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The Molecular Structure of Trimethylamine-Borane as Studied from Gas Electron Diffraction and Spectroscopic Data

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The molecular structure of trimethylamine-borane $(CH_3)_3N \cdot BH_3$ has been determined from gas electron-diffraction data with spectroscopic data. The molecular parameter values and their uncertainties are r_g(B–H)= 1.261±0.006 Å, r_g(N–B)=1.656±0.002 Å, r_g(C–N)=1.485±0.001 Å, r_g(C–H)=1.108±0.002 Å, ∠HBH=112.8±0.4°, and ∠CNC=109.2±0.2°. The potential barrier around the N–B bond has been estimated to be larger than 5 kcal mol^{-1} (1 cal=4.183 J). The isotope effects on the B–D bond distance and the DBD angle have also been estimated to be −0.006 Å and 0.4°, respectively, in r_a^0 parameters.

Trimethylamine-borane $(CH_3)_3N \cdot BH_3$ is one of stable molecular complexes, and the gaseous molecular structure has been determined from microwave spectroscopic data by two research groups.[1,2] The N–B distances obtained from both studies, 1.609 and 1.638 Å, are considerably different from each other. On the other hand the N–B distances in $(CH_3)_3N \cdot BX_3$ (where X is F, Cl, Br, and I), on which we have studied by electron diffraction,[3] fall into the range of 1.65—1.67 Å. The N–B distances of $(CH_3)_3N \cdot BH_3$ obtained by MW spectra are out of this range, though it appears to be difficult to determine precisely the molecular parameters of this compound from MW data because only one rotational constant is available for one isotope species and the center of mass in this compound locates close to the nitrogen atom.

The acceptor power of borane for trimethylamine or pyridine has been discussed in relation with heat of formation,[4,5] dipole moment,[6] chemical shift of NMR spectra,[7] and displacement reaction.[8] We have also reported that on complex formation the changes of molecular structure of the donor and the acceptor molecules have some relation with the acceptor power of boron trihalides.[3] In order to discuss the acceptor power of borane in this point of view, it is necessary to know the precise values of molecular parameters of $(CH_3)_3N \cdot BH_3$. We undertook thus the structure analysis by a gas electron-diffraction method in combination with microwave spectroscopic data.

Experimental

The sample of trimethylamine-borane was purified by sublimation in vacuum. Electron diffraction photographs were taken by the use of an r^3-sector on Kodak Electron-Image plates at camera distances of 293.30 and 143.60 mm. The sample is highly volatile and a nozzle was heated at 346 K to introduce the vaporized sample to vacuum from a warmed sample holder. An accelerating voltage was 40 kV and the wavelength was determined from the diffraction patterns of thallium(I) chloride.[9] The exposure times were about 135 and 280 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 5×10^{-6} Torr (1 Torr=133.322 Pa) during the experiment. Three plates and four plates were selected for the long and short camera distance photographs, respectively, 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.[10]

Analysis and Results

Molecular Intensity and Radial Distribution. The scattering intensities in the range of s=2.8—16.5 Å^{-1} were obtained from the long camera-distance plates and those in the range of s=10.1—33.3 Å^{-1} from the short camera-distance plates. They were leveled by using theoretical backgrounds, and the intensities for each camera distance were averaged. The elastic and inelastic scattering factors were taken from the tables prepared by Schäfer *et al.*[11] and by Cromer and Mann,[12] respectively. The inelastic scattering factor for the hydrogen atom was taken from the table by Tavard *et al.*[13] The experimental background curve was drawn smoothly,[14] and the experimental molecular intensities obtained are shown in Fig. 1. Figure 2 shows the experimental radial distribution function calculated from the experimental molecular intensities. The molecular model of $(CH_3)_3N \cdot BH_3$ and the numbering of the atoms are shown in Fig. 3.

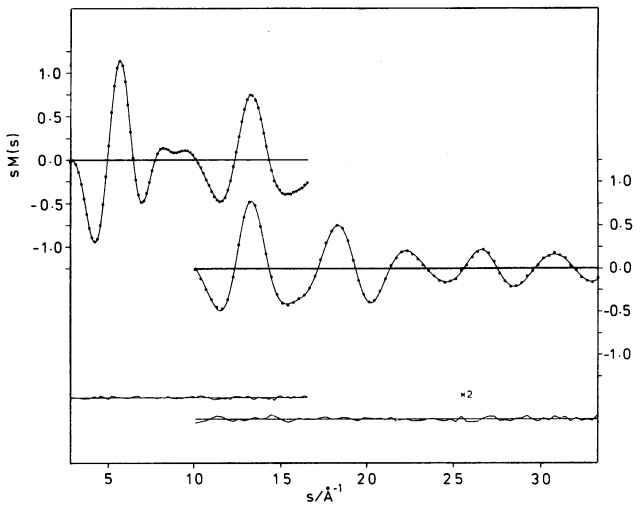

Fig. 1. Molecular intensities for trimethylamine-borane. The two upper curves are long and short camera-distance data. Dots represent observed intensities, solid curves calculated intensities, and the lower curves are their residuals.

