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Molecular Structure and Internal Rotation of Trimethylamine-Boron Trifluoride. A Combination of Electron Diffraction and Spectroscopic Data

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The molecular structure of trimethylamine-boron trifluoride $(CH_3)_3N\cdot BF_3$ was determined from gas electron-diffraction data with vibrational and rotational spectroscopic data. The geometric parameters of the molecule were found to be very close to those inferred from the preliminary analysis of the diffraction data alone. The structural parameters and uncertainties were r_g(N–B) = 1.674(4) Å, r_g(B–F) = 1.374(2) Å, r_g(C–N) = 1.485 (2) Å, r_g(C–H) = 1.100(3) Å, r_g(F···F) = 2.288(2) Å, and r_g(C···C) = 2.420(4) Å. The potential barrier about the N–B axis was estimated to be 4.3±0.3 kcal/mol in the gas phase; this value is much larger than that from NMR spectra.

Several studies have recently been carried out on the gas-phase structure of trimethylamine-boron trifluoride $(CH_3)_3N\cdot BF_3$,[1–3] which is a representative of donor-acceptor molecular complexes, in order to clarify the difference in the molecular structure between the gas and the solid. However, there are considerable discrepancies among the results from electron diffraction[2,3] and microwave spectra:[1] *e.g.*, the N–B distance determined by microwave spectroscopy is about 0.03 Å shorter than that from electron diffraction. The electron diffraction study by Hargittai and Hargittai[3] also gave different results from ours,[2] especially for the B–F and C–N distances, though the rotational constant calculated using their results did not agree well with the observed one. On the other hand, this molecule has an internal rotation about the N–B bond, and the rotational barrier was found to be 1.7 kcal/mol from the NMR study in the solid phase.[4] The height of the barrier seems to be too small, compared with those in other ethane-like molecules.[5] The height of the potential barrier about the N–B bond cannot be estimated from IR or Raman vibrational spectroscopic studies, because the torsional vibration is inactive in these spectra. It is therefore very desirable to estimate it from a combined analysis of electron diffraction intensities with spectroscopic data. Thus, the molecular structure of $(CH_3)_3N\cdot BF_3$ was reinvestigated in order to determine more accurate molecular parameters as well as the height of the potential barrier about the N–B bond, by means of a joint analysis of gas-electron diffraction and spectroscopic data.

Experimental

Trimethylamine and boron trifluoride gases, which were prepared by the procedures described in the literature,[6,7] were condensed in a flask cooled by liquid air and were allowed to react while being warmed slowly to room temperature. A white product was purified by sublimation under vacuum, and its infrared spectrum[8,9] revealed no impurities. In the electron-diffraction experiment the sample was vaporized at about 130 °C by means of a high tepmerature nozzle, and photographs were taken with an r^3-sector at the camera distances of 144 and 294 mm. The accelerating voltage was 40 kV. The exposure time at the short camera distance was 60 s, using an electron-beam current of 0.8 μA, and that at the long camera distance was 20 s, using a beam current of 0.6 μA. The pressure of the diffraction chamber was below 1×10^{-5} Torr during the experiment. The electron wavelength was measured using diffraction patterns of thallium chloride powder.[10] Photographs were recorded on Fuji spectroscopic plates, and the optical densities of four short and three long camera distance plates were measured at 0.4 mm intervals by means of a digital microphotometer. The electron-diffraction unit and digital microphotometer used in the present study were described elsewhere.[11]

Analysis and Results

Molecular Intensity and Radial Distribution. The scattering intensities were obtained in the range of s=2.5—17.3 and 5.0—33.0 Å^{-1} from the photographic plates at long and short camera distances, respectively. They were leveled by the theoretical backgrounds, and then the leveled intensities of several plates for each camera distance were averaged. The background curves were drawn smoothly by hand for the long distance data and were fitted by a polynomial of 7th degree[12] for the short distance data, and then the molecular intensities for each camera distance were joined at s = 14.8 Å^{-1}. Figure 2 shows the observed intensities and Fig. 3 shows the experimental radial distrubution curve. The elastic and inelastic scattering factors were taken from the tables prepared by Kimura *et al.*[13] and Cromer and Mann,[14] respectively. The inelastic scattering factor for the hydrogen atom was taken from Ref. 15.

