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Molecular Structure of Trimethylphosphine-Borane as Determined from Electron Diffraction and Microwave Spectroscopic Data

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The molecular structure of trimethylphosphine-borane has been determined from gas electron diffraction and spectroscopic data. The molecular parameters and their uncertainties are r_g(B-H)=1.225±0.011 Å, r_g(P-B)=1.899±0.006 Å, r_g(C-P)=1.815±0.003 Å, r_g(C-H)=1.103±0.002 Å, ∠HBH=108.6±0.6°, and ∠CPC=104.6±0.3°. The P-B distance of this complex is about 0.04 Å shorter than those of trimethylphosphine-boron trihalides.

Molecular structures of trimethylamine-borane and trimethylamine-boron trifluoride have been sudied by electron diffraction and microwave spectroscopic methods in the gas phase.[1-6] The molecular structures determined from microwave spectroscopic data, however, were found to be significantly different from those determined from electron diffraction data. Since a trimethylamine complex with borane or boron trifluoride has C_{3v} symmetry, the number of the rotational constants used in the structural analysis was limited and some molecular parameters had to be assumed in the microwave spectroscopic method. These assumptions were not necessary in electron diffraction, though electron diffraction data were less precise than microwave spectroscopic data. Therefore the joint analysis of electron diffraction and microwave spectroscopic data yielded highly accurate molecular parameters.[2,3]

The structural parameters of trimethylphosphine-borane have also been determined from the rotational constants of $(CH_3)_3P\cdot{}^{11}BH_3$, $(CH_3)_3P\cdot{}^{10}BH_3$, $CD_3(CH_3)_2P\cdot{}^{11}BH_3$, and $(CH_3)_3P\cdot{}^{11}BDH_2$.[7] We have reported in the study of $(CH_3)_3N\cdot BH_3$ that the substitution of D for H causes shortening of the B-H distance and opening of the HBH angle.[3] The microwave spectroscopic study, where isotopic molecules were assumed to have the same molecular dimension as the normal species, might have given incorrect molecular parameters as shown in the studies on trimethylamine complexes. Thus we reinvestigated the molecular structure of gaseous trimethylphosphine-borane by using both electron diffraction and microwave spectroscopic data.

Experimental

Diborane was prepared by the reaction of orthophosphoric acid and potassium tetrahydroborate,[8] and trimethylphosphine was obtained by the decomposition of trimethylphosphine-silver iodide complex at 200 °C.[9] The diborane and trimethylphosphine were allowed to react in a glass tube cooled by Dry Ice-acetone. The crude complex was purified by sublimation under reduced pressure. The purity was checked from the IR absorption spectra.

Electron diffraction photographs were taken by the use of an r³-sector on Kodak Electron-Image plates at camera distances of 293.79 and 143.85 mm. The sample was sublimed at 349 K by a high temperature nozzle. The accelerating voltage was about 40 kV and the wavelength was determined from the diffraction patterns of thallium(I) chloride.[10] The exposure times were about 30 and 105 s for the long and the short camera-distance photographs, respectively, with an electron-beam current of 0.8 μA. The pressure in the diffraction chamber was 1.5×10^{-3} Pa during the experiment. Two photographic plates taken at the long camera distance and three plates taken at the short camera distance were selected for the intensity measurement by a digital microphotometer. The electron diffraction unit and the digital microphotometer used in the present study have been described elsewhere.[11]

Analysis and Results

The scattering intensities in the range of q=10.0—53.5 Å^{-1} were obtained from the long camera-distance plates and those in the range of q=20.0—107.0 Å^{-1} from the short camera-distance plates. Here q represents $(40/\lambda)\sin(\theta/2)$, where λ is the wavelength

