

Molecular Structures of Complexes of Trimethylamine with Boron Trichloride and Boron Tribromide as Determined by Gas Electron Diffraction

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The molecular structures of trimethylamine-boron trichloride $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and trimethylamine-boron tribromide $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ were determined from gas electron diffraction and vibrational-spectroscopic data. The molecular parameters and their uncertainties for $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ were $r_g(\text{B}-\text{Cl})=1.836\pm0.002$ Å, $r_g(\text{N}-\text{B})=1.652\pm0.009$ Å, $r_g(\text{C}-\text{N})=1.497\pm0.003$ Å, $r_g(\text{C}-\text{H})=1.107\pm0.005$ Å, $\angle\text{ClBCl}=110.9\pm0.2^\circ$, $\angle\text{CNC}=108.1\pm0.3^\circ$, while those for $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ were $r_g(\text{B}-\text{Br})=2.001\pm0.003$ Å, $r_g(\text{N}-\text{B})=1.663\pm0.013$ Å, $r_g(\text{C}-\text{N})=1.500\pm0.005$ Å, $r_g(\text{C}-\text{H})=1.095\pm0.007$ Å, $\angle\text{BrBBr}=110.3\pm0.3^\circ$, $\angle\text{CNC}=107.8\pm0.5^\circ$. The potential barriers around the N-B bonds in $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ were also estimated to be higher than 18 kcal mol⁻¹ and about 12 kcal mol⁻¹ respectively.

The molecular structures of several N-B and P-B donor-acceptor complexes have been determined recently in the gas phase¹⁻⁴⁾ and in the solid phase;⁵⁻⁸⁾ it was found that the N-B bond length in trimethylamine-boron trifluoride is appreciably longer in the gas phase³⁾ than that in the solid phases,⁵⁾ while the P-B bond length in trimethylphosphine-boron trichloride is similar in the two phases.^{4,8)} It was also noted that, on the formation of the complex, the structural changes in trimethylamine are quite different from those in trimethylphosphine; that is, in both complexes the CNC angle decreases and the CN distance increases,³⁾ but the CPC angle increases and the CP distance decreases⁴⁾ in comparison with the molecular parameters of free molecules. In order to understand the complicated properties of these molecular complexes, it is necessary to determine the molecular structures of trimethylamine and trimethylphosphine complexes with various boron compounds, BX_3 . The present study will report the molecular structures of trimethylamine-boron trichloride $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and trimethylamine-boron tribromide $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$, as determined by means of gas electron diffraction.

The molecular structures of gaseous trimethylamine-boron trifluoride $(\text{CH}_3)_3\text{N}\cdot\text{BF}_3$ and trimethylamine-boron trichloride $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ have been reported by several workers.¹⁻³⁾ The molecular parameters of $(\text{CH}_3)_3\text{N}\cdot\text{BF}_3$ previously obtained by the present authors³⁾ were consistent with the microwave spectroscopic data,¹⁾ but these parameters were systematically different from those obtained by Hargittai and Hargittai.²⁾ Thus, we tried to determine the molecular structure of $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ as well as that of $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ in order to compare its molecular parameters with those reported by them. The rotational barriers about the N-B bonds in $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ were also estimated from the electron-diffraction and vibrational-spectroscopic data in the present study.

Experimental

The trimethylamine was prepared by the method described in Ref. 9; it was allowed to react in dry benzene with boron trichloride and boron tribromide, which were commercially available from Wako Pure Chemical Industries, Ltd. The complexes were recrystallized from ethanol and

then sublimed under a vacuum. Their infrared spectra revealed no impurities.¹⁰⁾

The electron-diffraction photographs were recorded on Kodak Electron-Image plates using an r^3 -sector. The accelerating voltage was 40 kV. Samples of $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ were vaporized at 192 °C and 212 °C respectively. The beam current was about 0.8 μA; the exposure time at a long camera distance of 294 mm was 20 s, and that at a short camera distance of 144 mm was 40 s. The pressure in the diffraction chamber was below 1×10^{-5} Torr during the experiment. The electron wavelength was measured from the diffraction patterns of thallium chloride.¹¹⁾ The optical densities of the plates were measured at 0.4 mm intervals by means of a digital microphotometer. The electron-diffraction unit and the digital microphotometer have been described elsewhere.¹²⁾