Mean Amplitude of Vibration and Shrinkage Effect. Several workers have measured the vibrational spectra of $(CH_3)_3N\cdot BF_3$ in the solid phase and calculated the force field.[9,16] However, these calculations seem not to be reasonable because a large number of

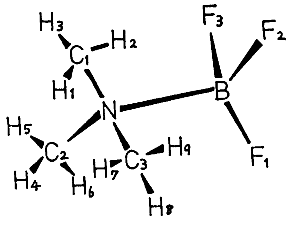

Fig. 1. Numbering of atoms in trimethylamine-boron trifluoride (symmetry C_{3v}).

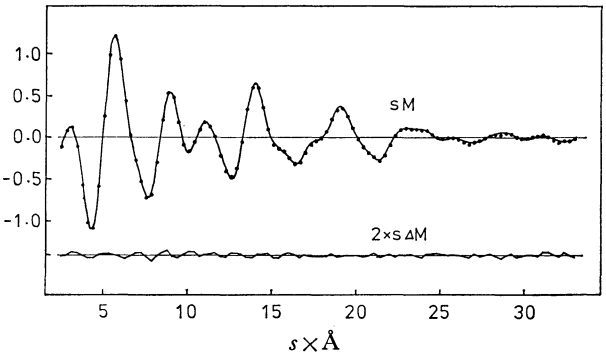

Fig. 2. Molecular intensities for trimethylamine-boron trifluoride. Solid curve, calculated; dotted curve, experimental. Lower curve, two times the residuals with respect to the experimental curve.

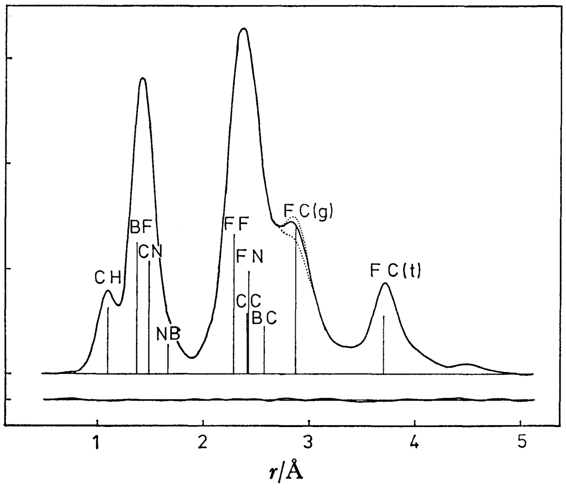

Fig. 3. Radial distribution curve for trimethylamine-boron trifluoride. Solid curve, experimental; lower curve, the residual curve; dotted curves, calculated using V_0=6.0 kcal/mol (upper) and V_0=3.0 kcal/mol (lower).

unknown parameters were used; *e.g.*, Laswick and Taylor obtained forty force constants on the basis of twenty wave numbers measured for each of five isotopic species.[9] In the present study, a modified Urey-Bradley force field was adopted in order to reduce the variable parameters. The force constants used are shown in Table 1, and the calculated wave numbers are listed in Table 2, where the spectra were assigned according to the notation suggested by Laswick and Taylor.[9] The mean amplitudes of vibration and shrinkage effects,[17] r_a-r_α, at 130 °C, which were calculated using the above force constants, are shown in Table 3. The calculated mean amplitudes of most atomic pairs agreed well with the observed ones, but the observed mean amplitude of the N–B bond is significantly larger than the calculated one. The reason for this disagreement is that the calculation was carried out on the basis of the vibrational spectra observed in the solid state, where the N–B bond strength is probably enhanced.

Torsional Vibration and Height of Potential Barrier. Torsional vibrations around the N–B and C–N bonds

TABLE 1. FORCE CONSTANTS FOR $(CH_3)_3N \cdot BF_3$

K(B-F)	2.8	*H*(CNC)	0.36
K(N-B)	1.5	*H*(CNB)	0.65
K(C-N)	3.3	*H*(HCH)	0.35
K(C-H)	4.5	*H*(NCH)	0.33
p_1	0.6	*F*(FF)	0.70
p_2	−0.02	*F*(FN)	0.70
Y(N-B)	0.134	*F*(CC)	0.05
Y(C-N)	0.18	*F*(CB)	0.50
H(FBF)	0.38	*F*(HH)	0.20
H(FBN)	0.42	*F*(HN)	0.40

K, p, H, F: mdyn/Å unit; *Y*: mdyn·Å unit. p_1: cross term between Δr(N-B) and Δr(B-F). p_2: cross term between Δr(N-B) and Δr(C-N).