Vibrational Amplitude and Shrinkage Correction. Root-mean-square amplitudes of the atomic pairs in $(CH_3)_3N \cdot BH_3$ with the staggered form were calculated by using the Urey-Bradley force field for related molecules,[3] which was changed slighly so as to obtain better agreement with the observed mean amplitudes. The force constants are listed in Table 1, and the calculated mean amplitudes and the shrinkage corrections, $r_a - r_\alpha$,[15] are listed in Table 2.

The height of the rotational barrier around the N-B bond, V_3, was estimated to be about 10 kcal mol^{-1} from the force constant of Y by the relation $V_3=(2/9)Y$. The lower limit was calculated to be 5 kcal mol^{-1} from the lower limit of the Y value which was estimated from the error of the observed mean amplitude of the *gauche* $C_2 \cdots H_1$ atomic pair, because the Y value has the main contribution to the mean amplitude of that atomic pair.[16]

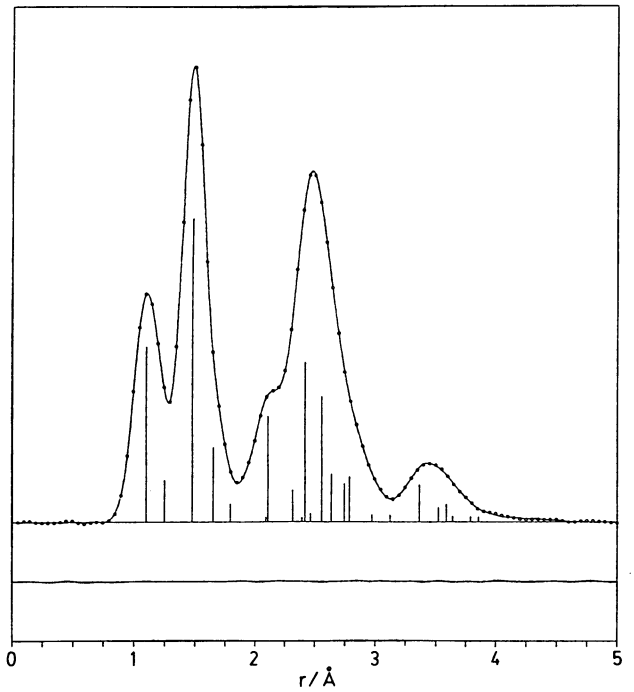

Fig. 2. Radial distribution for trimethylamine–borane. Dot represents the experimental one, the solid curve the calculated one, and the difference is shown below. The vertical bars represent bond distances and the scattering powers.

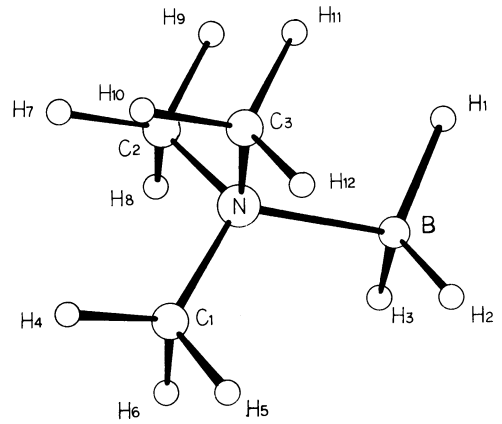

Fig. 3. Numbering of atoms in trimethylamine–borane.

Analysis of Electron Diffraction Intensities and Rotational Constant. At first the molecular parameters of $(CH_3)_3N \cdot BH_3$ were determined by the least-squares analysis of the molecular intensities. Here it was assumed that the molecule has the C_{3v} symmetry in a staggered form, and the methyl and the borane groups also have the C_{3v} symmetry. The geometrical parameters and the root-mean-square amplitudes listed in Tables 3 and 4 were refined. The mean amplitudes of the other atomic pairs and the shrinkage corrections were fixed to the calculated values listed in Table 2. The asymmetry parameters, κ, for the B-H, N-B, C-N, and C-H bonds were estimated to be 21, 4.7, 2.1, and 12×10^{-6} Å, respectively, by the diatomic approximation[17] and were fixed throughout the analysis. Those for the other atomic pairs were ignored.

