CONTRIBUTION NO. 200 FROM THE RESEARCH AND DEVELOPMENT DIVISION, EASTERN LABORATORY,
EXPLOSIVES DEPARTMENT, E. I. DU PONT DE NEMOURS AND COMPANY, GIBBSTOWN, NEW JERSEY

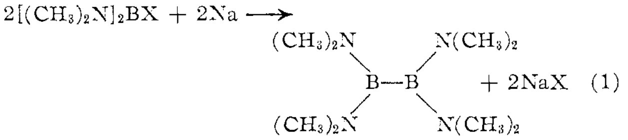
The Chemistry of Tetrakis(dimethylamino)diboron[1]

BY S. C. MALHOTRA

Received December 2, 1963

Tetrakis(dimethylamino)diboron reacts with certain protonic acids to give substituted diboron compounds. With hydrogen sulfide, a six-membered ring compound containing two boron–boron bonds is formed. Hydrogen cyanide, chloride, and bromide react to yield tetrasubstituted products which are stabilized by dimethylamine molecules firmly attached to the boron atoms by coordination linkages. The physical and chemical properties characterizing these compounds are given and structures are discussed.

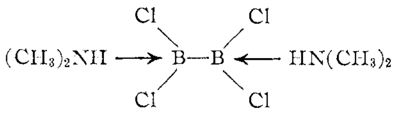
The readily available and remarkably air stable tetrakis(dimethylamino)diboron is an ideal starting material to prepare certain compounds containing boron–boron linkages. Reaction of chloro or bromobis(dimethylamino)borane with highly dispersed alkali metals to give excellent yields of the diboron compound has only recently been reported.[2,3]



(1)

This technique has been used to obtain certain other compounds containing boron–boron bonds such as tetraalkoxydiborons[4] and 1,2-dialkyl- or 1,2-diphenyl-1,2-bis(dimethylamino)diboron.[5,6] The method is applicable only to relatively thermally stable compounds. On the other hand, tetrakis(dimethylamino)diboron can be used to prepare certain derivatives at or below room temperature.

Tetrakis(dimethylamino)diboron is a colorless liquid, extremely sensitive to moisture. Complex reactions were observed when it was heated with oxygen above 200°.[7] It is monomeric in benzene solution and gives one mole of hydrogen per mole of diboron compound when hydrolyzed in 10% sodium hydroxide.[2] It is known[8] to give, upon acid hydrolysis, tetrahydroxydiboron; with alcohol in the presence of acid, it forms tetraalkoxydiboron. When heated at 300° in the absence of oxygen and water, it gives bis- and tris-(dimethylamino)boranes.[9] Other aminodiborons are prepared from it readily by transamination.[2,10] With boron trichloride, it forms diboron tetrachloride and bis(dimethylamino)dichlorodiboron.[3] Hydrogen chloride reacts to yield products in which dimethylamino groups are replaced with chlorine; excess acid gives a compound of the suggested formula[11]



Brown and Silver,[12] however, give the latter a salt-like structure, $B_2Cl_2[N(CH_3)_2]_2\cdot 2HCl$, on the basis of the absence of analogy with the known complex $[B_2Cl_4\cdot(N(CH_3)_3)_2]_4$.[13,14] We have also prepared the same compound and have shown it to have the covalent properties.

An excellent review[15] on boron subhalides has recently appeared. Addition rather than substitution products are formed in the reactions of diboron tetrachloride with hydrogen sulfide[16] and hydrogen cyanide.[14] The sulfide adducts, $B_2Cl_4\cdot H_2S$ and $B_2Cl_4\cdot 2H_2S$, are unstable at or above room temperature, decomposing to give hydrogen and boron sulfide, among other products. The product of reaction between diboron tetrachloride and cyanogen, $B_2Cl_4\cdot 1.5(CN)_2$, does not contain a boron–boron linkage.[17]

We have used tetrakis(dimethylamino)diboron successfully to prepare cyano and sulfo diboron compounds. The synthesis and characterizations of these compounds as well as those of the chloro and bromo analogs are described below.

Experimental

All materials employed in this work were reagent grade chemicals. Gases were dried over anhydrous calcium sulfate before use and the reactions were carried out in an atmosphere of dry nitrogen.

