BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 52 (11), 3204—3207 (1979)

# Molecular Structure of Trimethylphosphine-boron Trichloride by Gas Electron Diffraction

Kinya IIJIMA and Shuzo SHIBATA*

*Department of Chemistry, Faculty of Science, Shizuoka University, Oya, Shizuoka 422*

(Received March 22, 1979)

The molecular structure of trimethylphosphine-boron trichloride $(CH_3)_3P\cdot BCl_3$ has been determined from gas electron-diffraction data. The structure parameters and uncertainties are $r_g$(P–B)=1.941(16) Å, $r_g$(B–Cl)=1.851(7) Å, $r_g$(C–P)=1.800(4) Å, $r_g$(C–H)=1.099(5) Å, $r_g$(Cl···Cl)=3.022(5) Å, and $r_g$(C···C)=2.936(10) Å. The potential barrier about the P–B axis is 3.8±0.7 kcal $mol^{-1}$ in the gas phase. The data show that the molecular structure in the gas phase is nearly equal to that in the solid phase.

The molecular structures of several phosphorus-boron donor-acceptor complexes have been investigated in the gas and solid phases by microwave spectroscopy$^{1-5)}$ and X-ray diffraction,$^{6)}$ respectively. According to these studies the distances of the P–B dative bond in the complexes are very different from each other. The experimental data showed that the P–B distances in $F_3P\cdot BH_3$$^{1)}$ and $H_3P\cdot BH_3$$^{2)}$ are 1.836±0.006 Å and 1.937±0.005 Å, respectively, and the P–B distances of the other complexes are somewhat between these values. Therefore, the P–B dative bond appears to considerably change in length according to circumstances surrounding the bonded atoms. It has been noted that there appears to be no correlation between the distance of the P–B dative bond and the stability of the complex.$^{4)}$ For example, the $F_3P\cdot BH_3$ complex is extensively dissociated in the gas phase at room temperature, while the $(CH_3)_3P\cdot BH_3$ complex, which has a greater P–B distance, 1.901±0.007 Å,$^{4)}$ is more stable and can be heated to approximately 200 °C without appreciable decomposition.$^{7)}$ Rudolph and Parry have proposed a theory to account for the unusual properties of the P–B bond,$^{8)}$ but more structural data appears to be necessary in order to understand the nature of the P–B dative bond. It has been reported that the distance of the N–B dative bond in trimethylamine-boron trihalide is significantly larger in the gas phase than in the solid phase.$^{9-11)}$ It is therefore of interest to compare the P–B distance of trimethylphosphine-boron trihalide in the gas phase with that in the solid phase.$^{6)}$ Thus the present study was undertaken in order to determine the molecular structure of gaseous trimethylphosphine-boron trichloride $(CH_3)_3P\cdot BCl_3$.

## Experimental

Trimethylphosphine was prepared by the dropwise addition of phosphorus trichloride into an ethereal solution of methyllithium, and the distilled trimethylphosphine solution added to an ethereal solution of boron trichloride. After removal of the ether, the trimethylphosphine-boron trichloride complex was recrystallized from acetone and water, and sublimed under vacuum. The purity of the complex was verified by IR analysis.$^{12)}$ In the electron-diffraction experiment the sample was vaporized at approximately 190 °C by means of a high temperature nozzle, and photographs taken with an $r^3$-sector at camera distances of 144 and 294 mm. The accelerating voltage was 40 kV, and the exposure time for the long camera distance was 25 s using an electron-beam current of 0.7 μA. For the short camera distance the exposure time was 80 s using a beam current of 0.9 μA. The pressure in the diffraction chamber was approximately $1\times10^{-5}$ Torr during the experiment. The electron wavelength was measured by means of diffraction patterns of thallium chloride powder.$^{13)}$ Photographs were recorded on Kodak electron-image plates, and the optical densities of the three plates taken at each camera distance 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 have been described elsewhere.$^{14)}$

## Analysis and Results

The scattering intensities were obtained in the ranges of $s$=2.5—17.3 $Å^{-1}$ and 5.0—34.2 $Å^{-1}$ from the photographic plates at long and short camera distances, respectively. The intensities were divided by the theoretical backgrounds, and 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.*$^{15)}$ and Cromer and Mann,$^{16)}$ respectively. The background curves were drawn by hand for the long distance data and fitted to a 7th degree polynomial for the short distance data. The molecular intensities for each camera distance were joined at $s$=14.8 $Å^{-1}$, and the curve, shown in Fig. 2, used for the analysis. Figure 3 shows the radial distribution curve, which suggests that the molecular structure of $(CH_3)_3P\cdot BCl_3$ is staggered.