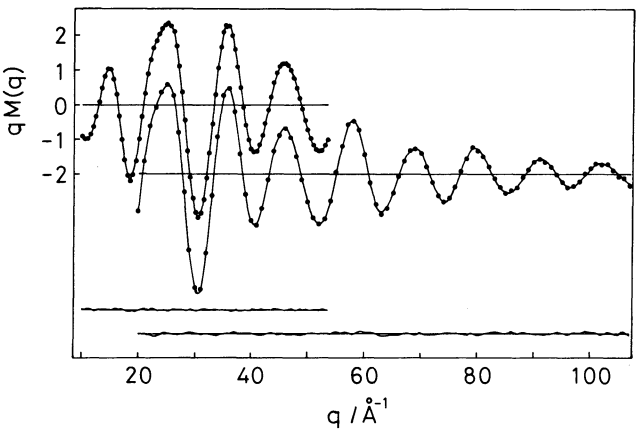

Fig. 1. Molecular intensities for trimethylphosphine-borane. The upper curve is the long camera-distance data and the lower the short camera-distance data. Dots represent the observed ones and solid curves the calculated ones. The residuals are shown at the lower part of the figure.

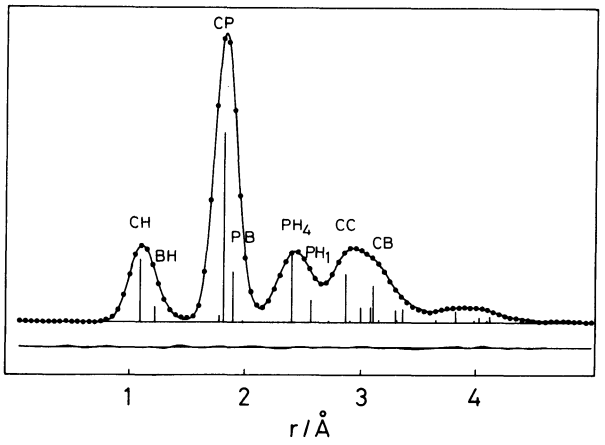

Fig. 2. Radial distribution curve for trimethylphosphine-borane. Dots represent the experimental one, solid curve the theoretical one, and the difference is shown below. The vertical bars represent bond distances and the scattering powers.

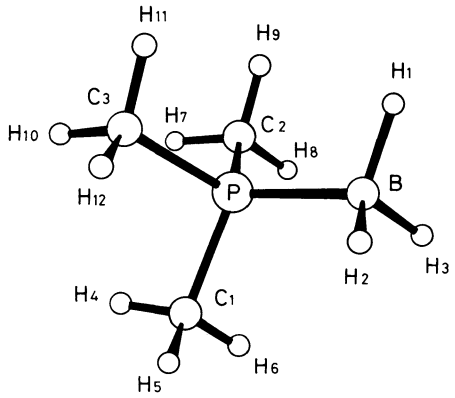

Fig. 3. Molecular model and numbering of atoms in trimethlphosphine-borane.

and θ is the scattering angle. 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 Refs. 12—14. The experimental molecular intensities obtained are shown in Fig. 1. Figure 2 shows the experimental radial distribution function. The molecular model of trimethylphosphine-borane and the numbering of the atoms are shown in Fig. 3.

It was assumed that the molecule of $(CH_3)_3P \cdot BH_3$ has C_{3v} symmetry in a staggered form and the methyl groups also have C_{3v} symmetry. The latter local C_3 axes were assumed to be coincident with the C–P bond. The r_α parameters[15] determined by least-squares analyses were r(B–H), r(P–B), r(C–P), r(C–H), r(C–C), r(H–(B)–H), and $\angle$PCH. Vibrational mean amplitudes and shrinkage corrections, $r_a - r_\alpha$,[15] were calculated from the reported force field,[16] where the force constants for the torsional vibration around the C–P and P–B bonds had not been estimated. The force

Table 1. Root-Mean-Square Amplitudes and Shrinkage Corrections for $(CH_3)_3P \cdot BH_3$ (in 10^{-4} Å unit)

	l	$r_a - r_\alpha$		l	$r_a - r_\alpha$
B–H_1	883	375	P–C_1	557	23
P–B	598	37	P–H_4	1110	164
B–C_1	1105	−12	C_1–C_2	1096	−10
B–H_4	1228	85	C_1–H_4	783	376
B–H_5	2067	1	C_1–H_7	2059	6
H_1–H_2	1419	572	C_1–H_8	2085	0
H_1–P	1265	176	C_1–H_9	1255	93
H_1–C_1	1394	86	H_4–H_5	1289	579
H_1–C_2	2062	24	H_4–H_7	2883	−23
H_1–H_4	1608	138	H_4–H_8	3187	−115
H_1–H_5	2117	103	H_4–H_9	2130	101
H_1–H_7	2087	110	H_5–H_8	2094	103
H_1–H_8	3190	−91	H_5–H_9	1474	148
H_1–H_9	2903	−3	H_5–H_{12}	2973	−47

