

methyl groups, around the central Cu(II) ion, if it is assumed that all the rings are coplanar, and lie in the plane defined by the C-N bonds. The nature of the steric hindrance involved is shown in Fig. 5, in which the C-H distance is taken as 1.09 Å., and the van der Waals radius of the hydrogen atoms as 1.10 Å. The marked overlapping shown between the van der Waals radii of the adjacent imidazole rings in Fig. 5 obviously cannot be obviated by any reasonable change in the assumed dimensions. Presumably some or all of the imidazole rings must be rotated out of the plane of the figure, around the Cu-N bonds, so as to make mutual accommodation easier. Probably there is also some distortion of the orientation of the Cu-N bonds, so that they do not all lie in a single plane.²⁴

The insertion of a methyl group in the 4-position on the ring gives rise to new stereochemical problems and also to new possibilities of isomerism, as illustrated in Fig. 6. To minimize steric hindrance it seems probable that the binding will occur chiefly with the 1-nitrogen, as for the imidazole ring shown on the right hand side of Fig. 6. This places the methyl group as far away as possible from the central copper ion. In the binding of 2,4-dimethylimidazole, however, it is inevitable that one of the methyl groups must be on a nitrogen atom immediately adjacent to the copper ion. Neverthe-

(24) Bjerrum, *et al.*,²² conclude that the Cu(NH₃)₄⁺⁺ complex, and other analogous complexes, are distorted octahedral structures, with attached water molecules above and below the plane defined by the 4 Cu-N bonds. If this is true for the imidazole complexes, the stereochemical problem is not very much changed from that outlined in the text here. The two attached water molecules, however, may make the attachment of 4 imidazole molecules involve an even tighter fit than we have suggested.

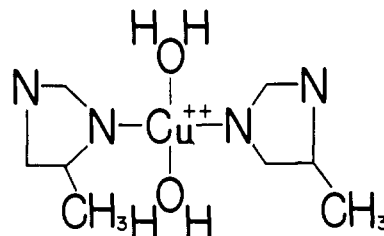


Fig. 6.—Combination of 4-methylimidazole with Cu(II), showing the two possible isomeric arrangements; the one shown on the right is presumably preferred. The other two coordination positions are shown as being occupied by water molecules.

less the rather incomplete studies reported here on 2,4-dimethylimidazole indicate only a slight decrease in its tendency to coordinate with copper as compared with imidazole or 4-methylimidazole. These findings reinforce the conclusion that the Cu-N bonds cannot be coplanar in the tri- and tetra-coordinated complexes. X-ray diffraction and spectroscopic studies on these complexes may serve to clarify these problems, to which we can give no definite answer here.²⁵

Acknowledgment.—We are indebted to Mr. Charles Lipson for much work on the preparation and purification of the imidazole derivatives studied in this paper, and for some of the preliminary measurements upon them.

(25) Compare the structure of the CuCl₄⁻ ion in cesium chlorocuprate, reported by L. F. Helmholz and R. F. Kruh, *THIS JOURNAL*, **74**, 1176 (1952).

CAMBRIDGE AND BOSTON, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

Amine Chemistry of the Pentaborane B₅H₉

BY ANTON B. BURG

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The structure of B₅H₉ suggests certain modes of reaction which its amine chemistry appears to confirm. It adds trimethylamine at -78° to form B₅H₉·2Me₃N, which on heating *in vacuo* is partly dissociated into the original components and partly converted to Me₃NBH₃ and (BH)_x. On heating with excess Me₃N, the adduct yields 2Me₃NBH₃ and BH polymers incorporating Me₃N, which lends thermoplastic character. Either Me₂NH or aminoboron hydrides such as Me₂NBH₂ or (Me₂N)₂BH remove BH₃ from B₅H₉ on heating, and much of the new (Me₂N)₃B₃H₄ (m.p. 95°; b.p. est. 220°) is formed. Small yields of the new liquid (Me₂N)₂B₄H₆, of similar volatility, also are obtained. Both compounds, which seem to represent a large new class, are presumed to have cross-ring structures wherein all B and N atoms are four-coordinate. The (Me₂N)₂B₃H₄ is especially unreactive and thermally stable but can be converted by heat to still more inert new materials.