Analysis and Results

Molecular Intensity and Radial Distribution. The scattering intensities for both complexes were obtained in the ranges of $s=2.5$ –14.8 and 7.5–34.2 Å⁻¹ from the photographic plates taken at the long and short camera distances respectively. They were leveled by theoretical backgrounds, and then the leveled intensities of several plates for each camera distance were averaged. The elastic and inelastic scattering factors were taken from the tables prepared by Schäfer *et al.*¹³⁾ and by Cromer and Mann¹⁴⁾ respectively. The inelastic scattering factor for the hydrogen atom was taken from the table prepared by Tavard *et al.*¹⁵⁾

The experimental background curves were drawn smoothly; the experimental molecular intensities shown in Figs. 2 and 3 were thus obtained.¹⁶⁾ The radial distribution curves for $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and $(\text{CH}_3)_3\text{N}\cdot$

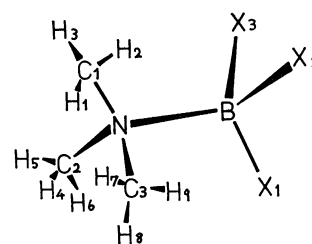


Fig. 1. Numbering of atoms in trimethylamine-boron trihalide (symmetry C_{3v}).

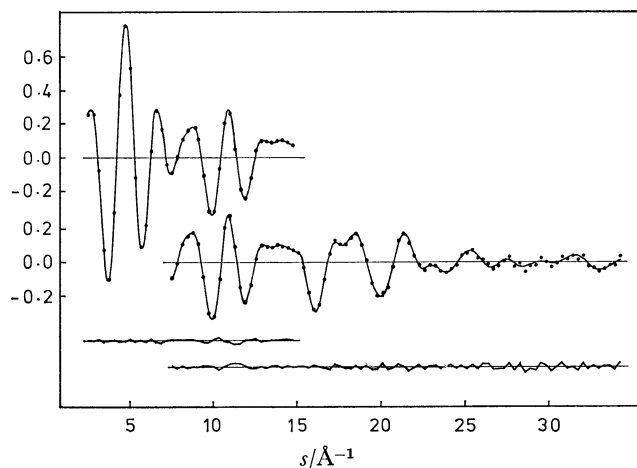


Fig. 2. Molecular intensities for trimethylamine-boron trichloride. The two upper curves are long and short camera-distance data, respectively. Dots represent observed ones, solid curves calculated ones, and the two lower curves the residuals.

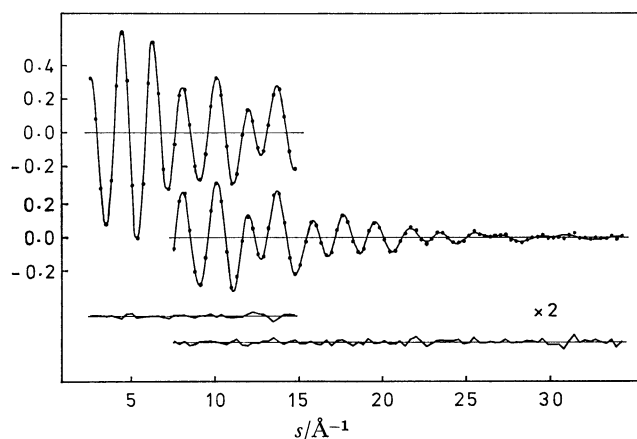


Fig. 3. Molecular intensities for trimethylamine-boron tribromide. The two upper curves are long and short camera-distance data, respectively. Dots represent observed ones, solid curves calculated ones, and the two lower curves two times the residuals.