Boron analyses were performed by the Parr bomb fusion method. Melting points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Infracord spectrophotometer.

2,3,5,6-Tetrakis(dimethylamino)1,4-dithiatetraborinane.—Excess hydrogen sulfide (>54.8 mmoles) was bubbled through a dilute solution of tetrakis(dimethylamino)diboron (2.7 g., 13.7 mmoles) in ether at 0°, to which hydrogen chloride (27.4 mmoles, B_2:HCl = 1:2) in ether solution was then slowly added with constant stirring of the reaction mixture.[18] The mixture was filtered and the solution evaporated to dryness. (The ether-

---

[1] We thank U. S. Borax for the sample of tetrakis(dimethylamino)diboron.

[2] R. J. Brotherton, *et al.*, *J. Am. Chem. Soc.*, **82**, 6242 (1960).

[3] H. Nöth and W. Meister, *Ber.*, **94**, 509 (1961).

[4] E. Wiberg and W. Rushmann, *ibid.*, **70b**, 1393 (1937).

[5] H. Nöth and P. Fritz, *Angew. Chem.*, **73**, 408 (1961).

[6] R. J. Brotherton, *et al.*, *Inorg. Chem.*, **1**, 749 (1962).

[7] A. G. Massey and N. R. Thompson, *J. Inorg. Nucl. Chem.*, **25**, 175 (1963).

[8] A. L. McCloskey, *et al.*, *J. Am. Chem. Soc.*, **83**, 4750 (1961).

[9] L. L. Petterson and R. J. Brotherton, *Inorg. Chem.*, **2**, 423 (1963).

[10] M. P. Brown, *et al.*, *J. Chem. Soc.*, 4648 (1962).

[11] H. Nöth and W. Meister, *Z. Naturforsch.*, **17b**, 714 (1962).

[12] M. P. Brown and H. B. Silver, *Chem. Ind.* (London), 85 (1963).

[13] G. Urry, *et al.*, *J. Am. Chem. Soc.*, **76**, 5293 (1954).

[14] A. K. Holliday, *et al.*, *J. Chem. Soc.*, 3348 (1961).

[15] A. K. Holliday and A. G. Massey, *Chem. Rev.*, **62**, 303 (1962).

[16] T. Wartik and E. F. Apple, *J. Am. Chem. Soc.*, **80**, 6155 (1958).

[17] E. F. Apple and T. Wartik, *ibid.*, **80**, 6158 (1958).

[18] The title compound was also formed upon treating the ether solution of tetrakis(dimethylamino)diboron in an autoclave with hydrogen sulfide under pressure without the use of the strong acid.

insoluble solid was shown to be dimethylamine hydrochloride by its X-ray diffraction pattern.) The residue from the evaporation was extracted with benzene at room temperature. The benzene solution yielded a white crystalline solid upon concentration and cooling, m.p. 112° dec. The estimated yield was above 90%.

Anal. Calcd. for $B_4[N(CH_3)_2]_4S_2$: C, 33.9; H, 8.5; N, 19.7; B, 15.3; S, 22.6; mol. wt., 283. Found: C, 32.7; H, 8.5; N, 18.5; B, 15.6; S, 21.8; mol. wt., 285, 288 (in benzene by osmometer method). The test for chlorine was negative.

Infrared spectrum (KBr, cm.$^{-1}$): 2942 (w), 2858 (s), 2778 (w), 2382 (w), 1493 (s), 1428 (s), 1389 (s), 1235 (m), 1190 (s), 1150 (s), 1112 (s), 1055 (m), 1020 (w), 980 (s), 893 (w), 870 (s), 800 (m), 793 (m), and 742 (m).

X-Ray diffraction data, d (I/I_0): 8.5 (1.00), 7.0 (0.70), 6.4 (0.05), 5.3 (0.10), 4.73 (0.10), 4.42 (0.15), 4.21 (0.80), 3.96 (0.30), 3.51 (0.50), 3.19 (0.80), 2.91 (0.05), 2.70 (0.05), 2.53 (0.05), 2.42 (0.10), and 2.37 (0.05).

