THE BORON HYDRIDES AND RELATED COMPOUNDS

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The boron hydrides owe their special position among inorganic compounds both to the variety and interest of their reactions and to the structural problems which they present. The reactions of the hydrides are described in the first, and the structural problems in the second part of this article. The more recent contributions to the subject are given special prominence throughout : this is because the classical work of A. Stock and his co-workers, most of which was done before 1930, has been admirably summarised in his book,[1] which also described in detail the special vacuum technique still essential in all work in this field.

Methods of Preparation.—The hydrides of boron were first prepared by decomposing salt-like borides with acids. Stock used magnesium boride and hydrochloric acid, or better, phosphoric acid, and obtained a mixture, the chief component of which was tetraborane, B_4H_{10}. Admixed with this were smaller proportions of the stable pentaborane, B_5H_9, hexaborane, B_6H_{10}, and decaborane, $B_{10}H_{14}$. The yields were very low and the separation of the products from one another and from impurities (*e.g.*, silicon hydrides) was difficult. Diborane, B_2H_6, which is rapidly decomposed by water and is therefore not formed in the acid decomposition of borides, was prepared by the thermal decomposition of tetraborane.

A greatly improved preparative method yielding diborane directly was described by A. B. Burg and H. I. Schlesinger.[2] Boron trichloride (or bromide) mixed with excess of hydrogen was streamed at a pressure of 10 mm. through an electrical discharge, yielding a mixture of monochlorodiborane (or monobromodiborane) mixed with a small amount of diborane, hydrogen chloride, or bromide and unchanged boron halide and hydrogen. The haloborane admixed with boron halide was isolated and decomposed at room temperature, forming diborane (*e.g.*, $6B_2H_5Br = 5B_2H_6 + 2BBr_3$).

A new method of preparing diborane from boron trichloride [3] is reported as giving an almost theoretical yield. It is based on the reaction between lithium aluminium hydride (see below) and boron trichloride, which occurs according to the equation $3LiAlH_4 + 4BCl_3 = 3LiCl + 3AlCl_3 + 2B_2H_6$. The lithium aluminium hydride is dissolved in ether and cooled in an evacuated vessel by means of liquid nitrogen. The boron halide, dissolved in ether, is distilled in a vacuum on to the cooled lithium compound, reaction,

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[1] " Hydrides of Boron and Silicon ", Oxford University Press, 1933.

[2] *J. Amer. Chem. Soc.*, 1931, **53**, 4321.

[3] A. E. Finholt, A. C. Bond, junr., and H. I. Schlesinger, *ibid.*, 1947, **69**, 1199.

with liberation of diborane, taking place on allowing the reactants to melt and come to room temperature. This method and the electrical discharge method both yield diborane, and it is important that there should be methods for converting it into the other hydrides, the formulæ, melting points, and boiling points of which are shown in Table I.[4] These six volatile hydrides are the only ones known with certainty at present. Several non-volatile hydrides, which were described by Stock [5] and have been little studied since, appear to have a lower H : B ratio than have the volatile compounds.

TABLE I

Physical constants of the boranes

Name.	Formula.	M.p.	B.p.
Diborane	B_2H_6	– 165·5°	– 92·5°
Tetraborane	B_4H_{10}	– 120	18
Stable pentaborane	B_5H_9	– 46·6	48
Unstable pentaborane . . .	B_5H_{11}	– 123	63
Hexaborane	B_6H_{10}	– 65	(V.p. at 0°, 7·2 mm.)
Decaborane	$B_{10}H_{14}$	99·7	213

Stock showed that when tetraborane was heated to 100° in glass vessels it decomposed in part, forming diborane with a small proportion of the unstable pentaborane and of decaborane. More recent work has shown that a series of reversible reactions occurs between the hydrides and that by carefully controlling the conditions a reasonable yield of any member of the series (except hexaborane) may be obtained. Hexaborane is best prepared by Stock's method. As an example of the interconversion, the preparation of the stable pentaborane, B_5H_9, from diborane may be described. Diborane at an initial pressure of 120 mm. is circulated by means of a pump through a hot tube at 300°, the less volatile product being removed by condensation as it is formed. A high proportion of the stable pentaborane, together with some B_5H_{11}, is collected.[6] The conditions of these interconversions have been arrived at empirically and there is as yet no definite information as to the reaction mechanism, though free radicals are presumably involved.

Reactions.—The boron hydrides considered as a group have certain reactions in common. For instance, all are decomposed quantitatively at a red heat into boron and hydrogen ; all are hydrolysed, though at widely different rates ; diborane, for example, is instantly decomposed by water ($B_2H_6 + 6H_2O = 2H_3BO_3 + 6H_2$), whereas tetraborane and the unstable pentaborane are fairly readily hydrolysed, but complete decomposition of the stable pentaborane, hexaborane, and decaborane takes place only on prolonged heating with water. The resistance to hydrolysis does not

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[4] These data are taken from a review by H. I. Schlesinger and A. B. Burg (*Chem. Rev.*, 1942, **31**, 1).