The structure of the pentaborane B₅H₉^{1,2} is such that the removal of two BH₃ groups from the molecule—as by the use of a tertiary amine to form 2R₃NBH₃—could occur by breaking only bonds of order less than one, and without shifting any hydrogen atoms from one boron atom to another. The remainder of the molecule then would be a B₃H₃ unit which could not persist as a simple B-B-B chain hydride, but would convert immediately to a high-polymer form. These ideas correlate with some experimental results obtained by the author

(1) K. Hedberg, M. E. Jones and V. Schomaker, *THIS JOURNAL*, **73**, 3538 (1951).

(2) W. J. Dulmage and W. N. Lipscomb, *ibid.*, **73**, 3539 (1951).

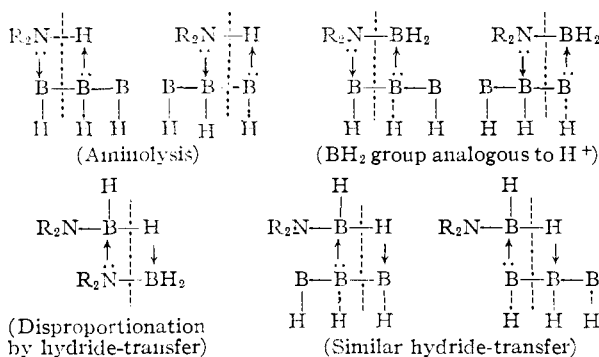
in the year 1937, during a period of collaboration with Professor H. I. Schlesinger at the University of Chicago. It was found that the adduct B₅H₉·2(CH₃)₃N would form slowly at -79° and upon warming *in vacuo* it would decompose in two ways: dissociation into the original components and the formation of (CH₃)₃NBH₃ and a yellow residue. The two ways of decomposition, occurring simultaneously, suggested the possibility that the adduct had two forms with different types and strengths of bonding. On heating with more trimethylamine, the yellow solid became almost colorless, with slight production of (CH₃)₃NBH₃, and approached the composition (BH)_x, containing only a very

small proportion of amine. For each unrecovered B_5H_9 there now were two $(CH_3)_3NBH_3$, and the equivalent of a B_3H_3 unit in the solid residue. This $(BH)_x$ polymer would not react further on heating with more amine, and it was only slightly affected by aqueous acids or bases.

In more recent experiments, the adduct $B_5H_9 \cdot 2(CH_3)_3N$ was slowly heated to temperatures above 100° in the presence of excess trimethylamine, again always producing $2(CH_3)_3NBH_3$ per B_5H_9 . In such experiments some of the excess amine became incorporated in the polymer, which exhibited thermoplastic behavior above 100° . This effect can be understood by assuming that a $(BH)_x$ polymer has a highly cross-linked chain structure of icosahedral or possibly octahedral boron hydride clumps, the interlinking of which can be decreased by amine-complex bonding to boron. Thus it would be possible to have a rubber-like chain instead of a stiff network. Polymers of similar composition were obtained earlier from the reaction of tetraborane with trimethylamine,³ although their physical character was not closely observed.

Such aminated boron hydride polymers, ranging from three to five BH units per amine molecule, can neither absorb nor lose amine on heating; indeed one sample was heated *in vacuo* to 400° , losing methane rather than trimethylamine, and forming a very difficultly volatile sublimate. This product would seem to be a dimethylaminopolyborane, a member of a new class of compounds whose prototype was obtained by experiments using dimethylamine.

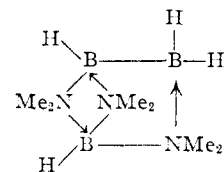
The reaction of pentaborane with dimethylamine present in excess led only to the previously known aminoboron hydrides,⁴ but the reaction with a carefully limited proportion of this amine produced new volatile products wherein direct B-B bonding can be recognized. The yields of such products were improved by the use of the compounds $(CH_3)_2NBH_2$ and $[(CH_3)_2N]_2BH$ with pentaborane, for these pick up the BH_3 group to form $(CH_3)_2NB_2H_5$ and $(CH_3)_2NBH_2$, respectively⁴; and they can react with the B_3H_3 remainder with no net destruction of B-B bonding. The latter aspect can be recognized by comparing with aminolysis or hydride-transfer reactions the attack by an aminoborane upon the B_3H_3 remainder, thus



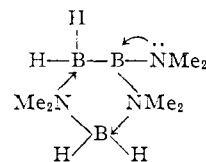
(3) A. B. Burg and F. C. A. Stone, *THIS JOURNAL*, **75**, 228 (1953).