The numbering of atoms is shown in Fig. 3.

constant for the C–P torsion was estimated to be 0.081×10^{-18} N m from the potential barrier height of 2.6 kcal mol^{-1} in trimethylphosphine.[17] From the preliminary analysis assuming a low potential barrier approximation[18] the potential barrier around the P–B bond was about 3 kcal mol^{-1}, though it might include a large error. The force constant for the torsional vibration around the P–B bond was 0.09×10^{-18} N m. Thus the torsional vibrations around the C–P and P–B bonds were treated in a high potential barrier approximation.[18] The calculated mean amplitudes and shrinkage corrections are listed in Table 1. The asymmetry parameters, κ, for the B–H, P–B, C–P, and C–H bonds were estimated to be 20, 4.3, 3.2, and 13×10^{-6} Å^3, respectively, by the diatomic approximation[19] and those for the other atomic pairs were ignored.

The results of the least-squares analysis from the electron diffraction data are listed in Table 2. The rotational constant of a normal species of trimethylphosphine–borane was calculated by using the r_α°[15] parameters transformed from the r_α parameters in Table 2. Although it was in good agreement with the observed one as shown in Table 3, 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 the standard deviation of the rotational constant obtained from the least-squares calculation is nearly equal to the uncertainty in B_z, which is a rotational constant corrected for the vibrational effect.[15] The geometrical parameters and the mean amplitudes obtained from the joint analysis are listed in Tables 2 and 4, respectively. The limits of error in the distances were taken to be the square root of the sum of the squares of the random and systematic errors, while those in the angles and the mean amplitudes were taken to be the

Table 2. Molecular Parameters Obtained from Least-Squares Analysis for $(CH_3)_3P \cdot BH_3$

	r_α[a]	r_g[b]	r_α°[c]	r_g[d]	r_o[e]
r(B–H)/Å	1.183(11)	1.227	1.201(11)	1.225	1.212(10)
r(P–B)/Å	1.892(7)	1.899	1.894(6)	1.899	1.901(7)
r(C–P)/Å	1.810(3)	1.815	1.811(3)	1.815	1.819(10)
r(C–H)/Å	1.059(2)	1.103	1.077(2)	1.103	1.08(2)
r(H–(B)–H)/Å	1.931(26)	1.999	1.957(23)	1.990	
r(C–C)/Å	2.868(4)	2.870	2.870(4)	2.870	
∠PCH/°	109.9(2)		109.7(2)		109.6(10)
∠HBH/°[f]	109.5(10)	109.1	109.2(6)	108.6	113.5(5)
∠CPC/°[f]	104.8(4)	104.5	104.8(3)	104.6	105.0(4)
∠PBH/°[f]	109.5(10)	109.8	109.8(7)	110.3	105.1(6)
∠BPC/°[f]	113.9(3)	114.1	113.8(3)	114.0	113.6(4)

Limits of error are in parentheses. Parameters r_α, r_α°, 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 constants of the normal species. d) r_g parameters transformed from r_α° parameters. The limits of error are equal to those in the r_α° parameters. e) Results from the microwave spectroscopic study. Ref. 7. f) Dependent parameters in the present analysis.

Table 3. Observed and Calculated Rotational Constants of $(CH_3)_3P \cdot {}^{11}BH_3$

B_o/MHz[a]	3215.63(3)
B_z/MHz[b]	3216.0(4)
B_α°/MHz[c]	3217(5)
B_{av}/MHz[d]	3216.1(3)

Uncertainties in parentheses are attached to the last digit of the values. a) Observed rotational constant for the ground vibrational state. Ref. 7. b) Rotational constant corrected for the vibrational effect. The uncertainty was assumed to be 100% the vibrational correction. 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. The error means the standard deviation in the least-squares calculation.