TABLE 2. OBSERVED AND CALCULATED WAVE NUMBERS FOR $(CH_3)_3N \cdot BF_3$[a] (cm^{-1} UNIT)

		Obsd	Calcd	$\Delta\nu/\nu$
A_1	ν_3	1486	1488	−0.1%
	ν_4	1453	1453	0.0
	ν_5	1271	1269	0.2
	ν_6	843	844	−0.1
	ν_7	694	696	−0.3
	ν_8	330	319	3.3
	ν_9	929	931	−0.2
E	ν_{19}	1478	1491	−0.9
	ν_{20}	1469	1454	1.0
	ν_{21}	1412	1438	−1.8
	ν_{22}	1255	1351	−7.6
	ν_{23}	1105	1064	3.7
	ν_{24}	990	990	0.0
	ν_{25}	1144	1129	1.3
	ν_{26}	432	431	0.2
	ν_{27}	343	343	0.0
	ν_{28}	300	275	8.3
	ν_{29}	520	521	−0.2
	ν_{30}	323	321	0.6

a) Assignment is according to the notation in Ref. 9.

TABLE 3. MEAN AMPLITUDES AND SHRINKAGE EFFECTS FOR $(CH_3)_3N \cdot BF_3$ (IN 10^{-4} Å)

	l	r_a-r_α		*l*	r_a-r_α
$B-F_1$	528	86	$N-C_1$	501	81
B-N	589	−6	$N\cdots H_1$	1041	171
$B\cdots C_1$	714	39	$C_1\cdots C_2$	807	113
$B\cdots H_1$	1030	108	C_1-H_1	778	238
$B\cdots H_2$	1632	86	$C_1\cdots H_4$	1620	128
$F_1\cdots F_2$	681	140	$C_1\cdots H_5$	1635	137
$F_1\cdots N$	665	39	$C_1\cdots H_6$	1071	227
$F_1\cdots C_1$	717	−1	$H_1\cdots H_2$	1262	362
$F_1\cdots C_2$	1532	12	$H_1\cdots H_4$	2399	98
$F_1\cdots H_1$	1109	48	$H_1\cdots H_5$	2476	72
$F_1\cdots H_2$	1669	12	$H_1\cdots H_6$	1700	236
$F_1\cdots H_4$	1653	85	$H_2\cdots H_5$	1778	246
$F_1\cdots H_5$	2682	−97	$H_2\cdots H_6$	1408	299
$F_1\cdots H_6$	2387	60	$H_2\cdots H_9$	2384	92

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

TABLE 4. MOLECULAR PARAMETERS

	$(CH_3)_2N\cdot BF_3$					$(CH_3)_3N$[f]	BF_3[g]	$(CH_3)_3N\cdot BF_3$[h]
	r_α[a]	r^0_α[b]	r_g[c]	r_g[d]	r_0[e]	r^0_α	r^0_α	(solid)
B–F	1.363 (2)	1.370 (2)	1.374	1.356 (6)	1.387 (5)		1.311 (1)	1.39
N–B	1.669 (6)	1.669 (4)	1.674	1.666(11)	1.636 (4)			1.585
C–N	1.476 (3)	1.481 (2)	1.485	1.470(10)	1.476 (5)	1.458 (2)		1.50
C–H	1.072 (3)	1.081 (3)	1.100	1.104 (8)	1.10 (3)	1.100 (5)		
F···F	2.272 (3)	2.285 (2)	2.288	2.261 (6)	2.305(10)		2.271	2.24
C···C	2.407 (5)	2.417 (4)	2.420	2.383(12)	2.400(10)	2.401 (6)		
∠NCH	110.0 (8)	110.2 (6)	110.2	106.3(18)	109 (2)	110.2(13)		
∠FBF	113.0 (3)	113.1 (3)	112.6	113.1 (9)	112.4 (2)		120	107
∠CNC	109.3 (4)	109.4 (4)	109.2	108.5 (7)	108.6 (2)	110.9 (6)		114