(4) A. B. Burg and C. L. Randolph, Jr., *ibid.*, **73**, 953 (1951), and earlier papers there cited.

A major product of such reactions was shown by analyses and a molecular weight determination to have the molecular formula $[(CH_3)_2N]_3B_3H_4$. It is a slightly volatile white solid, reasonably stable in the open air, and on heating to 300° , both thermally stable and unreactive toward hydrogen. The only molecular structure which seems both appropriate and sterically possible would be



wherein the two nitrogen atoms in the B_2N_2 ring would be in a line perpendicular to the plane of the B_3N chain. However, it seems necessary to find some explanation for the failure of the substance to react with diborane at 90° , as happens when the B_2N_2B ring dimer of $(CH_3)_2NBH_2$ is converted to $(CH_3)_2NB_2H_5$. But this difficulty would seem greater if one considered the conceivable alternative pattern



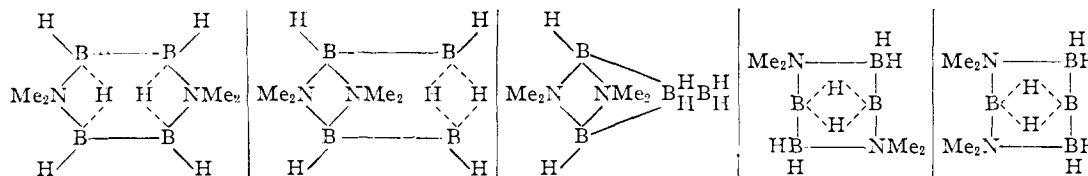
In any case a formal name for this new compound would be cumbersome; hence in this paper it will be called simply the triaminotriborane, the -ane ending being adopted in view of the probable analogy to a hydrocarbon somewhat like pinane.

Another product of the aminoborane-pentaborane reaction is a somewhat less stable and more reactive liquid, slightly more volatile than the solid triaminotriborane. Its molecular formula was determined as $[(CH_3)_2N]_2B_4H_6$. If it be assumed that B and N always are four-coördinate in such compounds, the following five structural patterns might be considered.

The last three of these structures are sterically not favored, and the second would be less stable than the first, by analogy to the reaction of $[(CH_3)_2NBH_2]_2$ with B_2H_6 to form $(CH_3)_2NB_2H_5$. However, the first pattern might well be less stable than still another form wherein the B-B bonds are along opposite edges of a B_4 -tetrahedron. A second pair of opposite edges would be $B^H B$ bridged and the third pair of edges would be $B^N B$ bridged. A final decision on the structure must come from physical methods, for which it will be necessary to find a way to make larger samples. Hereinafter the compound will be designated as diamino-bis-diborane.

Experimental

The Reaction of Pentaborane with Trimethylamine.—In the 1937 experiment, 0.504 mmole of B_5H_9 and 13.12 mmoles of $(CH_3)_3N$ were allowed to react during 10 days at -79° . Then 12.05 mmoles of the amine could be recovered by distillation at -79° , leaving a loose white solid of average composition $B_5H_9 \cdot 2.12(CH_3)_3N$. This was warmed to room temperature under high vacuum, with the vapors led through a fractional-condensation train, and finally with warming to 66° . The volatile products were 0.290 mmole



of B₅H₉, 0.629 mmole of (CH₃)₃N and 0.361 mmole of (CH₃)₂NBH₃. Thus 58% of the 2:1 adduct was recovered as the original reactants, while the remainder was partially converted to (CH₃)₂NBH₃. The glassy brilliant-yellow residue next was heated for 8 hr. at 100°, in an atmosphere of 3.00 mmoles of amine, converting 0.063 mmole of this to (CH₃)₂NBH₃ and leaving a nearly-white residue of composition (BH)₂ with possibly as much as 3 mole % of amine content. The yield of (CH₃)₂NBH₃ was 1.98 per unrecovered B₅H₉. The polymer did not react further with trimethylamine, but aqueous hydrochloric acid attacked it slightly, giving off 0.09 mmole of hydrogen, and a sodium hydroxide solution first turned it slightly brown, and then white, without appreciable dissolving.

In more recent experiments the 2:1 adduct was formed in 50 ml. sealed tubes at -78° and simply allowed to warm slowly to room temperature or higher, usually in the presence of excess amine. At intervals in the course of heating to higher temperatures, the volatile products were removed and determined, and the residue was heated further in the resealed tube or with connection to an automatic Sprengel pump for collection of non-condensable gases. The results of four such experiments are shown in Table I.