BBr_3 , shown in Figs. 4 and 5 respectively, were calculated by using the molecular intensities in $s=2.5$ – 14.8 \AA^{-1} from the long camera-distance data and those in $s=15.1$ – 34.2 \AA^{-1} from the short camera-distance data.

Root-Mean-Square Amplitude of Vibration and Shrinkage Effect. The vibrational spectra for $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ were observed by Laswick and Taylor in the solid phase.¹⁰⁾ In the present study, the Urey-Bradley force field was adopted, and the vibrational wave numbers were calculated by using the values listed in Table 1. The σ 's ($\sigma = [\sum(\bar{\nu}_{\text{obsd}} - \bar{\nu}_{\text{calcd}})^2 / \sum \bar{\nu}_{\text{obsd}}^2]^{1/2}$) were 0.017 and 0.021 for $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ respectively. The root-mean-square amplitudes of the vibration and shrinkage effects,¹⁷⁾ $r_a - r_s$, based on this force field were also calculated; they are listed in Table 2.

Torsional Vibration and Height of the Potential Barrier. The torsional vibration around the N–B bond cannot

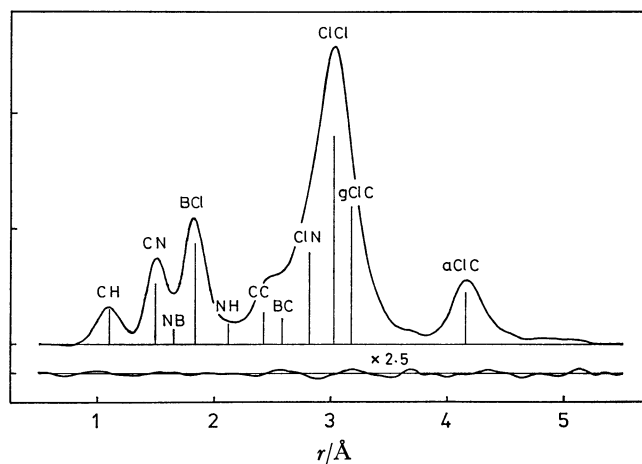


Fig. 4. Radial distribution curve for trimethylamine-boron trichloride. Solid curve, experimental; lower curve, 2.5 times the residuals.

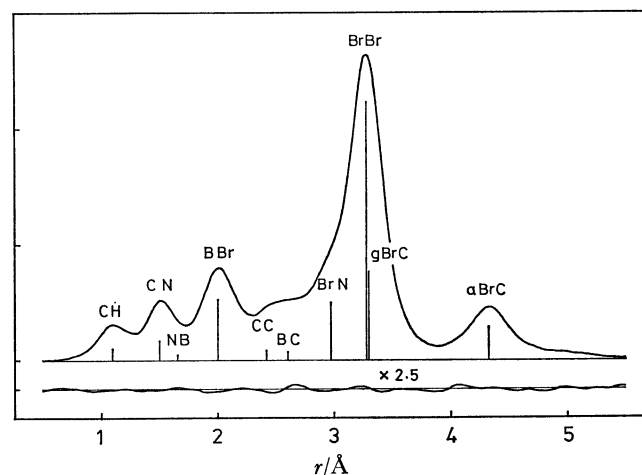


Fig. 5. Radial distribution curve for trimethylamine-boron tribromide. Solid curve, experimental; lower curve, 2.5 times the residuals.

be observed directly in the vibrational spectra of these complexes. However, the potential barrier around the N–B bond, V_0 , can be estimated from a comparison of the observed mean amplitude for the *gauche* halogen-carbon atomic pair, $l(\text{gauche } \text{X}\cdots\text{C})$, with that calculated from the force field,³⁾ since this vibration contributes greatly to the $l(\text{gauche } \text{X}\cdots\text{C})$ value.¹⁸⁾

The $l(\text{gauche } \text{Br}\cdots\text{C})$ value of $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ was found to be $0.164 \pm 0.018 \text{ \AA}$ from the least-squares analysis of the electron-diffraction data. This value corresponds to the V_0 value of 12 kcal mol^{-1} . The lower and upper limits of the V_0 values were estimated to be about 6 kcal mol^{-1} and about 40 kcal mol^{-1} respectively from the error in the observed mean amplitude. The V_0 value in $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ was also estimated to be higher than 18 kcal mol^{-1} from the observed $l(\text{gauche } \text{Cl}\cdots\text{C})$ value of $0.140 \pm 0.008 \text{ \AA}$.