[5] *Op. cit.*, p. 87.

[6] A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1933, **55**, 4009 ; see also A. Stock and W. Mathing, *Ber.*, 1936, **69**, 1456.

parallel the thermal stability, since the least stable on heating are the unstable pentaborane, B_5H_{11}, tetraborane, and hexaborane. The reactions of the hydrides with oxygen occur readily and will almost certainly be found to show the characteristics of branching-chain reactions. Diborane does not inflame spontaneously in air at atmospheric pressure, but, as in the case of the silicon hydrides, the higher members of the series appear to be more inflammable.

Halogenation of the boron hydrides may be effected by reaction with either a free halogen or a halogen halide, most of the experimental work on this group of reactions being due to Stock and his co-workers.[7] Other substitution reactions have been studied in the greatest detail in the case of diborane, and have an important bearing on structural problems. Thus, four methyl-substituted derivatives of diborane were formed in the reaction between diborane and trimethylboron at room temperature.[8] Even with a large excess of boron alkyl, no penta- or hexa-methyldiborane was obtained. The four derivatives, all of which were volatile, were characterised by vapour-density determinations, analysis, and hydrolysis to known methylboric acids [*e.g.*, $BHMe_2{\cdot}BH_2Me \rightarrow Me_2B{\cdot}OH + Me{\cdot}B(OH)_2$]. The four derivatives were found to be 1-methyl-, 1 : 1-dimethyl-, 1 : 1 : 2-trimethyl-, and 1 : 1 : 2 : 2-tetramethyl-diborane. Other alkyl boranes were prepared by an analogous reaction. The symmetrical dimethylborane is not formed in the above reaction and must be prepared by reaction of the monomethyl derivative with dimethyl ether, whereupon the borine radical, BH_3, forms the compound dimethyl ether–borine, Me_2O,BH_3, leaving two methylborine radicals, which do not combine with ether, to combine together forming the symmetrical dimethyldiborane. These alkylated diboranes resemble the halogenated diboranes in the ease with which they disproportionate : for instance, monomethyldiborane changes rapidly at room temperature into diborane and trimethylboron, just as the monochloro-derivative changes into diborane and boron trichloride.

The reaction of diborane with methyl alcohol is different, in that fission of the molecule into two parts occurs with formation of dimethoxyborine, $BH(OMe)_2$, which also disproportionates readily.[9] No volatile monomethoxy-derivative is formed in this reaction. Acetaldehyde reacts in a somewhat similar way forming a diethoxyborine

$$[4CH_3{\cdot}CHO + B_2H_6 = 2BH(OEt)_2],$$

and with acetone the main product is di*iso*propylborine

$$[4COMe_2 + B_2H_6 = 2BH(OPr^i)_2].$$

The borine radical, BH_3, which has been referred to already in several connections, is incapable of an independent existence in the sense of its forming a stable molecule in equilibrium with the dimeric form B_2H_6. A number of different substances do, however, react with diborane yielding products in which a molecule containing a donor group is co-ordinated

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[7] A. Stock, *op. cit.*

[8] H. I. Schlesinger and A. O. Walker, *J. Amer. Chem. Soc.*, 1935, **57**, 621.

[9] A. B. Burg and H. I. Schlesinger, *ibid.*, 1933, **55**, 4020.

with the boron (in BH_3). One of the simplest instances of this occurs in the reaction between diborane and carbon monoxide at pressures of the order of 20 atm., wherein the equilibrium $B_2H_6 + 2CO \rightleftharpoons 2H_3B,CO$ becomes established fairly rapidly at 100°.[10] If the equilibrium mixture is cooled quickly the compound borine carbonyl, H_3B,CO (b.p. – 64°), may be isolated. Borine carbonyl reacts with ammonia forming a solid ammoniate, $BH_3,CO,2NH_3$, which appears from its reaction with sodium in liquid ammonia solution to contain two NH_4^+ ions. With trimethylamine, carbon monoxide is displaced and a new co-ordination derivative, BH_3,NMe_3, produced. Diborane reacts with trimethylamine to give the same derivative, trimethylamine–borine, which is much more stable than the carbonyl. Methylated diboranes give exactly analogous reactions with trimethylamine,[11] the products (BH_2Me,NMe_3, $BHMe_2,NMe_3$, BMe_3,NMe_3) becoming more stable with progressive substitution of the borine radical. The compound BMe_3,NMe_3, prepared from trimethylboron and a slight excess of trimethylamine, is sufficiently stable to be sublimed in a vacuum.