In all of these experiments the initial heating (usually slowly, to 100°) gave a polymer-residue having a B:H ratio near to 1:1 and this changed very little on heating up to the 200° range. When there was plenty of amine, this initial heating always produced very nearly 2(CH₃)₂NBH₃ per B₅H₉. However in the exceptional expt. 2 the excess

Formation of Aminoboron Compounds from Pentaborane.—The experiments on the reactions of B₅H₉ with dimethylamine and with dimethylaminoboron compounds are summarized in Table II. Experiment 1 was done in a vertical tube having an internal cold finger at 0° and attached to the high-vacuum manifold. The others were done in sealed tubes which could be opened to the vacuum system for isolation and measurement of the volatile products and possible reheatings of the residues with volatile materials in the resealed tubes. It is apparent that the best conversion of B₅H₉ to the triaminotriborane occurred in expt. 5, wherein more than two-thirds of the boron was recovered in that form. The sixth run did nearly as well, and gave also some of the diamino-bis-diborane—a product which could not be expected from expt. 5 because it has been found to react with [(CH₃)₂N]₂BH. Methods for obtaining high yields of this diamino-bis-diborane are yet to be found.

Physical Properties of the Aminopolyboranes.—The triaminotriborane and the diamino-bis-diborane apparently have nearly the same normal boiling point, but their vapor tensions at room temperature or lower are so different as to permit easy separation under high vacuum. The triaminotriborane was purified by fractional condensation at 15–20°, and the diamino-bis-diborane was isolated from it by a slow distillation from a tube at 0°.

The triaminotriborane melted sharply at 95.0°, and the vapor tensions of the solid, shown in Table III, determined the equation $\log_{10} p_{\text{mm.}} = 11.424 - 3723/T$. Assuming a normal value of the Trouton constant, the normal b.p.

TABLE I
THE PENTABORANE-TRIMETHYLAMINE REACTION

Expt. no.	Reactants (mmoles)		Latest heat treatment	Volatile components (mmoles)		Composition of residue (mmoles)			
	B ₅ H ₉	(CH ₃) ₃ N		(CH ₃) ₃ N	(CH ₃) ₂ NBH ₃	H ₂	B	H	(CH ₃) ₂ N
1	0.988	4.149	30 min., 165°	1.446	1.936	0.098	3.003	2.887	0.769
2	1.013	2.681	10 min., 210°	0.576	1.363	.569	3.703	3.890	0.742
3	1.630	5.684	10 min., 200°	1.031	3.165	.140	4.985	4.895	1.488
4	1.542	11.29	70 hr., 208°	7.11	3.11 ^a	.127	4.60	4.29	1.07
			2 hr., vac. 210°	7.14	3.27 ^a	.146	4.44	3.77	0.86
			2 hr., vac., 290°	7.24	3.28 ^a	.525	4.43	2.63	.75
			3 hr., vac. → 402°	7.25	3.28 ^a	1.087	4.43	1.04	.74

^a Includes 0.29 mmole converted to (CH₃)₂NBH₂ and CH₄; the next-to-last heating of the residue gave 0.36 mmole of CH₄ and no other volatile products, and the final heating gave 0.46 mmole more CH₄; total CH₄ from residue, 1.11 mmoles.

amine had been removed at -78°, establishing the composition of the adduct as 2.04(CH₃)₃N per B₅H₉, and then the initial heating of this adduct (24 hr. in a sealed tube at 102°) gave only 1.3(CH₃)₂NBH₃ per B₅H₉, and 0.494 mmole of H₂ was produced. Thus it appears that the forming polymer competes with BH₂ groups for possession of the amine; but once formed, the polymer does not absorb any significant proportion of amine after being formed with a low amine content. And from expt. 4 it is apparent that the amine cannot be removed from its incorporation in the polymer by vacuum heating; instead there is a loss of methane to produce some (CH₃)₂NBH₂ and a far less volatile sublimate, presumably formed at the expense of the N-CH₃ and B-H linkages. Attempts to analyze this sublimate have not been successful, and there is no evidence that it is a pure substance.