The molecular parameters were determined by a least-squares analysis of the molecular intensities. It was assumed that the $(CH_3)_3P\cdot BCl_3$ molecule has $C_{3v}$ symmetry in the staggered form, and that the methyl group has local $C_{3v}$ symmetry and is staggered with respect to the P–B bond. The mean amplitudes and the corrections for the shrinkage effects,$^{17)}$ $r_a-r_\alpha$, were calculated on the basis of the force field for $(CH_3)_3P\cdot BCl_3$$^{12)}$ and are given in Table 1. The

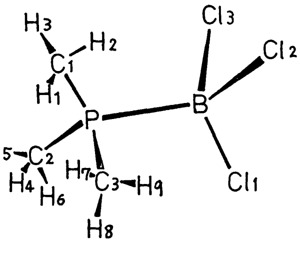

Fig. 1. Numbering of atoms in trimethylphosphine-boron trichloride (symmetry $C_{3v}$).

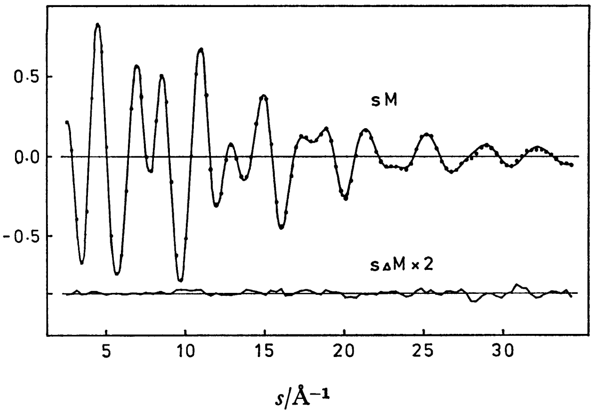

Fig. 2. Molecular intensities for trimethylphosphine-boron trichloride. Solid curve, calculated; dotted curve, experimental. Lower curve, two times the residuals with respect to the experimental curve.

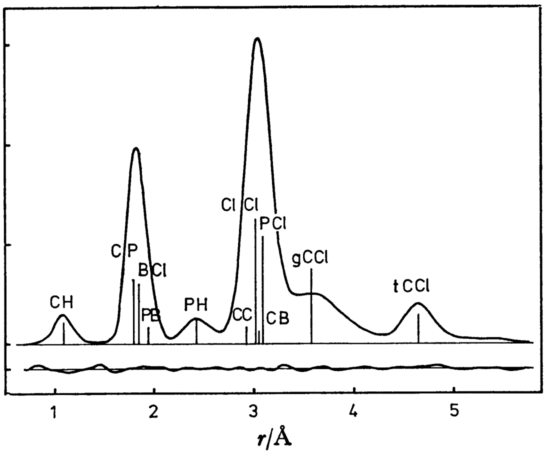

Fig. 3. Radial distribution curve for trimethylphosphine-boron trichloride. Solid curve, experimental; lower curve, 2.5 times the residuals.

geometrical parameters and the mean amplitudes determined by the least-squares analysis are as follows: $r$(B–Cl), $r$(P–B), $r$(C–P), $r$(C–H), $r$(Cl···Cl), $r$(C···C), ∠PCH, $l$(B–Cl), $l$(C–P), $l$(C–H), $l$(Cl···Cl), $l$(*trans* C···Cl), $l$(*gauche* C···Cl), $l$(P···H). The mean amplitudes for the other atomic pairs were fixed to the calculated values shown in Table 1. The asymmetry parameter, $\kappa$, for the C–H bond was assumed to be $1.2 \times 10^{-5}$ Å$^3$ by a diatomic approximation.[18] The asymmetry parameters for the other atomic pairs were neglected.

Table 1. Calculation of mean amplitudes and shrinkage effects for $(CH_3)_3P \cdot BCl_3$ (in $10^{-4}$ Å)