Dimethyl ether–borine, which is formed in the low-temperature reaction between dimethyl ether and diborane, is similarly constituted, though it is much less stable than the trimethylamine derivative. A further reaction of the same type is that between methyl cyanide and diborane. The product $CH_3{\cdot}CN,BH_3$ is a solid, from which methyl cyanide is set free by trimethylamine, which forms the more stable trimethylamine–borine.

Reaction with ammonia. The reactions of the boron hydrides with ammonia were studied in considerable detail by Stock. A number of derivatives were isolated, and have been further characterised by later workers. The formulæ of the ammoniates described by Stock are given in Table II. These compounds are salt-like solids, the derivatives of B_2H_6 and B_5H_9 being particularly stable. All are formed by treating the hydride with liquid ammonia and distilling off the excess, and the existence of such salt-like derivatives has been taken as evidence for the " acidic " character in the hydrides. This point has been followed up mainly on diborane ammoniate, which forms a conducting solution in liquid ammonia at – 75°.

TABLE II

Ammoniates of the boron hydrides

Hydride.	Compound formed.	Stability.
B_2H_6	$B_2H_6,2NH_3$	Stable
B_4H_{10}	$B_4H_{10},4NH_3$	Loses H_2 and NH_3 at room temp.
B_5H_9	$B_5H_9,4NH_3$	Stable
B_5H_{11}	$B_5H_{11},2{\cdot}7NH_3$	Products depend on reaction conditions
B_6H_{10}	Not known	
$B_{10}H_{14}$	$B_{10}H_{14},6NH_3$	All NH_3 lost at room temp.

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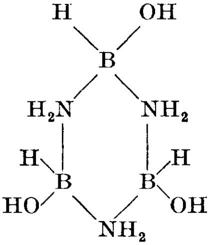
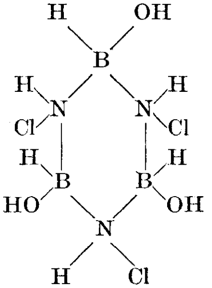
[10] *Idem, ibid.*, 1937, **59**, 780.

[11] H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *ibid.*, 1939, **61**, 1078.

The earlier formulation of the ammoniate of diborane as the salt $(NH_4)_2B_2H_4$ is not, however, generally accepted, since H. I. Schlesinger and A. B. Burg's observation that 1 g.-mol. of the *pure* ammoniate dissolved in liquid ammonia at − 77° reacts with 1 equiv. of sodium, liberating 1 equiv. of hydrogen. When the ammoniate is not pure, further hydrogen is liberated slowly in secondary reactions. It thus appears that the ammoniate is a mono-ammonium salt, the probable constitution of which is $NH_4^+(H_3BNH_2BH_3)^-$. Reaction of excess of diborane with the ammoniate at 88° gives a second compound B_2H_7N (b.p. 76·2°) which is believed to have the constitution $BH_2NH_2BH_3$.

The ammoniates of B_2H_6, B_4H_{10}, and B_5H_9 undergo a remarkable reaction when heated for several hours at 200°. Hydrogen is set free and a volatile substance of the molecular formula $B_3N_3H_6$ remains. The same compound (borazole) is formed when diborane and ammonia are heated to 200°. It has a six-membered ring structure in which BH and NH groups alternate, and from which either addition or substitution products may be prepared. With excess of ice-cold water, for example, borazole yields $B_3N_3H_6,3H_2O$, to which Stock attributed the structure (I). With excess of anhydrous hydrogen chloride the trihydrate forms $B_3N_3H_3Cl_3,3H_2O$ (II), whilst borazole itself with hydrogen chloride at room temperature forms $B_3N_3H_9Cl_3$ (III).


(I.)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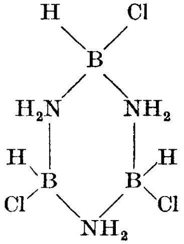
(III.)

If in place of diborane a methylborane is used in the reaction with ammonia, compounds analogous to the ammoniates of diborane are again formed.[12] These decompose at 180—200° forming aminodimethylborine, $BMe_2{\cdot}NH_2$, and a mixture of $B_3N_3H_6$, $MeB_3N_3H_5$, $Me_2B_3N_3H_4$, and $Me_3B_3N_3H_3$, the last three compounds being *B*-methyl derivatives of borazole. These compounds are also obtained by heating the alkyldiborane with ammonia at 180—200°. Analogous *N*-methylborazoles are formed when mixtures of diborane, ammonia, and methylamine are heated at 200°.[13] In this case the compounds *N*-$MeB_3N_3H_5$ (b.p. 84°), *NN'*-$Me_2B_3N_3H_4$ (b.p. 108°), and *NN'N''*-$Me_3B_3N_3H_3$ (b.p. 134°) have been characterised.