The force constant of the torsional vibration around the C–N bonds was $0.14 \times 10^{-18} \text{ N m}$ in both of the

present complexes. This value corresponds to the V_0 value of 4.4 kcal mol⁻¹, in good agreement with that in the trimethylamine molecule, 4.41 kcal mol⁻¹.¹⁹⁾

Analysis of the Electron-diffraction Intensities. The molecular parameters of $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ were determined from the least-squares analysis of the molecular intensities. It was assumed that these molecules have a staggered form with C_{3v} symmetry in the gas phase and that the methyl groups also have C_{3v} symmetry in a staggered form with respect to the C-N bonds. The shrinkage effects for the bonds in the complexes were fixed to the values listed in Table 2. The asymmetry parameters, κ , for the C-H, C-N, N-B, and B-Cl bonds in $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ were estimated to be 12, 2.5, 6.6, and $8.3 \times 10^{-6} \text{ \AA}^3$ respectively by means of a diatomic approximation.²⁰⁾ The κ parameters for the C-H, C-N, N-B, and B-Br bonds in $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ were estimated to be 12, 2.6, 7.1, and $12 \times 10^{-6} \text{ \AA}^3$ respectively, while those for the other bonds were assumed to be zero in both the present complexes.

The geometrical parameters, r_a , refined by the

TABLE 1. UREY-BRADLEY FORCE FIELD FOR $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ AND $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$

	$(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$	$(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$		$(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$	$(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$
$K(\text{NB})$	1.1	1.2	$F(\text{XX})$	0.65	0.75
$K(\text{BX})$	1.1	0.9	$F(\text{XN})$	0.7	0.7
$K(\text{CN})$	2.1	2.1	$F(\text{CC})$	0.3	0.3
$K(\text{CH})$	4.4	4.4	$F(\text{CB})$	0.15	0.15
$H(\text{XBX})$	0.1	0.1	$F(\text{HH})$	0.1	0.1
$H(\text{XBN})$	0.35	0.2	$F(\text{NH})$	0.6	0.6
$H(\text{CNC})$	0.45	0.45	$Y(\text{NB})$	—	0.35
$H(\text{CNB})$	0.3	0.3	$Y(\text{CN})$	0.14	0.14
$H(\text{HCH})$	0.4	0.4	p	-0.05	-0.05
$H(\text{NCH})$	0.3	0.3			

The torsional force constants, 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} .

least-squares analysis were as follows: $r(\text{B-X})$, $r(\text{X}\cdots\text{X})$, $r(\text{N-B})$, $r(\text{C-N})$, $r(\text{C}\cdots\text{C})$, $r(\text{C-H})$, and $\angle\text{NCH}$. The r_g parameters were calculated from the r_a parameters obtained in the least-squares calculations;¹⁷⁾ they are

TABLE 2. MEAN AMPLITUDES AND SHRINKAGE EFFECTS FOR $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ AND $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ (IN 10^{-4} \AA)