Experiment 1 was of special interest because the polymer showed plastic character in the range 100–165°: in losing traces of volatile products *in vacuo* it slowly formed large bubbles which slowly collapsed and reformed in the manner of bubble gum. At room temperature the material was a brittle solid, very slightly yellow, and apparently unaffected by the open air. Thermoplastic behavior in such materials may be critically dependent upon their amine content, for in expt. 4 (B:N ratio, 5.16) the only such effect was the temporary appearance of a fine foam during the vacuum heating to 200°.

would be estimated as 220° and the heat of fusion approximately 6750 cal./mole. A preliminary crystal-structure determination by Professor Jerry Donohue showed orthorhombic symmetry and a density of 0.945 for a unit cell containing four molecules (*a*₀ = 8.03 Å.; *b*₀ = 11.14 Å.; *c*₀ = 13.22 Å., all ±0.8%). A complete structure determination from the X-ray data would be very time-consuming, but it could be argued from the Weissenberg photographs that the space group could be either C_{2h}²-Pbc or D_{2h}²-Pbcm—the latter affording the possibility of a mirror-plane in accord with the preferred molecular pattern.

The melting point of the diamino-bis-diborane was uncertain, for the transition from a glassy state to a viscous oil was hard to observe. There seemed to be melting in the range 11–15°. The vapor tensions of the liquid, shown in Table IV, determined the equation $\log_{10} p_{\text{mm.}} = 8.070 - 2475/T$. This would imply a normal boiling point near 203°—probably lower than the true value, since the Trouton constant has the high value 23.8 cal./deg. mole.

Proofs of Formulas.—The molecular weights of the new aminoboron hydrides were determined from their gas densities: for the triaminotriborane the result was 169.3 (calcd., 168.7); for the diamino-bis-diborane, 140 ± 2 (calcd., 137.5). Each of these compounds was analyzed by heating with methanol and a measured quantity of HCl, in a sealed glass tube at 80–90°. The resulting H₂ was Sprengel-pumped into a gas-measuring tube. Methyl chloride, representing

TABLE II
 REACTIONS OF AMINO COMPOUNDS WITH B₅H₉

Expt. no.	B ₅ H ₉	Reactants (mmoles)	Heating conditions	Volatile remainders and products (mmoles)					
				H ₂	(CH ₃) ₂ -NB ₂ H ₅	(CH ₃) ₂ -NBH ₂	[(CH ₃) ₂ N] ₂ BH	[(CH ₃) ₂ N] ₃ B ₃ H ₄	[(CH ₃) ₂ -N] ₂ B ₄ H ₆
1	11.13	49.34 (CH ₃) ₂ NH	See below	30.8	2.3	21.7	0.38	uncertain	
2	5.76	17.20 (CH ₃) ₂ NH	160°, 72 hr.	4.5	8.3	3.4	nil.	0.57	0.10
3	4.46	13.38 (CH ₃) ₂ NH	150°, 2 hr.	4.0	5.8	0.5	nil.	0.14	nil.
4	1.42	3.03 (CH ₃) ₂ NBH ₂	100°, 14 hr.	0.06	0.37	2.22	0.02	present 0.20	
5	1.41	3.95 [(CH ₃) ₂ N] ₂ BH	111°, 94 hr.	.15	.03	1.62	0.01	1.57	nil.
		+1.71 [(CH ₃) ₂ N] ₂ BH	112°, 282 hr.	.003	1.62	trace	..
6	7.384	36.23 (CH ₃) ₂ NBH ₂	95°, 21 hr.	3.12	7.91	5.77 ^a	nil.	6.58	0.64
		+5.77 (CH ₃) ₂ NBH ₂	133°, 96 hr.	1.5	..	1.74	..	1.50	..

^a Same sample re-used on the glassy residue. Expt. 1 (cold-finger apparatus): first, 15 hr. at 95–100° with frequent removal of volatile products; finally 20 min. at 150°; cold-finger always at 0°.

TABLE III

VAPOR TENSIONS OF SOLID [(CH₃)₂N]₂B₃H₄

t (°C.)	Obsd. p _{mm}	Calcd. p _{mm}
43.3	0.41	0.46
54.0	1.10	1.11
69.0	3.52	3.49
80.2	7.76	7.73
87.8	12.6	12.9
90.9	15.66	15.77
97.3	24.0 (1.)	23.7 (s.)