A 0.21-g. sample of the product was treated with 6 N HCl (25 ml.) at 0° whereupon a trace of hydrogen gas was collected. The acid solution was evaporated to dryness and the residue extracted with chloroform. The chloroform-insoluble product was shown to be tetrahydroxydiboron containing a small amount of boric acid (infrared analysis).

The boron n.m.r. spectrum showed a single peak at 11.2 p.p.m. above TMB.[19] (N.m.r. for tetrakis(dimethylamino)diboron showed a single peak at 17 p.p.m. below TMB.)

Bis(dimethylamine)tetracyanodiboron.—In a typical experiment, 2.3 g. (85.2 mmoles) of hydrogen cyanide was distilled from anhydrous calcium sulfate into an ether solution of tetrakis(dimethylamino)diboron (1.9 g., 9.6 mmoles) at 0–25°. The precipitate that was formed after a few minutes' stirring was separated by filtration and was extracted with chloroform. The insoluble solid (1.9 g., 8.8 mmoles, 92% yield) was purified by crystallization from ethanol, m.p. 202° dec.

Anal. Calcd. for $B_2(CN)_4 \cdot 2HN(CH_3)_2$: C, 44.5; H, 6.5; N, 38.8; B, 10.2; mol. wt., 216. Found: C, 44.4; H, 6.4; N, 38.3; B, 10.1; mol. wt., 213 (in water by osmometer method).

Infrared spectrum (KBr, cm.$^{-1}$): 3177 (s), 3032 (vw), 2818 (w), 2740 (w), 2470 (vw), 2215 (m), 1627 (w), 1470 (s), 1410 (m), 1343 (m), 1228 (w), 1150 (s), 1055 (w), 1015 (s), 925 (s), 893 (w), 830 (s), 758 (w), 747 (w), and 700 (w).

X-Ray diffraction data, d (I/I_0): 8.6 (0.10), 7.5 (1.00), 6.2 (0.70), 6.0 (0.70), 5.4 (0.70), 4.83 (0.20), 4.18 (0.30), 3.74 (1.00), 3.50 (0.40), 3.43 (0.30), 3.30 (0.30), 3.10 (0.50), 2.49 (0.30), and 2.08 (0.10).

A 0.10-g. sample of the product upon treatment with 6 ml. of 5% NaOH solution at 115° for 2 days gave 8.09 cc. (STP)[20] of hydrogen, indicating that 78% of the boron–boron linkage was oxidized under these conditions (calcd.: 10.39 cc.).

Another sample of the product was treated with excess silver nitrate in aqueous solution in the presence of dilute HNO_3. The precipitate thus formed was washed thoroughly with water. *Anal.* Calcd. for $B_2(CN)_4 \cdot 2HN(CH_3)_2 \cdot AgNO_3$: C, 24.9; N, 25.4. Found: C, 24.8; N, 24.6. Infrared analysis was identical with that of the starting material except for an additional absorption at 1370 cm.$^{-1}$ due to the nitrate ion. The X-ray diffraction data showed the absence of free silver, silver nitrate, and silver cyanide: d (I/I_0): 6.7 (0.70), 6.2 (0.80), 6.0 (0.70), 5.9 (0.60), 5.7 (0.20), 5.4 (0.10), 5.3 (1.00), 4.86 (0.70), 4.31 (0.20), 4.11 (0.70), 4.00 (0.10), 3.95 (0.10), 3.91 (0.10), 3.82 (0.50), 3.73 (0.70), 3.66 (0.30), 3.60 (0.10), 3.42 (0.30), 3.33 (0.20), 3.24 (0.50), 3.09 (0.50), 2.99 (0.10), 2.57 (0.40), 2.52 (0.10), 2.41 (0.20), 2.33 (0.10), 2.28 (0.10), 2.11 (0.10), and 2.00 (0.10).