	$(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$		$(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$	
	l	$r_a - r_a$	l	$r_a - r_a$
B-X ₁	667	14	699	11
B-N	655	-5	654	4
B...C ₁	937	0	932	75
B...H ₁	1139	118	1139	186
B...H ₂	1827	25	1811	173
X ₁ ...X ₂	846	0	812	0
X ₁ ...N	765	0	798	-1
X ₁ ...C ₁	892	-2	902	27
X ₁ ...C ₂	1312	-31	1643	-13
X ₁ ...H ₁	1231	66	1275	95
X ₁ ...H ₂	1656	31	1709	93
X ₁ ...H ₄	1738	35	1935	64
X ₁ ...H ₅	2414	-76	2863	-59
X ₁ ...H ₆	2379	-77	2665	9
N-C ₁	548	37	551	144
N...H ₁	1033	200	1035	283
C ₁ ...C ₂	811	31	824	225
C ₁ -H ₁	784	332	784	351
C ₁ ...H ₄	1758	64	1781	236
C ₁ ...H ₅	1769	55	1811	267
C ₁ ...H ₆	1060	138	1068	417
H ₁ ...H ₂	1286	489	1287	569
H ₁ ...H ₄	2590	17	2605	192
H ₁ ...H ₅	2843	-41	2894	142
H ₁ ...H ₆	1875	159	1916	412
H ₂ ...H ₅	1848	152	1879	460
H ₂ ...H ₆	1349	194	1352	552
H ₂ ...H ₉	2639	4	2718	188

The numbering of the atoms is shown in Fig. 1.

TABLE 3. MOLECULAR PARAMETERS OBTAINED FROM LEAST-SQUARES ANALYSIS FOR $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ AND $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$

	$(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$				$(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$		
	Present study			H and H ^{a)}	Present study		
	r_a	r_g	σ	r_g	r_a	r_g	σ
B-X	1.833	1.836	0.002	1.841 (4)	1.997	2.001	0.003
N-B	1.650	1.652	0.009	1.663 (6)	1.656	1.663	0.013
C-N	1.491	1.497	0.003	1.497 (4)	1.483	1.500	0.005
C-H	1.067	1.107	0.005	1.118 (4)	1.054	1.095	0.007
X...X	3.022	3.025	0.005	3.030 (6)	3.280	3.283	0.003
C...C	2.417	2.423	0.006	2.433 (8)	2.398	2.424	0.010
$\angle\text{NCH}$	108.9		1.0	107.0 (7)	109.2		1.7
$\angle\text{XBX}^b)$	111.1	110.9	0.2	110.8 (3)	110.4	110.3	0.3
$\angle\text{CNC}^b)$	108.3	108.1	0.3	108.7 (5)	107.9	107.8	0.5

Bond distance: \AA unit; bond angle: degree unit.

a) Results reported by Hargittai and Hargittai.²⁾ The r_a parameters given by them are transformed to r_g parameters by the $r_g = r_a + l^2/r_a$ relation. The numbers in parentheses represent the limits of error. b) Calculated from independent parameters.

TABLE 4. ROOT-MEAN-SQUARE AMPLITUDES FOR $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ AND $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ (IN Å UNIT)

	$(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$		$(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$	
	Obsd	Calcd	Obsd	Calcd
B-X	0.060 (4)	0.067	0.065 (7)	0.070
N-B	0.070 (26)	0.066	0.101 (43)	0.065
C-N	0.056 (5)	0.055	0.058 (6)	0.055
C-H	0.083 (6)	0.078	0.075 (8)	0.078
X...X	0.092 (3)	0.085	0.101 (2)	0.081
C...C	0.075 (7)	0.081	0.0824 (assumed)	
<i>anti</i> X...C	0.091 (6)	0.089	0.092 (8)	0.090
<i>gauche</i> X...C	0.140 (8)	0.131	0.164 (18)	0.164
X...N	0.090 (5)	0.077	0.092 (8)	0.080

listed in Table 3, together with their limits of error. The errors were estimated from random errors in the least-squares calculations and systematic errors originating from the measurements of the camera distance and the electron wavelength. The mean amplitudes obtained by the least-squares analysis are listed in Table 4. The other mean amplitudes were fixed to the values listed in Table 2 throughout the analysis. The best-fit theoretical intensity curves are shown in Figs. 2 and 3, while the correlation matrices are listed in Tables 5 and 6. The calculations of the mean amplitudes and the shrinkage effects and the least-squares analysis were carried out on a HITAC 8800/8700 computer in the Computer Center of the University of Tokyo.

