the N–B bond seems to be mainly hindered by repulsion between the methyl groups and the halogen atoms. The distances of $X_1\cdots H_6$ (see Fig. 1), which are considerably shorter than their van der Waals distances, increase as the atomic numbers of the halogen atoms involved become larger, and therefore their potential barriers are considered to become smaller. However, the barrier height of $(CH_3)_3N\cdot BF_3$ is much smaller than that of $(CH_3)_3N\cdot BCl_3$. This may be due to that the van der Waals radius of a fluorine atom is comparatively small and the $X_1\cdots H_6$ distance is nearly equal to the van der

Waals distance.

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