| | $l$ | $r_a - r_\alpha$ | | $l$ | $r_a - r_\alpha$ |
|---|---|---|---|---|---|
| B–Cl | 696 | 62 | P–$C_1$ | 534 | 277 |
| B–P | 645 | 3 | P···$H_1$ | 1181 | 428 |
| B···$C_1$ | 1187 | 117 | $C_1$···$C_2$ | 1189 | 410 |
| B···$H_1$ | 1340 | 242 | $C_1$–$H_1$ | 782 | 518 |
| B···$H_2$ | 2276 | 253 | $C_1$···$H_4$ | 2329 | 401 |
| $Cl_1$···$Cl_2$ | 808 | 93 | $C_1$···$H_5$ | 2341 | 450 |
| $Cl_1$···P | 1001 | 15 | $C_1$···$H_6$ | 1330 | 685 |
| $Cl_1$···$C_1$ | 1160 | 20 | $H_1$···$H_2$ | 1299 | 900 |
| $Cl_1$···$C_2$ | 2390 | 3 | $H_1$···$H_4$ | 3292 | 356 |
| $Cl_1$···$H_1$ | 1498 | 111 | $H_1$···$H_5$ | 3621 | 271 |
| $Cl_1$···$H_2$ | 2141 | 107 | $H_1$···$H_6$ | 2373 | 665 |
| $Cl_1$···$H_4$ | 2476 | 123 | $H_2$···$H_5$ | 2319 | 740 |
| $Cl_1$···$H_5$ | 3850 | −106 | $H_2$···$H_6$ | 1561 | 889 |
| $Cl_1$···$H_6$ | 3456 | 112 | $H_2$···$H_9$ | 3360 | 363 |

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

In the force field treatment by Drake *et al.*[12] the torsional vibrations around the C–P and P–B bonds were not taken into consideration. In the present study the force constant for the torsional vibration around the C–P bond was assumed to be 0.08 mdyne Å. This value was estimated from the potential barrier for trimethylphosphine, 2.6 kcal mol$^{-1}$.[19] Since the torsional vibration around the P–B bond contributes considerably to the mean amplitude of the *gauche* C···Cl pair, the force constant for this motion, $Y$(P–B), was adjusted to fit the calculated mean amplitude of the *gauche* C···Cl pair to the observed one from the analysis of electron-diffraction intensities.[11] Thus $Y$(P–B) was estimated to be 0.12± 0.02 mdyne Å, and the potential barrier of the torsional vibration around the P–B bond was evaluated as 3.8±0.7 kcal mol$^{-1}$.

The $r_\alpha$ parameters and mean amplitudes determined by the analysis are given in Tables 2 and 3 together

Table 2. Molecular parameters

| | $(CH_3)_3P \cdot BCl_3$ (gas)$^{a)}$ | | | (solid)$^{c)}$ | $(CH_3)_3P^{d)}$ | $BCl_3{}^{e)}$ |
|---|---|---|---|---|---|---|
| | $r_\alpha{}^{b)}$ | $r_g$ | $\sigma^{f)}$ | $r$ | $r_g$ | $r_g$ |
| B–Cl | 1.843 | 1.851 | 0.007 | 1.855 (5) | | 1.742 (4) |
| P–B | 1.939 | 1.941 | 0.016 | 1.957 (5) | | |
| C–P | 1.771 | 1.800 | 0.004 | 1.81 (1) | 1.846 (3) | |
| C–H | 1.042 | 1.099 | 0.005 | | 1.091 (6) | |
| Cl···Cl | 3.010 | 3.022 | 0.005 | | | 3.013 (6) |
| C···C | 2.890 | 2.936 | 0.010 | | 2.800 (5) | |
| ∠PCH | 113.7 | | 0.9 | | 110.7 (5) | |
| ∠ClBCl | 109.5 | | 0.4 | 111.4 (4) | | 120 |
| ∠CPC | 109.3 | | 0.3 | 107.9 (4) | 98.6 (3) | |

Bond distance: Å unit; bond angle: degree unit. a) Present study. b) Angles were calculated using $r_\alpha$ parameters. c) Ref. 6. d) Ref. 21. e) Ref. 22. f) See text.

TABLE 3. ROOT-MEAN-SQUARE AMPLITUDES FOR $(CH_3)_3P\cdot BCl_3$ (in Å unit)

| | $l_{\mathrm{obsd}}$ | $l_{\mathrm{calcd}}$ |
|---|---|---|
| B-Cl | 0.067 (6) | 0.070 |
| C-P | 0.048 (4) | 0.053 |
| C-H | 0.073 (5) | 0.078 |
| C···Cl | 0.092 (4) | 0.081 |
| *trans* C···Cl | 0.106 (8) | 0.116 |
| *gauche* C···Cl | 0.238 (10) | 0.239 |
| P···H | 0.113 (10) | 0.118 |

with their 99% confidence errors, respectively. 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 comparatively large errors of $r$(B–Cl), $r$(P–B), and $l$(B–Cl) are attributable to the large correlations between other parameters. The correlation matrix is listed in Table 4, and the best-fit theoretical intensity curve is shown in Fig. 2.[20] The calculations of mean amplitudes, shrinkage effects, and method of least-squares were conducted on a HITAC 8800/8700 computer in the Computer Center of the University of Tokyo.