The observed $l(\text{N-B})$ and $l(\text{Br}\cdots\text{Br})$ values in $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ are found to be larger than their calculated values. This disagreement may be due to the fact that the calculation was based on the force field estimated in the solid phase. A large $l(\text{N-B})$ value has also been observed in the analysis of gaseous $(\text{CH}_3)_3\text{N}\cdot\text{BF}_3$,³⁾ therefore, it may be suggested that the N-B bond is strengthened in the solid phase in comparison with that in the gas phase.

The bond distances of $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ obtained in the present study are shorter by about 0.3% than those obtained by Hargittai and Hargittai.²⁾ This value is greater than the systematic error in the present study (0.1%), but if random errors are taken into account, the molecular parameters obtained in these independent studies are in essential agreement with each other.

Discussion

The molecular parameters for gaseous trimethylamine-boron trihalide complexes are listed in Table 7 in comparison with those for the complexes in the solid phase and those for the free molecules. When a trimethylamine molecule and a boron trihalide molecule form a complex, the distances of the B-X and C-N bonds increase, while the XBX and CNC angles decrease. The experimental results show that such structural changes are greater in the acceptor molecule than in the donor molecule, and that the magnitude of the changes on the complex formation

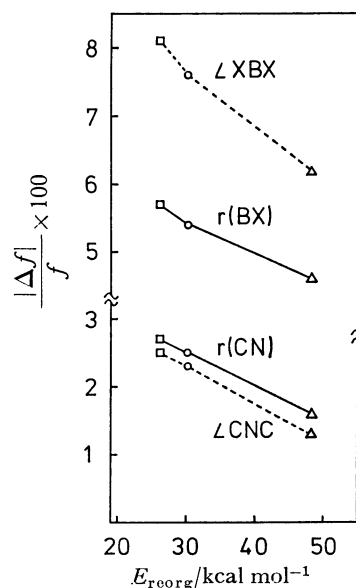


Fig. 6. Parameter changes on complex formation *versus* reorganization energies for acceptor molecules. Solid curves represent positive Δf and dashed curves negative Δf . \triangle : $(\text{CH}_3)_3\text{N}\cdot\text{BF}_3$, \circ : $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$, \square : $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$. The reorganization energies for BF_3 , BCl_3 , and BBr_3 are 48.4, 30.3, and 26.2 kcal mol⁻¹, respectively.²⁵⁾

is in the order of $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3 > (\text{CH}_3)_3\text{N}\cdot\text{BCl}_3 > (\text{CH}_3)_3\text{N}\cdot\text{BF}_3$. The fractional difference, $\Delta f/f$, between the parameter in the complex and that in the corresponding free molecule²¹⁻²⁴⁾ is plotted in Fig. 6 against the reorganization energies calculated by Cotton and Leto²⁵⁾ for boron trihalides. The figure shows a correlation of the structural changes in the donor and acceptor molecules with the reorganization energy of the acceptor molecule. However, no systematic relation can be observed with respect to the N-B bond distance.

In the solid phase,⁵⁻⁷⁾ the B-X and C-N distances are larger and the XBX angles are smaller than the corresponding values in the gas phase. Furthermore, the N-B dative bonds are much shorter in the solid phase than in the gas phase. These facts indicate that, in the solid phase, the charge transfer occurs to a larger extent, thereby enhancing the dative bonding. This trend is also in accord with our foregoing remarks with regard to its mean amplitude.

The rotational barrier around the N-B bond, V_0 , is considerably larger in $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ and $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$ than in $(\text{CH}_3)_3\text{N}\cdot\text{BF}_3$, 4.3 ± 0.3 kcal mol⁻¹.³⁾ As has been described above, the potential barrier for $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$ seems to be larger than that for $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$, though these barriers could not be determined very accurately in the present study. Thus, the magnitudes of the potential barriers about the N-B bonds are in the order of $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3 \geq (\text{CH}_3)_3\text{N}\cdot\text{BBr}_3 > (\text{CH}_3)_3\text{N}\cdot\text{BF}_3$, in agreement with that obtained from an NMR study.²⁶⁾ This order seems to be consistent with the inverse order of the observed N-B bond lengths in the gas phase.