Table 1. Urey-bradley force field for $(CH_3)_3N \cdot BH_3$

K(N-B)	1.0	H(HCH)	0.4
K(B-H)	4.0	H(NCH)	0.3
K(C-N)	2.0	F(H(B)H)	0.1
K(C-H)	4.7	F(N(B)H)	0.3
Y(C-N)	0.14	F(CC)	0.3
Y(N-B)	0.33	F(CB)	0.15
H(HBH)	0.2	F(H(C)H)	0.1
H(NBH)	0.3	F(N(C)H)	0.5
H(CNC)	0.3	p	−0.05
H(CNB)	0.25		

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 $(CH_3)_3N \cdot BH_3$ (in 10^{-4} Å)

Atomic pair	l	$r_a - r_\alpha$	Atomic pair	l	$r_a - r_\alpha$
B-H_1	809	170	N-C	541	13
B-N	659	8	N$\cdots$$H_4$	1040	121
B$\cdots$$C_1$	915	−12	$C_1\cdots C_2$	792	−4
B$\cdots$$H_4$	1127	61	C_1-H_4	774	247
B$\cdots$$H_5$	1785	−7	$C_1\cdots H_7$	1673	9
$H_1\cdots H_2$	1354	200	$C_1\cdots H_8$	1669	10
$H_1\cdots$N	1144	78	$C_1\cdots H_9$	1051	70
$H_1\cdots C_1$	1149	44	$H_4\cdots H_5$	1264	353
$H_1\cdots C_2$	1676	−8	$H_4\cdots H_7$	2470	−33
$H_1\cdots H_4$	1457	77	$H_4\cdots H_8$	2594	−72
$H_1\cdots H_5$	1805	56	$H_4\cdots H_9$	1780	76
$H_1\cdots H_7$	1859	48	$H_5\cdots H_8$	1775	76
$H_1\cdots H_8$	2532	−67	$H_5\cdots H_9$	1369	103
$H_1\cdots H_9$	2500	−58	$H_5\cdots H_{12}$	2461	−30

The numbering of the atoms is shown in Fig. 3. The mean amplitudes and shrinkage corrections were calculated for the same temperature (346 K) as in the experiment.

The r_α parameters for bonds obtained by the analysis of electron diffraction data were transformed to r_α^0 parameters at 0 K by the relation $r_\alpha^0 = r_\alpha + K_T - K_0 - 3/2\, a(l_T^2 - l_0^2)$,[15] and the angle parameters were assumed to be equal to those at 0 K. The rotational constant, B_α^0, which was calculated from these r_α^0 parameters was 0.15065(68) cm^{-1}. The rotational constant observed for the normal species was 0.1506482 cm^{-1},[2] and the value corrected for the vibrational effect, B_z,[18] was 0.150629 (19) cm^{-1}, as listed in Table 5. The uncertainty in the correction was tentatively assumed to be 100%. Although the B_α^0 value from the electron diffraction data was in agreement with the observed one, B_z, within the limits of error, the joint analysis of electron diffraction data and rotational constant was performed. The relative weight for the observed rotational constant in the least-squares calculation was estimated to be 1×10^7 in such a way that 2.6 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 the mean amplitudes obtained from the joint analysis are listed in Tables 3 and 4, respectively, with their errors. 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 (0.03%) and wavelength (0.08%). The best-fit molecular intensities and the theoretical radial distribution function are shown in Figs. 1 and 2, respectively. The experimental intensities, the experimental smooth backgrounds, and the correlation matrix for the molecular parameters are deposited as Document No. 8452 at the Office of the Editor of the Bulletin of the Chemical Society of Japan. The least-squares calculations were carried out on a HITAC M-200H computer in the Computer Center of the University of Tokyo.

Table 6 lists the observed rotational constants of the isotope species[2] and the corresponding ones calculated by the use of the r_α^0 parameters in Table 3. The

Table 3. Molecular parameters obtained from least-squares analysis for $(CH_3)_3N \cdot BH_3$

	r_α [a]	r_g [b]	r_α^0 [c]	r_g [d]
B-H/Å	1.239 (6)	1.260	1.243 (6)	1.261
N-B/Å	1.652 (3)	1.656	1.651 (2)	1.656
C-N/Å	1.482 (1)	1.485	1.482 (1)	1.485
C-H/Å	1.078 (2)	1.108	1.088 (2)	1.108
H···(B)···H/Å	2.071 (14)	2.100	2.078 (13)	2.100
C···C/Å	2.419 (3)	2.421	2.419 (3)	2.421
∠NCH/°	109.2 (2)		109.0 (2)	
∠HBH/° [e]	113.5 (6)	112.9	113.4 (4)	112.8
∠CNC/° [e]	109.4 (2)	109.2	109.4 (2)	109.2

Limits of error are in parentheses. Parameters r_α, r_α^0, and r_g are defined in Ref. 15. a) Results from electron diffraction data. b) r_g parameters transformed from r_α parameters. The limits of error are equal to those in the r_α parameters. c) Results from the joint analysis of electron diffraction data and rotational constant. d) r_g parameters transformed from r_α^0 parameters. The limits of error are equal to those in the r_α^0 parameters. e) Dependent parameters.