TABLE IV

VAPOR TENSIONS OF LIQUID [(CH₃)₂N]₂B₄H₆

t (°C.)	Obsd. p _{mm}	Calcd. p _{mm}
8.3	0.18	0.19
13.1	0.27	.27
27.0	.69	.68
33.3	1.02	1.00
36.4	1.20	1.21
51.3	2.82	2.82
66.0	6.04	6.03
73.1	8.48	8.52
82.1	12.92	12.92
86.5	15.6	15.7

the excess of the HCl over the amine, was isolated and measured. Methyl borate was distilled into water and titrated as the mannitol boro-spirane. In various experiments the amine hydrochloride was determined by direct weighing, by a micro-Kjeldahl analysis, by a chloride titration, or from the decrease of volatile chloride.

For the triaminotriborane, the two samples averaged 2.94 amine, 2.92 boron and 5.08 H₂ per molecule, no deviation being higher than 0.17 unit. These results uniquely require the equation [(CH₃)₂N]₃B₃H₄ + 9 CH₃OH + 3 HCl → 5H₂ + 3(CH₃O)₃B + 3(CH₃)₂NH₂Cl, for conformity to the observed molecular weight of the compound.

For the diamino-bis-diborane the ratio of amine to B to H₂ was 200:370:803. Boron usually runs a little low by the method here employed, for Pyrex glass is avoided and the formation of CH₃Cl from CH₃OH and the excess HCl produces a trace of water which interferes with the complete volatilization of boron as methyl borate. The results are consistent only with the equation [(CH₃)₂N]₂B₄H₆ + 12CH₃OH + 2HCl → 8H₂ + 4(CH₃O)₃B + 2(CH₃)₂NH₂Cl, requiring that the compound have two B-B links per molecule.

Chemical Behavior of the Aminopolyboranes.—The triaminotriborane [(CH₃)₂N]₃B₃H₄ proved to be inert toward water, acid, and methanol at room temperature, requiring

many hours of heating for the analytical break-down by acid methanolysis. With an equi-molar proportion of dimethylamine in a sealed tube it failed to react during 100 hr. at 180°; but after 102 hr. at 300° the mixture had formed mole-for-mole yields of H₂, (CH₃)₂NBH₂ and [(CH₃)₂N]₂BH, the remaining aminoborane material appearing as a colorless non-volatile film on the tube-wall. Unlike some other B-B compounds,⁵ the triaminotriborane is inert toward hydrogen, for a 0.245-mmole sample, after a series of heatings with 1.56 mmoles of H₂ (ending with 24 hr. at 300°) still had the same melting point. After 102 hr. at 360°, however, there was a considerable formation of a colorless oily film and the H₂ had increased to 1.88 mmoles. There was also 0.14 mmole of CH₄ and a trace of (CH₃)₂NBH₂. Thus it appears that the triaminotriborane is stable at 300°, but at 360° is converted to a still more stable material—probably a high polymer.

With 0.141 mmole of diborane, a 0.128-mmole sample of the triaminotriborane showed no effect of heating in a space of 130 ml. for 3 hr. at 99°; the recovery of diborane was 0.137 mmole. This result indicates that the nitrogen atoms are very firmly bonded in a four-coordinate situation, contrasting with the comparatively reactive state of nitrogen in [(CH₃)₂NBH₂]₂.

Little is known of the chemistry of the diamino-bis-diborane, for the samples so far have been too small for extensive study; but it does seem to be considerably less stable and more reactive than the triaminotriborane. Its presumed structure would permit the possibility of conversion to the triaminotriborane by reaction with [(CH₃)₂N]₂BH but when 0.763 mmole of this was heated with 0.348 mmole of the diamino-bis-diborane for 5 hr. at 95°, only 2.2 mg. (0.013 mmole) of the triaminotriborane could be found, the main yield being a yellow resinous solid.

Such a yellow resinous solid was the chief by-product of the preparation of the triaminotriborane in expts. 5 and 6, Table II. From the reaction-balance of expt. 6 (first part), its empirical formula would be approximately [(CH₃)₂N]₄-B₁₁H₁₈. As indicated in Table II, its further treatment with the bis-aminoborane gave a further yield of dimethylaminoborane and the triaminotriborane. At various points in this study trace amounts of very difficultly volatile aminoborane hydrides were noticed, indicating that a considerable variety of such compounds, probably merging into polymeric types, can be produced.

Acknowledgment.—The generous support of this work by the Office of Naval Research is gratefully acknowledged. Reproduction of this paper in whole or in part is permitted for any purpose of the United States Government.

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(5) G. Urry, T. Wartik, R. E. Moore and H. I. Schlesinger, THIS JOURNAL, **76**, 5293 (1954).