Bond distance: Å unit; bond angle: degree unit. a) Results from electron diffraction data. b) Results from the joint analysis of electron diffraction data and rotational constant. c) r_g parameters transformed from r^0_α parameters.[17] The limits of error are equal to those in the r^0_α parameters. d) Results reported by Hargittai and Hargittai.[3] r_a parameters given by them are transformed to r_g parameters by the relation of $r_g = r_a + l^2/r_a$. e) Results from microwave spectroscopic study. Ref. 1. f) Ref. 24. g) Ref. 25. The F···F distance was calculated by the relation of $r^0_\alpha(F\cdots F) = \sqrt{3}\cdot r^0_\alpha(B\text{–}F)$. h) Ref. 26. Limits of error are not clear.

TABLE 5. ROOT-MEAN-SQUARE AMPLITUDES FOR $(CH_3)_3N\cdot BF_3$ (IN Å UNIT)

	l_{obsd}[a]	l_{calcd}
B–F	0.051 (3)	0.053
N–B	0.083 (9)	0.059
C–N	0.054 (3)	0.050
C–H	0.074 (3)	0.078
F···F	0.064 (2)	0.068
F···N	0.066 (2)	0.067
trans F···C	0.081 (3)	0.072
gauche F···C	0.154 (3)	0.153

a) Results from joint analysis of electron diffraction data and rotational constant.

were treated in a high barrier approximation.[18] However, the torsional vibration around the N–B axis which was completely isolated from other vibrations contributes greatly to the *gauche* F···C mean amplitude. The mean amplitude of the *gauche* F···C calculated without consideration of this motion resulted in 0.099 Å. The electron diffraction experiment gave the mean amplitude of 0.154±0.003 Å, as listed in Table 5. The difference between the two values suggests a significant contribution of the torsional vibration around the N–B bond. Therefore, the force constant Y in the formula $V=(1/2)Y\Delta t^2$, where V is a potential energy and Δt is an internal coordinate in the torsional vibration, was chosen so that the calculated mean amplitude of the *gauche* F···C was in agreement with the observed one. Thus the force constant Y and the wave number of the vibration were estimated to be 0.134±0.010 mdyn·Å and 67±3 cm^{-1}, respectively. The errors were estimated from that of the observed *gauche* F···C mean amplitude. If the potential function around the N–B bond is assumed to be $V(t)=(1/2)V_0(1-\cos 3t)$, where V_0 is the height of the potential barrier, V_0 can be estimated to be 4.3±0.3 kcal/mol using the relation $V_0=(2/9)Y$.

On the other hand, the torsion around the N–B bond was also treated in a low barrier approximation,[18] and then the molecular intensities were calculated by the average over the torsional angle at 5° intervals, using the weight of the Boltzmann factor $\exp(-V/kT)$. The *gauche* F···C mean amplitude was assumed to be 0.099 Å at each torsional angle. Thus radial distributions were obtained from the molecular intensites calculated using assumed values of V_0, as shown in Fig. 3. The radial distribution obtained from $V_0=$ 4.5 kcal/mol gave the same shape of the *gauche* F···C peak as in the experimental radial distribution, and the value of V_0 was consistent with that obtained from the analysis of a high barrier approximation.

Analysis of Electron Diffraction Intensities and Rotational Constants. Shrinkage effects were considered and the molecular parameters in the r_α structure were determined by the least-squares analysis of the molecular intensities; these are shown in Table 4. It is assumed that the molecule of $(CH_3)_3N\cdot BF_3$ has a staggered form with C_{3v} symmetry, and that the methyl group also has local C_{3v} symmetry in the staggered form with respect to the C–N axis. The mean amplitudes (except those listed in Table 5) were fixed as shown in Table 3, and the asymmetry parameters κ for the C–H, B–F, N–B, and C–N bonds were estimated to be 12, 2.4, 11, and 2.5×10^{-6} Å^3, respectively, by a diatomic approximation.[19] The κ parameters for other atomic pairs were ignored.