Table 4. Root-mean-square amplitudes for $(CH_3)_3N \cdot BH_3$

	l_{obsd}/Å [a]	l_{calcd}/Å [b]
$N-C_1$	0.057 (1)	0.054
C_1-H_4	0.076 (2)	0.077
$C_1 \cdots C_2$	0.080 (3)	0.079
N-B	0.072 (3)	0.066
$B \cdots C_1$	0.091 (5)	0.092
$B-H_1$	0.077 (7)	0.081
$N \cdots H_4$	0.104 (2)	0.104
$C_2 \cdots H_1$	0.168 (12)	0.168

a) Results obtained from the joint analysis of electron diffraction data and rotational constant. b) Values calculated from the force constants in Table 1.

Table 5. Observed and calculated rotational constants of $(CH_3)_3N \cdot BH_3$

B_0/cm^{-1} [a]	0.1506482 (2)
B_z/cm^{-1} [b]	0.150629 (19)
B_α^0/cm^{-1} [c]	0.15065 (68)
B_{av}/cm^{-1} [d]	0.150630 (20)

a) Observed rotational constant for the ground vibrational state. Ref. 2. b) Rotational constant corrected for the vibrational effect. c) Rotational constant calculated from the parameters obtained by the analysis of electron diffraction data. d) Best-fit rotational constant obtained from the joint analysis.

Table 6. Rotational constants of isotope species of $(CH_3)_3N \cdot BH_3$

	B_0/cm^{-1} [a]	B_z/cm^{-1} [b]	B_α^0/cm^{-1} [c]	$(B_z - B_\alpha^0)/10^{-5}$ cm^{-1}
$(CH_3)_3{}^{15}N \cdot {}^{11}BH_3$	0.150662	0.15064	0.15063 (15)	1
$(CH_3)_3{}^{14}N \cdot {}^{10}BH_3$	0.154367	0.15434	0.15438 (15)	−4
$(CH_3)_3{}^{15}N \cdot {}^{10}BH_3$	0.154381	0.15437	0.15438 (15)	−1
$(CH_3)_3{}^{14}N \cdot {}^{11}BD_3$	0.134857	0.13484	0.13453 (10)	31
$(CH_3)_3{}^{15}N \cdot {}^{11}BD_3$	0.134862	0.13485	0.13452 (10)	33
$(CH_3)_3{}^{14}N \cdot {}^{10}BD_3$	0.137540	0.13753	0.13723 (10)	30
$(CH_3)_3{}^{15}N \cdot {}^{10}BD_3$	0.137548	0.13754	0.13722 (10)	32

a) Observed rotational constants, Ref. 2. b) Rotational constants corrected for the vibrational effect. c) Rotational constants calculated from the r_α^0 parameters in Table 3. The correlations between the parameters were taken into consideration in calculating the errors.

Table 7. Comparison of molecular parameters

	r(N-B)/Å	r(B-X)/Å	r(C-N)/Å	∠XBX/°	∠CNC/°
$(CH_3)_3N\cdot BH_3$[a]	1.656 (2)	1.261 (6)	1.485 (1)	112.8 (4)	109.2 (2)
$(CH_3)_3N\cdot BF_3$[b]	1.674 (4)	1.374 (2)	1.485 (2)	112.6 (3)	109.2 (4)
$(CH_3)_3N\cdot BCl_3$[b]	1.652 (9)	1.836 (2)	1.497 (3)	110.9 (2)	108.1 (3)
$(CH_3)_3N\cdot BBr_3$[b]	1.663 (13)	2.001 (3)	1.500 (5)	110.3 (3)	107.8 (5)
$(CH_3)_3N\cdot BI_3$[b]	1.663 (13)	2.245 (4)	1.497 (5)	108.6 (4)	106.0 (8)
$(CH_3)_3N$[c]			1.461 (2)		110.6 (6)
B_2H_6[d]		1.196 $\binom{+8}{-6}$		120.2 (18)	