## Discussion

From a comparison of the molecular structure of the $(CH_3)_3P\cdot BCl_3$ complex to those of the component molecules of $(CH_3)_3P$[21] and $BCl_3$[22] (Table 2), it can be seen that complex formation increases the CPC angle by 11% and the B–Cl distance by 6%, and decreases the C–P distance by 3% and the ClBCl angle by 9%. Both the CPC and the ClBCl angles in the complex are almost tetrahedral. The above changes can be interpreted in terms of the valence-shell electron-pair repulsion theory.[23]

The structural change of the donor molecule by the formation of $(CH_3)_3P\cdot BCl_3$ is quite different from that by the formation of the trimethylamine complex, since in the former the CPC angle increases and the C–P distance decreases while in the latter the CNC angle decreases (2°) and the C–N distance increases (0.04 Å).[10] With respect to the acceptor molecule, however, the structural change is rather similar in both complexes (a decrease of 8% in the ClBCl angle and an increase of 6% in the B–Cl distance in the $(CH_3)_3N\cdot BCl_3$ complex[10]). There is another difference between both complexes. The molecular structure of $(CH_3)_3N\cdot BCl_3$ in the gas phase[10] differs from that in the solid phase.[24] For example, the N–B dative bond is much greater in the gas phase than in the solid phase. The molecular structure of gaseous $(CH_3)_3P\cdot BCl_3$ is however nearly equal to that in the solid phase.[6]

The rotational barrier of $H_3P\cdot BH_3$ about the P–B bond is 2.47±0.05 kcal mol$^{-1}$ according to a MW spectroscopic study.[2] The fluorine-substituted compounds of $F_3P\cdot BH_3$ and $H_3P\cdot BF_3$ have slightly larger barriers, 3.24±0.15 and 3.39±0.40 kcal mol$^{-1}$, respectively.[1,3] The H···H distance in $H_3P\cdot BH_3$, the F···H distance in $F_3P\cdot BH_3$ and that in $H_3P\cdot BF_3$ are virtually identical, which suggests that the increment in the barrier for the fluorine-substituted compounds is probably due to the large steric repulsion of the fluorine atoms. On this bases, it might be expected that in $(CH_3)_3P\cdot BCl_3$ the methyl groups and chlorine atoms increase the barrier around the P–B bond through large steric effects. The barrier was however found to be 3.8±0.7 kcal mol$^{-1}$, which is equal to that reported for $F_3P\cdot BH_3$ and $H_3P\cdot BF_3$ within the limits of experimental error. This could be attributed to the considerably large C···Cl distances in $(CH_3)_3P\cdot BCl_3$.

## References

1) R. L. Kuczkowski and D. R. Lide, *J. Chem. Phys.*, **46**, 357 (1967).

TABLE 4. CORRELATION MATRIX OF $(CH_3)_3P\cdot BCl_3$

| | $r$(BCl) | $r$(PB) | $r$(CP) | $r$(CH) | $r$(ClCl) | $r$(CC) | ∠PCH | $l$(CH) | $l$($t$CCl) | $l$($g$CCl) | $l$(PH) | $l$(BCl) | $l$(CP) | $l$(ClCl) | $R_1$[a] | $R_2$[a] |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $r$(BCl) | 1.0 | | | | | | | | | | | | | | | |
| $r$(PB) | −0.95 | 1.0 | | | | | | | | | | | | | | |
| $r$(CP) | −0.65 | 0.51 | 1.0 | | | | | | | | | | | | | |
| $r$(CH) | −0.06 | 0.07 | −0.03 | 1.0 | | | | | | | | | | | | |
| $r$(ClCl) | 0.12 | −0.27 | −0.01 | −0.04 | 1.0 | | | | | | | | | | | |
| $r$(CC) | −0.18 | 0.18 | 0.49 | −0.02 | −0.32 | 1.0 | | | | | | | | | | |
| ∠PCH | 0.17 | −0.18 | −0.16 | −0.33 | 0.03 | −0.11 | 1.0 | | | | | | | | | |
| $l$(CH) | −0.10 | 0.11 | 0.10 | −0.02 | −0.20 | 0.07 | −0.03 | 1.0 | | | | | | | | |
| $l$($t$CCl) | −0.07 | 0.09 | 0.06 | 0.03 | −0.15 | 0.05 | −0.07 | 0.18 | 1.0 | | | | | | | |
| $l$($g$CCl) | 0.03 | −0.09 | −0.03 | −0.09 | 0.13 | −0.09 | 0.18 | −0.09 | −0.10 | 1.0 | | | | | | |
| $l$(PH) | 0.02 | −0.01 | −0.04 | −0.04 | 0.10 | −0.02 | 0.05 | −0.14 | −0.10 | 0.00 | 1.0 | | | | | |
| $l$(BCl) | 0.25 | −0.39 | 0.46 | −0.05 | 0.04 | 0.33 | −0.01 | 0.15 | 0.10 | −0.04 | −0.13 | 1.0 | | | | |
| $l$(CP) | −0.75 | 0.79 | 0.22 | 0.09 | −0.31 | −0.01 | −0.12 | 0.25 | 0.19 | −0.10 | −0.13 | −0.42 | 1.0 | | | |
| $l$(ClCl) | −0.44 | 0.23 | 0.57 | 0.00 | 0.33 | 0.10 | −0.09 | 0.20 | 0.14 | 0.00 | −0.14 | 0.37 | 0.30 | 1.0 | | |
| $R_1$ | −0.30 | 0.33 | 0.24 | 0.02 | −0.41 | 0.04 | 0.06 | 0.32 | 0.24 | −0.28 | −0.09 | 0.19 | 0.45 | 0.30 | 1.0 | |
| $R_2$ | −0.22 | 0.24 | 0.21 | 0.06 | −0.42 | 0.14 | −0.08 | 0.48 | 0.35 | −0.17 | −0.32 | 0.32 | 0.53 | 0.42 | 0.63 | 1.0 |