Table 4. Observed Root-Mean-Square Amplitudes for $(CH_3)_3P \cdot BH_3$

	l_{obsd}/Å[a]	l_{calcd}/Å[b]
C_1–P	0.058(1)	0.056
C_1–C_2	0.094(3)	0.110
C_1–B	0.109(4)	0.111
C_1–H_4	0.084(2)	0.078
P–B	0.073(9)	0.060
P–H_9	0.112(2)	0.111

Limits of error are in parentheses. a) Results obtained from the joint analysis of electron diffraction data and rotational constant of the normal species. b) Values calculated from the force field.

random errors. The random errors were assumed to be 2.6 times as large as the standard errors in the least-squares calculation. The systematic errors in the distances were estimated from the errors in both the measurements of camera distance (0.03%) and wavelength (0.11%). The best-fit molecular intensities and the 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 in Document No. 8825 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-682H computer in the Computer Center of the University of Tokyo.

Discussion

The molecular parameters of gaseous trimethylphosphine–borane obtained from the present study are in agreement with those from the microwave spectroscopic study[7] except the parameters of r(B–H) and ∠HBH. The P–B bond distance of $(CH_3)_3P \cdot BH_3$, 1.90 Å, is greater than that of $F_3P \cdot BH_3$, 1.84 Å,[20] but the former complex is more stable than the latter. The unusually short but weak P–B bond of the latter complex has been discussed elsewhere.[7,21] The P–B bond distance of $(CH_3)_3P \cdot BH_3$ is about 0.04 Å shorter than those of $(CH_3)_3P \cdot BX_3$ (X=Cl,Br,I),[22–24] which are in the range of 1.94—1.95 Å, though the sequence of the stability of the complexes is $(CH_3)_3P \cdot BBr_3 > (CH_3)_3P \cdot BH_3 > (CH_3)_3P \cdot BCl_3$.[25] This close approach of boron to phosphorus in $(CH_3)_3P \cdot BH_3$ is probably achieved by a relatively small steric hindrance of borane to the donor molecule.

The magnitude of structural changes of donor molecules on the complex formation is one of the measures of the acid strength of acceptors. The structural parameters of trimethylamine and trimethylphosphine in the complexes with boron compounds are listed in Table 5 in decreasing order of the CNC or CPC angles. This order is almost the same as the increasing order of the C–N or C–P distances.

The order of trimethylamine boron trihalides is the same as that of trimethylphosphine boron trihalides in Table 5, but a free trimethylamine molecule is at the top of the corresponding series and a free

Table 5. Comparison of Molecular Parameters

Compound	r(C-N)/Å	∠CNC/°	Ref.	Compound	r(C-P)/Å	∠CPC/°	Ref.
$(CH_3)_3N$	1.461(2)	110.6(6)	26	$(CH_3)_3P \cdot BCl_3$	1.800(4)	109.3(3)	22
$(CH_3)_3N \cdot BH_3$	1.485(1)	109.2(2)	3	$(CH_3)_3P \cdot BBr_3$	1.804(4)	108.0(7)	23
$(CH_3)_3N \cdot BF_3$	1.485(2)	109.2(4)	2	$(CH_3)_3P \cdot BI_3$	1.809(3)	106.0(5)	24
$(CH_3)_3N \cdot BCl_3$	1.497(3)	108.1(3)	27	$(CH_3)_3P \cdot BH_3$	1.811(3)	104.8(3)	This work
$(CH_3)_3N \cdot BBr_3$	1.500(5)	107.8(5)	27	$(CH_3)_3P$	1.846(3)	98.6(3)	29
$(CH_3)_3N \cdot BI_3$	1.497(2)	106.0(8)	28				

The values represent r_g parameters.

trimethylphosphine molecule is at the bottom. The borane complexes are located at the position next to the free molecules. This fact means that both donor molecules require the least deformation energy on the complex formation with borane, and that the deformation energy of trimethylamine increases with the atomic number of halogens of the acceptor molecules while that of trimethylphosphine decreases. The different changes of the structures of trimethylamine and trimethylphosphine on the complex formation with boron trihalides will be explained by the ab initio molecular orbital calculation.

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