In another experiment, which was run under apparently similar conditions, a low yield product was obtained and was analyzed. *Anal.* Calcd. for $B_2(CN)_4 \cdot 2HN(CH_3)_2 \cdot 2AgNO_3$: C, 17.3; H, 2.5; N, 20.1; Ag, 38.9. Found: C, 17.6; H, 2.5; N, 20.5; Ag, 38.7. An infrared spectrum of the compound was identical with that of the previous product. X-Ray diffraction data, d (I/I_0): 10.0 (0.40), 8.1 (0.30), 7.8 (1.00), 6.6 (0.20), 6.2 (0.25), 5.9 (0.25), 5.0 (0.95), 4.83 (0.30), 4.30 (0.20), 4.07 (0.30), 3.91 (0.30), 3.85 (0.20), 3.79 (0.30), 3.69 (0.20), 3.49 (0.25), 3.43 (0.25), 3.39 (0.20), 2.83 (0.30), 2.66 (0.25), and 2.52 (0.15).

A sample of bis(dimethylamine)tetracyanodiboron was treated with 5 N HNO_3 at 25° for 24 hr. and the product was evaporated to dryness. The infrared analysis and X-ray diffraction pattern of the residue were essentially identical with those of the starting material.

Another sample of the cyano compound was heated in 6 N HCl at 95° for 24 hr. The infrared spectrum of the product showed the starting material containing a small amount of dimethylamine hydrochloride.

Thermal gravimetric analysis of the compound showed 61% weight loss at 775°. The residual product was a semicrystalline compound(s) and did not include B_4C or BN (X-ray).

The proton n.m.r. spectrum for a sample showed only one strong peak at 3.0 p.p.m. in pyridine solution.

Mixed Chlorocyanodiboron Compounds with Dimethylamine.—Tetrakis(dimethylamino)diboron (2.2 g., 11.1 mmoles) was treated with 2.7 g. (100.0 mmoles) of hydrogen cyanide as before except that 34.0 mmoles of hydrogen chloride was added to the mixture along with the hydrogen cyanide. A solid precipitated out and was separated by filtration. It was extracted with chloroform, and the chloroform solution was found to contain dimethylamine hydrochloride. The insoluble product was dried under reduced pressure.

Anal. Calcd. for a mixture of $B_2Cl_2(CN)_2 \cdot 2HN(CH_3)_2$ and $B_2(CN)_4 \cdot 2HN(CH_3)_2$ (1.5:1): C, 36.1; H, 6.2; N, 29.6; B, 9.5; Cl, 18.6; mol. wt., 227. Found: C, 35.3; H, 5.9; N, 27.3; B, 9.3; Cl, 17.1; mol. wt., 234, 238 (in dioxane by osmometer method).

Infrared spectrum (KBr, cm.$^{-1}$): 3207 (s), 3032 (vw), 2987 (w), 2818 (w), 2703 (w), 2470 (vw), 2198 (m), 1627 (w), 1472 (s), 1440 (w), 1408 (m), 1343 (m), 1228 (w), 1145 (s), 1058 (w), 1020 (s), 922 (s), 845 (m), 807 (w), 788 (w), 755 (m), 725 (w), and 690 (m).

X-Ray diffraction data, d (I/I_0): 7.8 (0.80), 6.3 (0.95), 5.8 (1.00), 5.4 (0.90), 5.3 (0.50), 3.92 (0.30), 3.88 (0.20), 3.70 (0.20), 3.53 (0.10), 3.41 (0.10), 3.22 (0.20), 3.08 (0.50), 3.00 (0.10), 2.94 (0.10), and 2.65 (0.10).

A sample of the product mixture was heated under reduced pressure at 200–210° for 1 hr. The residual solid was shown to be bis(dimethylamine)tetracyanodiboron by means of its infrared spectrum and X-ray diffraction pattern. *Anal.* Found: Cl, 0.7; B, 9.7. The volatiles were identified as dimethylamine hydrochloride, hydrogen cyanide, and a small amount of bis(dimethylamine)tetracyanodiboron. Thin-layer chromatography showed it to be a two-component mixture.

The boron n.m.r. spectrum showed two peaks at +24.4 and +37.0 p.p.m. with respect to TMB.

A sample of the mixture (0.14 g., 0.67 mg.-atom of chlorine) in dioxane solution was treated with 0.08 g. (0.60 mg.-atom of silver) of silver cyanide at 25° for 2 days. The reaction product isolated from the solution was identified as pure bis(dimethylamine)tetracyanodiboron by means of chemical and infrared analyses.