Bryan and Kuczkowski obtained the rotational constant B_0 value of 1756.073±0.01 MHz for the normal species of $(CH_3)_3N\cdot BF_3$.[1] The vibrational correction for the rotational constant[20] was made by the library program in the Computer Center of the University of Tokyo; B_z was 1756.17 MHz. The uncertainty in the vibrational correction was tentatively assumed to be 80%. The r_α parameters in Table 4 was transformed to r^0_α parameters by extrapolating $r_a - r_\alpha$ to zero kelvin.[17] Here the anharmonic contributions were estimated by a diatomic approximation. The rotational constant calculated from the r^0_α parameters was 1758±12 MHz, which was in good agreement with the experimental B_z. Although the parameters obtained from the above electron diffraction analysis

TABLE 6. CORRELATION MATRIX FOR MOLECULAR PARAMETERS OF $(CH_3)_3N \cdot BF_3$ a)

	r(BF)	r(NB)	r(CN)	r(CH)	r(FF)	r(CC)	∠NCH	l(BF)	l(CN)	l(FF)	l(FN)	l(FC(t))	l(FC(g))	l(NB)	l(CH)	R_1 b)	R_2 b)
r(BF)	1.0																
r(NB)	−0.59	1.0															
r(CN)	−0.31	−0.03	1.0														
r(CH)	−0.07	−0.01	0.33	1.0													
r(FF)	0.41	0.38	−0.10	0.04	1.0												
r(CC)	−0.27	0.29	0.87	0.31	0.19	1.0											
∠NCH	0.34	0.01	−0.35	−0.22	0.43	−0.04	1.0										
l(BF)	0.33	−0.14	−0.59	−0.38	0.02	−0.55	0.16	1.0									
l(CN)	0.48	−0.24	−0.53	−0.33	0.10	−0.50	0.21	0.92	1.0								
l(FF)	0.15	−0.19	−0.20	−0.12	0.07	−0.33	0.04	0.39	0.36	1.0							
l(FN)	0.23	−0.09	−0.17	−0.08	0.23	−0.25	−0.02	0.30	0.30	0.79	1.0						
l(FC(t))	−0.04	−0.01	0.03	−0.08	−0.07	−0.01	−0.08	0.24	0.22	0.14	0.09	1.0					
l(FC(g))	0.08	−0.02	−0.06	−0.02	0.14	0.08	0.52	−0.06	−0.03	−0.09	−0.15	−0.07	1.0				
l(NB)	0.36	−0.18	−0.37	−0.24	0.11	−0.30	0.33	0.54	0.67	0.17	0.11	0.10	0.09	1.0			
l(CH)	0.06	−0.23	0.29	−0.03	−0.13	0.19	−0.09	0.26	0.29	0.15	0.05	0.25	−0.06	0.19	1.0		
R_1	−0.26	0.18	0.04	−0.14	−0.18	−0.03	−0.38	0.35	0.26	0.35	0.35	0.25	−0.23	−0.05	0.16	1.0	
R_2	0.02	−0.20	0.13	−0.14	−0.19	0.03	−0.10	0.60	0.57	0.30	0.15	0.36	−0.11	0.33	0.76	0.38	1.0

a) Matrix elements are defined as $\rho_{ij}=B_{ij}^{-1}/(B_{ii}^{-1}\times B_{jj}^{-1})^{1/2}$. b) R_1 and R_2 are indices of resolution for the long and short camera-distance data, respectively.

TABLE 7. OBSERVED AND CALCULATED ROTATIONAL CONSTANTS FOR $(CH_3)_3N \cdot BF_3$ (IN MHz UNIT)

B_0 a)	1756.073 ± 0.01
B_z b)	1756.17 ± 0.08
B_α^0 c)	1758 ± 12
B_{av} d)	1756.17 ± 0.08

a) Observed rotational constant for the ground vibrational state. Ref. 1. b) Rotational constant corrected for vibrational effects. c) Rotational constant calculated from the parameters obtained by the analysis of electron diffraction data. See text. d) Best-fit rotational constant obtained by the joint analysis.