TABLE 5. CORRELATION MATRIX OF $(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$

	$r(\text{BCl})$	$r(\text{NB})$	$r(\text{CN})$	$r(\text{CH})$	$r(\text{ClCl})$	$r(\text{CC})$	$\angle\text{NCH}$	$l(\text{BCl})$	$l(\text{CN})$	$l(a\text{ClCl})$	$l(g\text{ClCl})$	$l(\text{CC})$	$l(\text{CH})$	$l(\text{ClCl})$	$l(\text{CIN})$	$l(\text{NB})$	R_1^a	R_2^a
$r(\text{BCl})$	1.0																	
$r(\text{NB})$	-0.13	1.0																
$r(\text{CN})$	0.03	-0.13	1.0															
$r(\text{CH})$	-0.07	-0.10	0.01	1.0														
$r(\text{ClCl})$	0.55	0.59	-0.09	-0.07	1.0													
$r(\text{CC})$	0.13	0.39	0.59	-0.11	0.26	1.0												
$\angle\text{NCH}$	0.54	0.07	0.18	-0.30	0.40	0.30	1.0											
$l(\text{BCl})$	0.04	-0.20	0.28	0.02	-0.02	-0.04	0.14	1.0										
$l(\text{CN})$	0.12	-0.36	0.35	-0.11	-0.14	-0.01	0.18	0.68	1.0									
$l(a\text{ClCl})$	-0.07	-0.13	-0.03	0.13	-0.07	-0.19	-0.21	0.24	0.17	1.0								
$l(g\text{ClCl})$	0.42	0.34	-0.16	-0.01	0.83	0.04	0.26	0.10	-0.02	0.08	1.0							
$l(\text{CC})$	-0.11	-0.18	-0.20	0.05	-0.28	-0.20	-0.41	0.00	0.02	0.13	-0.18	1.0						
$l(\text{CH})$	-0.08	-0.04	0.08	0.02	-0.03	-0.06	-0.14	0.21	0.12	0.17	0.08	0.09	1.0					
$l(\text{ClCl})$	0.24	0.04	-0.11	0.08	0.38	0.05	0.24	0.33	0.21	0.21	0.61	-0.09	0.20	1.0				
$l(\text{CIN})$	0.30	0.04	-0.04	-0.01	0.35	0.02	0.46	0.18	0.12	0.02	0.54	-0.26	0.04	0.73	1.0			
$l(\text{NB})$	0.12	-0.22	0.52	-0.15	-0.06	0.25	0.37	0.64	0.74	-0.02	-0.07	-0.16	-0.07	0.04	0.12	1.0		
R_1	0.08	-0.23	-0.05	0.24	0.11	-0.39	-0.17	0.36	0.25	0.35	0.39	0.11	0.24	0.46	0.28	0.02	1.0	
R_2	-0.06	-0.21	0.00	0.14	-0.07	-0.30	-0.20	0.59	0.46	0.43	0.16	0.26	0.43	0.47	0.12	0.07	0.54	1.0

a) R_1 and R_2 are the indices of resolution for the long and short camera distance data respectively. The indices of resolution and their uncertainties are $R_1=0.93\pm 0.02$ and $R_2=0.93\pm 0.04$.

TABLE 6. CORRELATION MATRIX OF $(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$