Bis(dimethylamine)tetrachlorodiboron.—An ether solution of tetrakis(dimethylamino)diboron (1.4 g., 7.0 mmoles) was treated with excess hydrogen chloride (B_2:HCl = 1:>6) at 0°. The contents of the reaction flask were evaporated to dryness after the completion of the reaction, and the residue was extracted with dry benzene in the absence of moisture. The benzene-insoluble solid was identified as dimethylamine hydrochloride (1.1 g.; calcd. on the basis of eq. 5, 1.2 g.) by means of its X-ray diffraction pattern. The benzene solution, upon concentration and cooling, gave a solid (1.5 g., 5.9 mmoles, 84% yield) which was dried under reduced pressure, m.p. 202°.

Anal. Calcd. for $B_2Cl_4 \cdot 2HN(CH_3)_2$: C, 18.9; H, 5.5; N, 11.0; B, 8.5; Cl, 56.1. Found: C, 18.2; H, 5.6; N, 10.6; B, 8.7; Cl, 53.3.

---

[19] Trimethyl borate reference.

[20] This does not include any dissolved gas in the solution.

Infrared spectrum (KBr, cm.$^{-1}$): 3205 (s), 3030 (w), 2960 (m), 1460 (s), 1435 (w), 1420 (m), 1390 (w), 1360 (m), 1300 (s), 1220 (w), 1118 (s), 1043 (w), 1010 (m), 990 (w), 902 (s), 813 (w), 795 (w), 763 (m), and 700 (m).

X-Ray diffraction data, d (I/I_0): 6.5 (1.00), 4.95 (0.40), 3.63 (0.20), 3.31 (0.15), 3.27 (0.60), 3.07 (0.40), 2.93 (0.50), and 2.81 (0.25).

The boron n.m.r. spectrum for the product showed one peak at +10.4 p.p.m. with respect to TMB.

A 1.51-g. (5.96 mmoles) sample of bis(dimethylamine)tetrachlorodiboron in benzene solution was treated with 4.00 g. (29.9 mmoles) of silver cyanide at 25° for 4 days. The mass was filtered and the insoluble solid was extracted with chloroform to free it from any soluble impurity. It was then extracted with tetrahydrofuran and the resulting solution evaporated to dryness. The product was identified as bis(dimethylamine)tetracyanodiboron by means of infrared spectrum, X-ray diffraction pattern, and chemical analysis.

Bis(dimethylamine)tetrabromodiboron.—The reaction between tetrakis(dimethylamino)diboron and hydrogen bromide was carried out in the manner described above, and the product was analyzed, m.p. 189° dec.

Anal. Calcd. for $B_2Br_4 \cdot 2HN(CH_3)_2$: C, 11.1; H, 3.2; N, 6.5; B, 5.0; Br, 74.2. Found: C, 11.3; H, 3.3; N, 6.3; B, 5.0; Br, 75.2.

The infrared spectrum of the compound was identical with that of the chloro analog up to 900 cm.$^{-1}$, after which the values for absorptions were (cm.$^{-1}$) 795 (w), 778 (w), 752 (m), and 725 (sh).

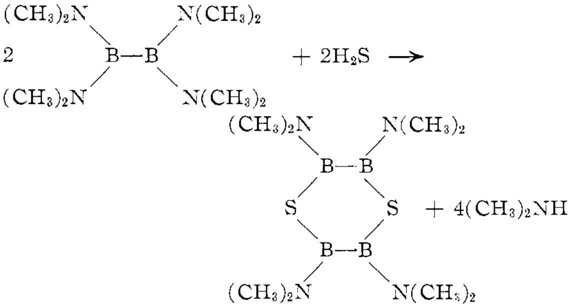
X-Ray diffraction data, d (I/I_0): 6.7 (1.00), 4.48 (0.10), 3.69 (0.20), 3.35 (0.80), 3.25 (0.10), 3.16 (0.40), 2.97 (0.40), 2.80 (0.20), 2.43 (0.10), 2.25 (0.20), and 2.06 (0.10).