TABLE 8. ROTATIONAL CONSTANTS OF $(CH_3)_3N \cdot BF_3$ (IN MHz UNIT)

	B_0 a)	B_0^α b)
$(^{13}CH_3)_3N \cdot {}^{11}BF_3$	1706.100	1706 (2)
$(^{13}CH_3)_3N \cdot {}^{10}BF_3$	1709.884	1710 (2)
$(CD_3)_3N \cdot {}^{11}BF_3$	1546.799	1545 (2) c)
$(CD_3)_3N \cdot {}^{10}BF_3$	1550.445	1548 (2) c)
$(CH_3)_3N \cdot {}^{10}BF_3$	1759.780	1760 (2)
$(CH_3)_3{}^{15}N \cdot {}^{11}BF_3$	1751.630	1752 (2)

a) Observed rotational constants, Ref. 1; the vibrational corrections, $\Delta B = B_0 - B_\alpha^0$, are adout 0.1 MHz. b) Rotational constants caluculated from the r_α^0 parameters in Table 4. The correlations between the parameters were taken into consideration in calculating the errors. c) The C–D distance and NCD angle were assumed to be equal to r(C–H)−0.0015 Å and ∠NCH −0.16°, respectively.[21]

were quite compatible with the rotational constant determined by the microwave experiment, the joint analysis of electron diffraction intensities and rotational constant was performed. The relative weight for the observed rotational constant in the least-squares calculation was estimated to be 6×10^8, in such a way that 2.5 times the standard deviation of the rotational constant obtained from the least-squares calculation is nearly equal to the uncertainty in B_z. The r_α^0 parameters and mean amplitudes determined by the joint analysis are given in Tables 4 and 5, together with the r_g parameters and their associated errors. The errors were estimated from random errors in the least-squares calculations and systematic errors originating from the measurements of camera distance and electron wavelength. The correlation matrix is listed in Table 6. The results from the joint analysis were the same as those obtained from the preliminary analysis.[2] The errors for the molecular parameters were much smaller than those from the study by Hargittai and Hargittai,[3] though there seems to be systematic devitation between the two sets of data. The calculated rotational constants were in quite good agreement with the observed ones, as listed in Table 7. Recently, the microwave spectra of deuterium and carbon-13 enriched samples of $(CH_3)_3N \cdot BF_3$ have been studied.[1] The rotational constants for these isotopic species were calculated using the parameters obtained by the above joint analysis, and their calculated values are also in agreement with the observed values, as shown in Table 8. The best-fit theoretical intensity curve is shown in Fig. 2.[22]

Discussion

The joint analysis of electron diffraction and vibrational spectra gave the result that the height of the potential barrier hindering the internal rotation of $(CH_3)_3N \cdot BF_3$ is 4.3 kcal/mol in the gas phase. This corresponds to that of Cl_3CSiCl_3.[18] The height of the potential barrier of $(CH_3)_3N \cdot BF_3$ is considerably larger than that of $H_3P \cdot BH_3$, 2.47 kcal/mol, which was obtained from microwave spectroscopy.[23] The increase of the potential barrier can be attributed to the large size of fluorine atoms and methyl groups and the smaller N–B distance in $(CH_3)_3N \cdot BF_3$. A wide line NMR study of $(CH_3)_3N \cdot BF_3$ in the solid phase showed that the barrier around the N–B axis was rather small, 1.7 kcal/mol.[4] The reason for this discrepancy is unknown, though one should be careful in comparing the values obtained by the two different methods.

Comparing the molecular structure of $(CH_3)_3N\cdot BF_3$ with those of the component molecules of $(CH_3)_3N$ and BF_3[24,25] (Table 4), the C–N and B–F distances increase by the complex formation by 1.6 and 4.5%, respectively, and the CNC and FBF angles decrease by 1.4 and 5.8%, respectively. This shows that the changes in the molecular parameters of the acceptor are much larger than those of the donor. In the solid phase, the molecule takes the same configuration as in the vapor phase, but the bond distances and the angles in the crystal[26] are considerably different from those in the vapor phase (Table 4). The C–N and B–F bond distances are longer and the N–B bond distance is shorter than those in the vapor phase. These changes indicate that the donor-acceptor bonding is enhanced in the solid state. The increments of the C–N and B–F bond distances are 2.9 and 6.0%, respectively, and the rate of the decrease of the FBF angle is 10.8%; these results are obtained by comparing the structural data from X-ray with those for the gaseous component molecules.

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