	$r(\text{BBr})$	$r(\text{NB})$	$r(\text{CN})$	$r(\text{CH})$	$r(\text{BrBr})$	$r(\text{CC})$	$\angle\text{NCH}$	$l(\text{BBr})$	$l(\text{CN})$	$l(\text{CH})$	$l(\text{BrN})$	$l(a\text{BrC})$	$l(g\text{BrC})$	$l(\text{BrBr})$	$l(\text{NB})$	R_1^a	R_2^a
$r(\text{BBr})$	1.0																
$r(\text{NB})$	-0.58	1.0															
$r(\text{CN})$	0.11	-0.35	1.0														
$r(\text{CH})$	-0.17	0.06	0.00	1.0													
$r(\text{BrBr})$	0.12	0.52	-0.42	-0.03	1.0												
$r(\text{CC})$	0.17	0.22	0.59	0.00	0.32	1.0											
$\angle\text{NCH}$	0.02	0.34	0.16	-0.14	0.17	0.42	1.0										
$l(\text{BBr})$	0.10	-0.23	-0.23	0.02	0.11	-0.29	-0.69	1.0									
$l(\text{CN})$	0.35	-0.36	0.28	-0.16	-0.09	0.13	0.08	0.06	1.0								
$l(\text{CH})$	0.00	-0.03	-0.04	-0.03	0.07	-0.06	-0.17	0.21	0.02	1.0							
$l(\text{BrN})$	0.17	0.21	-0.35	0.01	0.67	0.11	0.01	0.26	0.03	0.13	1.0						
$l(a\text{BrC})$	0.02	-0.06	-0.16	0.09	0.14	-0.15	-0.32	0.38	0.05	0.13	0.23	1.0					
$l(g\text{BrC})$	0.14	0.13	-0.42	0.03	0.55	-0.11	-0.33	0.58	0.06	0.23	0.73	0.43	1.0				
$l(\text{BrBr})$	-0.11	-0.42	0.09	0.10	-0.39	-0.33	-0.24	0.23	0.13	0.09	-0.17	0.09	-0.20	1.0			
$l(\text{NB})$	0.33	-0.30	0.66	-0.16	-0.21	0.48	0.36	-0.25	0.51	-0.17	-0.23	-0.19	-0.36	-0.02	1.0		
R_1	0.08	-0.10	-0.29	0.11	0.30	-0.24	-0.45	0.68	0.14	0.27	0.55	0.48	0.87	0.16	-0.32	1.0	
R_2	0.05	-0.09	-0.29	0.12	0.20	-0.29	-0.34	0.63	0.18	0.27	0.43	0.40	0.71	0.37	-0.29	0.82	1.0

a) R_1 and R_2 are the indices of resolution for the long and short camera distance data respectively. The indices of resolution and their uncertainties are $R_1=0.91\pm 0.03$ and $R_2=0.92\pm 0.03$.

TABLE 7. COMPARISON OF MOLECULAR PARAMETERS

	$(\text{CH}_3)_3\text{N}\cdot\text{BF}_3$		$(\text{CH}_3)_3\text{N}\cdot\text{BCl}_3$		$(\text{CH}_3)_3\text{N}\cdot\text{BBr}_3$		BF_3 , ^{e)} $(\text{CH}_3)_3\text{N}$ ^{d)}	BCl_3 ^{e)}	BBr_3 ^{f)}
	Gas	Solid ^{a)}	Gas	Solid ^{b)}	Gas	Solid ^{b)}			
$r(\text{N-B})$	1.674 (4)	1.585	1.652 (9)	1.609 (6)	1.663 (13)	1.60 (2)			
$r(\text{B-X})$	1.374 (2)	1.39	1.836 (2)	1.864 (4)	2.001 (3)	2.04 (2)	1.313 (1)	1.742 (4)	1.893 (5)
$r(\text{C-N})$	1.485 (2)	1.50	1.497 (3)	1.52 (1)	1.500 (5)	1.52 (1)	1.461 (2)		
$\angle\text{XBX}$	112.6 (3)	107	110.9 (2)	109.5 (2)	110.3 (3)	108.3 (7)	120	120	120
$\angle\text{CNC}$	109.2 (4)	114	108.1 (3)	108.6 (14)	107.8 (5)	107.7 (7)	110.6 (6)		

Bond distance: Å unit; bond angle: degree unit. The values in the gas phase represent r_g parameters.

a) Ref. 5. Limits of error are not clear. b) Ref. 7. c) Ref. 22. d) Ref. 21. e) Ref. 23. f) Ref. 24.

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