Discussion

It is clear from the above that tetrakis(dimethylamino)diboron reacts with certain weak and strong protonic acids to form substituted diboron compounds, liberating free dimethylamine or its salts. The formation of a π-bond between the boron atom and the group attached to it is important to the stability of the boron–boron linkage. Where such a bond does not exist, the liberated dimethylamine molecule is attached to the boron atom by coordinate linkage. The donation of a free pair of electrons from the nitrogen atom to the vacant 2p-orbital of the boron atom is so essential that even the strong acids, such as hydrogen chloride, do not liberate the attached amine from the products.

The reaction with hydrogen chloride or hydrogen bromide was instantaneous due to the formation of amine salt; with weak acids, the reactions proceeded slowly. In the latter case, slow addition of hydrogen chloride in ether solution to the reaction mixtures effected an increase in the reaction rates. Relatively rapid addition of the acid, however, resulted in the formation of compounds containing B–Cl bonds.

2,3,5,6-Tetrakis(dimethylamino)1,4-dithiatetraborinane (I) was prepared either by bubbling hydrogen sulfide through a solution of tetrakis(dimethylamino)diboron to which a solution of hydrogen chloride in ether was slowly added during the reaction or by treating the solution of the diboron compound in an autoclave with hydrogen sulfide under pressure without the use of the strong acid.

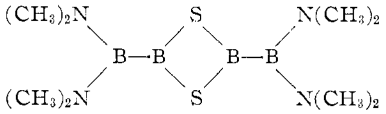


(2)

I

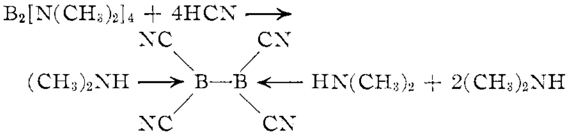
$$(CH_3)_2NH + HCl \longrightarrow (CH_3)_2NH \cdot HCl \qquad (3)$$

I can be sublimed under reduced pressure. It was characterized by molecular weight, boron n.m.r., which differentiates it from



elemental analysis, and its conversion to tetrahydroxydiboron upon acidic hydrolysis.

The reaction product of tetrakis(dimethylamino)diboron and hydrogen cyanide is a slightly volatile, crystalline solid, insoluble in ether, benzene, and chloroform, and slightly soluble in water, ethanol, acetone, and tetrahydrofuran.



(4)

II

Infrared absorption at 2215 cm.$^{-1}$ [21] is attributed to the C≡N stretching vibration and absorption at 3177 cm.$^{-1}$ is assigned to N—H stretching; the asymmetric stretching mode due to C—N shows absorption at 1015 cm.$^{-1}$ and absorption at 1150 cm.$^{-1}$ is due to B←N stretching. The possibility of equilibrium between the cyanide and the isocyanide forms may not be ruled out. The structure is further supported by molecular weight, proton n.m.r., and hydrogen evolution upon alkaline hydrolysis. The latter is a diagnostic test for the presence of boron–boron linkage.[15] The close similarity of the infrared spectrum with that of bis(dimethylamine)tetrachloro- or -bromodiboron also favors this structure.

II is probably the most stable diboron compound known so far. It undergoes only a slight decomposition in the presence of hot dilute HCl or cold dilute HNO_3.

In experiments not described here, an attempt was made to remove the coordinated dimethylamine groups from II by treating the latter with (a) sodium cyanide, (b) silver cyanide, and (c) boron trifluoride[13] in order to form sodium and silver salts of $B_2(CN)_6^{2-}$ and $(CH_3)_2NH \cdot BF_3$ (or products of intra-action), respectively. However, only decomposition products were

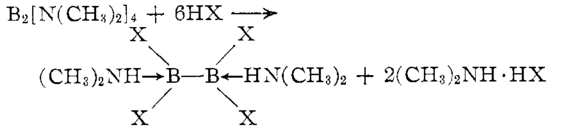
---

[21] B. M. Mikhailov and Yu. N. Bubnov, *Proc. Acad. Sci. USSR, Chem. Sect.*, **127**, 587 (1959).

obtained from the metal cyanides, and there was no reaction in the case of boron trifluoride.