The values represent r_g parameters.
a) Present study. b) Ref. 3. c) Ref. 22. d) The B-H bond and the HBH angle represent the B-H_t and the H_tBH_t in Ref. 23.

calculated rotational constants of the species with deuterium are significantly different from the observed ones, while those of the other species are in good agreement with the observed ones. These differences may indicate isotope effects on the B-D bond and the DBD angle. However, they cannot be estimated only from the rotational constant of $(CH_3)_3N\cdot BD_3$. The isotope effect on the B-D bond was thus estimated by the diatomic approximation and Δr_α^0 ($=r_\alpha^0$(B-D)$-r_\alpha^0$(B-H)) was assumed to be equal to Δr_g^0 ($=r_g^0$(B-D)$-r_g^0$(B-H)), because the force field used is not so reliable to calculate the precise perpendicular amplitude of the B-H bond, as described later. Thus, Δr_g^0 was obtained from $(3/2)a[l_0(\text{B-D})^2-l_0(\text{B-H})^2]$,[19] where a is Morse constant and was assumed to be 2.0 Å^{-1}. The mean amplitudes of the B-D and the B-H bonds at 0 K were calculated from the relation of $l_0^2=h/8\pi^2\mu c\nu$,[20] where h is Planck constant, μ is reduced mass, c is light velocity, and ν is the wave number for B-D (1656 cm^{-1}) or B-H (2267 cm^{-1}) bond stretching.[21] The isotope effect on the B-D bond distance was −0.006 Å. Then the isotope effect on the DBD angle was estimated so as to give the best agreement of the calculated rotational constant of $(CH_3)_3{}^{14}N\cdot{}^{11}BD_3$ with the observed one, and resulted in the value (=∠DBD−∠HBH) of 0.4±0.1°, where 100% uncertainty was assumed for the isotope correction to the B-D bond.

Discussion

The N-B bond distance of $(CH_3)_3N\cdot BH_3$, 1.656± 0.002 Å, is nearly equal to those of trimethylamine-boron trihalides, which were also determined by an electron-diffraction method,[3] as listed in Table 7. On the complex formation the B-H and the C-N bond distances of the complex increase by 4.4 and 1.6%, respectively, and the HBH and the CNC angles of the complex decrease by 6.1 and 1.1%, respectively, comparing the molecular parameters of $(CH_3)_3N\cdot BH_3$ with those of its component molecules,[22,23] in which BH_3 refers to the terminal part of diborane. These relative changes of the molecular parameters are nearly equal to the corresponding ones in $(CH_3)_3N\cdot BF_3$.[3] This seems to show that the acceptor power of borane is similar to that of boron trifluoride in accord with the result from the measurement of the enthalpy change.[5]

The rotational barrier around the N-B bond of this complex is higher than 5 kcal mol^{-1} and it seems to be larger than the barrier of a methyl group.[24] We deduced the V_3 value from the Y value, which was adjusted so that the calculated mean amplitude of the *gauche* $C_2\cdots H_1$ atomic pair agree with the observed one. Force constants for angle deformation, H(CNB) and H(NBH), also contributed to the mean amplitude of the *gauche* $C_2\cdots H_1$ pair. In the present study the H(CNB) was reasonably estimated from the observed mean amplitude of the C···B pair, but the H(NBH) could not be optimized. Therefore the deduced value of V_3 is not a reasonable one. However it should be noticed that the configuration around the nitrogen atom of this complex is nearly regular tetrahedral, but the observed mean amplitude of the C···B pair, 0.091± 0.005 Å, is considerably larger than that of the C···C pair, 0.080±0.003 Å. This fact shows that the BH_3 group vibrates more than the CH_3 group. Thus the mobility of the borane group seems to hinder the rotation around the N-B bond and increase the barrier height.

The isotope effects were found on the B-D bond distance and the DBD angle and they were estimated to be −0.006 Å and 0.4°, respectively, though the isotope effect on the B-D bond distance depends on the assumption of the diatomic approximation with the anharmonic constant of 2.0 Å^{-1}. The isotope effect on the C-D bond distance in CD_4 and that on the N-D bond distance in ND_3 have been estimated to be both −0.004 Å.[25,26] The isotope effect on the B-D bond distance of $(CH_3)_3N\cdot BD_3$ is comparable with them while the isotope effect on the DBD angle differs from that on the DND angle of ND_3, in which the DND angle is nearly equal to the HNH angle of NH_3.[26] It seems that in ND_3 the DND angle remains unchanged in spite of the shortening of the N-D distance because of the strong repulsion between the lone paired electrons of the N atom and the paired electrons of the N-D bond.

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