a) $R_1$ and $R_2$ are indices of resolution for the long and short camera distance data, respectively. The indices and uncertainties are $R_1=0.88(1)$ and $R_2=1.00(5)$.

2) J. R. Durig, Y. S. Li, L. A. Carreira, and J. D. Odom, *J. Am. Chem. Soc.*, **95**, 2491 (1973).

3) J. D. Odom, V. F. Kalasinsky, and J. R. Durig, *Inorg. Chem.*, **11**, 2837 (1975).

4) P. S. Bryan and R. L. Kuczkowski, *Inorg. Chem.*, **11**, 553 (1972).

5) J. P. Pasinski and R. L. Kuczkowski, *J. Chem. Phys.*, **54**, 1903 (1971).

6) D. L. Black and R. C. Taylor, *Acta Crystallogr.*, *Sect. B*, **31**, 1116 (1975).

7) A. B. Burg and R. I. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

8) R. W. Rudolph and R. W. Parry, *J. Am. Chem. Soc.*, **89**, 1621 (1967).

9) S. Shibata and K. Iijima, *Chem. Lett.*, **1977**, 29.

10) M. Hargittai and I. Hargittai, *J. Mol. Struct.*, **39**, 79 (1977).

11) K. Iijima and S. Shibata, *Bull. Chem. Soc. Jpn.*, **52**, 711 (1979).

12) J. E. Drake, J. L. Hencher, and B. Rapp, *Inorg. Chem.*, **16**, 2289 (1977).

13) W. Witt, *Z. Naturforsch.*, *Teil A*, **19**, 1363 (1964).

14) S. Shibata, K. Iijima, R. Tani, and I. Nakamura, *Rep. Fac. Sci. Shizuoka Univ.*, **9**, 33 (1974).

15) L. Schäfer, A. C. Yates, and R. A. Bonham, *J. Chem. Phys.*, **55**, 3055 (1971).

16) D. T. Cromer and J. B. Mann, *J. Chem. Phys.*, **47**, 1892 (1967); D. T. Cromer, *ibid.*, **50**, 4857 (1969).

17) K. Kuchitsu and S. J. Cyvin, "Molecular Structures and Vibrations," ed by S. J. Cyvin, Elsevier, Amsterdam (1972), Chap. 12.

18) K. Kuchitsu, *Bull. Chem. Soc. Jpn.*, **40**, 505 (1967).

19) "Kagaku Binran," 2nd ed, ed by the Chemical Society of Japan, Maruzen, Tokyo (1975), p. 1330.

20) Numerical experimental data of the leveled total intensity and background have been deposited with the Chemical Society of Japan (Document No. 7931).

21) L. S. Bartell and L. O. Brockway, *J. Chem. Phys.*, **32**, 512 (1960).

22) S. Konaka, Y. Murata, K. Kuchitsu, and Y. Morino, *Bull. Chem. Soc. Jpn.*, **39**, 1134 (1966).

23) R. J. Gillespie, *J. Chem. Educ.*, **40**, 295 (1963).

24) P. H. Clippard, J. C. Hanson, and R. C. Taylor, *J. Cryst. Mol. Struct.*, **1**, 363 (1971).