A mixture of II and bis(dimethylamine)dichlorodicyanodiboron (III) was obtained upon simultaneous addition of hydrogen chloride and hydrogen cyanide to tetrakis(dimethylamino)diboron. The exact conditions for the formation of III are, however, uncertain. The mixture could not be resolved due to close solubilities of the components. It was characterized by molecular weight, chemical analysis, conversion to pure II with silver cyanide, and thin-layer chromatography (which showed it to be a two-component mixture). The infrared spectrum shows N—H (3207 cm.$^{-1}$), C≡N (2198 cm.$^{-1}$), and B←N (1145 cm.$^{-1}$) absorptions. The absence of bis(dimethylamine)tetrachlorodiboron and the presence of II in the mixture are evident from their X-ray diffraction patterns. That the two boron atoms in III are equivalent is shown by the two peaks in the boron n.m.r. spectrum of the mixture (one for each constituent). The mixture upon treatment with water yielded solids which contained II and dimethylamine hydrochloride (infrared and X-ray). The same results were obtained when the mixture was heated under reduced pressure.

Both the tetrachloro (IV) and tetrabromo (V) derivatives of tetrakis(dimethylamino)diboron were obtained by treating the latter with excess hydrogen halide (B_2:HX = $1:\geqslant 6$) at 0°, according to the equation



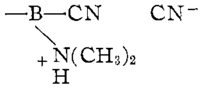
$$B_2[N(CH_3)_2]_4 + 6HX \longrightarrow (CH_3)_2NH\rightarrow BX_2-BX_2\leftarrow HN(CH_3)_2 + 2(CH_3)_2NH\cdot HX \quad (5)$$

IV, V

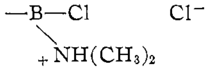
The products are crystalline, white solids, slightly soluble in ether and benzene. IV is identical with the compound recently reported in the literature.[11] Its melting point (202°) is in agreement with the published values (198, 204°[12]). There is, however, discrepancy between the originally assigned structure[11] and the one reported subsequently.[12] We have characterized it by its conversion to II with silver cyanide, formation of tetrahydroxydiboron on acidic hydrolysis, boron n.m.r., infrared, and elemental analysis. Although sodium cyanide did not react with it even upon heating the mixture in benzene at 50° for 4 days, silver cyanide gave a quantitative yield of II at room temperature, in accordance with the equation

$$B_2Cl_4\cdot 2HN(CH_3)_2 + 4AgCN \longrightarrow B_2(CN)_4\cdot 2HN(CH_3)_2 + 4AgCl \quad (6)$$

The product was identified as II by means of X-ray diffraction, infrared spectrum, and elemental analysis. The infrared absorption at 2215 cm.$^{-1}$ is characteristic of a covalent bond between boron and cyanide. An ionic bond between them would result in absorption at a much higher wave length, typical of inorganic cyanides.[22] The absence of this latter absorption rules out the possibility of the structure



and, hence, of



This is further supported by the absence of NH^+ stretching at 2735 cm.$^{-1}$ [23] and the presence of N–H stretching vibration at 3205 cm.$^{-1}$. In addition, the compound is slightly but appreciably soluble in ether and benzene. That IV is not $[(CH_3)_2NBCl_2]_2$ is evident from their different X-ray diffraction patterns, infrared spectra, and behavior toward water. $[(CH_3)_2NBCl_2]_2$ is unaffected by the latter[24] and does not contain boron–boron linkage.

In experiments not reported here, the reaction product of hydrogen fluoride and tetrakis(dimethylamino)diboron was shown to be a mixture of two components by means of thin-layer chromatography. Both were insoluble in ether, benzene, chloroform, methyl ethyl ketone, and tetrahydrofuran and soluble in acetonitrile. The chemical analysis was consistent with the equation

$$B_2[N(CH_3)_2]_4 + 10HF \longrightarrow B_2F_4\cdot 2HN(CH_3)_2 + 2(CH_3)_2NH\cdot 3HF \quad (7)$$

The infrared spectrum showed absorption at 2777 cm.$^{-1}$ attributed to NH^+ and/or NH_2^+, but the characteristic N-H absorption at about 3200 cm.$^{-1}$ was absent.

The existence of the $B\text{–}\overset{+}{N}H(CH_3)_2$ group is, therefore, probable in this case.

---

(22) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., London, New York, p. 346.

(23) Reference 22, p. 260.

(24) E. Wiberg and K. Schuster, *Z. anorg. allgem. Chem.*, **213**, 89 (1933).