Phosphine reacts with diborane to form the compound $B_2H_6,2PH_3$ which, though it shows some analogy to $B_2H_6,2NH_3$, is considerably less

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[12] H. I. Schlesinger, L. Horvitz, and A. B. Burg, *J. Amer. Chem. Soc.*, 1936, **58**, 409.

[13] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *ibid.*, 1938, **60**, 1296.

stable.[14] Since phosphonium salts evolve phosphine when dissolved in liquid ammonia whereas this compound does not do so, there is some doubt if it can be formulated as $PH_4(H_3B{\cdot}PH_2{\cdot}BH_3)$. Trimethylamine, however, displaces phosphine at − 40°, forming trimethylamine–borine. The phosphine derivative of diborane also reacts at − 80° with hydrogen chloride, forming PH_3,BH_2Cl, $PH_3,BHCl_2$, and PH_3,BCl_3.

Metal Derivatives.—Among the recent advances in the chemistry of the boron hydrides, the discovery of metal derivatives is one of the most striking. In this connection Stock's observations on the reaction of diborane with sodium, potassium, and calcium amalgams may first be recalled, since in each case metal addition compounds result.[15] Thus with sodium amalgams the reaction is : $2Na(Hg) + B_2H_6 = Na_2B_2H_6 + (Hg)$.

These metal derivatives are non-volatile, insoluble in organic solvents, and are decomposed by water. The simple formula (*e.g.*, $NaBH_3$) is excluded by the fact that the compounds are diamagnetic. The stability and lack of volatility suggest an ionic structure, which is reasonable since diborane, on gaining two electrons to form a doubly charged negative ion, acquires a stable saturated electronic structure similar to that of ethane. Similar but less stable compounds ($M^{I}_{2}B_4H_{10}$ and $M^{I}_{2}B_5H_9$) are formed by the reaction of alkali-metal amalgams with tetraborane and the stable pentaborane, B_5H_9. All of these salts react with hydrogen halides more readily than does diborane itself; with hydrogen bromide at room temperature, for example, the reaction $K_2B_2H_6 + 4HBr = K_2B_2H_2Br_4 + 4H_2$ goes to completion.

The discovery of a second group of metal boron hydride derivatives, the borohydrides, by Burg and Schlesinger represents perhaps the most important advance in the field since the hydrides themselves were isolated and characterised. Three only of these compounds, the borohydrides of lithium, beryllium, and aluminium, have as yet been fully described.[16] All are obtained by the reaction of diborane with the alkyl compound of the metal. In the case of lithium borohydride, for example, the reaction, which occurs between diborane and ethyl-lithium at room temperature, is represented by the equation $2LiC_2H_5 + 2B_2H_6 = 2LiBH_4 + (C_2H_5)_2B_2H_4$. The physical properties of these three derivatives, summarised in Table III,

TABLE III

Melting and boiling points of borohydrides of Li, Be, *and* Al

Compound.	M.p.	B.p.
$LiBH_4$	275° (decomp.)	—
$Be(BH_4)_2$	> 123	91·3°
$Al(BH_4)_3$	− 65·4	44·5
B_2H_6	− 165·5	− 92·5

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[14] E. L. Gamble and P. Gilmont, *ibid.*, 1940, **62**, 717.

[15] A. Stock, W. Sutterlin, and F. Kurzen, *Z. anorg. Chem.*, 1935, **225**, 225.

[16] *J. Amer. Chem. Soc.*, 1940, **62**, 3425 ; H. I. Schlesinger and H. C. Brown, *ibid.*, p. 3429 ; H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *ibid.*, 1939, **61**, 536, 3421.

show an increase in volatility in passing from lithium to aluminium. The lithium compound is a salt, $Li^+BH_4^-$, and this character is clearly lacking in the volatile aluminium derivative.

The mechanism of formation of these borohydrides is complex, and various intermediates have been isolated. Reaction at 95° between diborane and dimethylberyllium, for example, first yields a colourless non-volatile liquid which then forms a white volatile solid, $CH_3{\cdot}BeBH_4$, methylberyllium borohydride. This in turn undergoes further reaction with diborane to form beryllium borohydride. In the final stage of the reaction a non-volatile by-product with the empirical formula $BeBH_5$ is also produced and it is reported [17] that diborane and dimethylzinc yield a similar product ($ZnBH_5$).

The reactions of these borohydrides have been studied in some detail. The lithium compound is stable in dry air, but the beryllium and the aluminium compounds inflame. All are readily hydrolysed, and react with hydrogen chloride forming hydrogen (1 mole per g.-atom of B), diborane, and the metal chloride. Lithium borohydride with methyl alcohol forms lithium methoxide and trimethyl borate, but lithium boromethoxide, $LiB(OCH_3)_4$, may be isolated as an intermediate. It will be recalled that diborane itself forms similar methoxy-derivatives. A further reaction of very great interest is that between aluminium borohydride and ethyllithium in benzene solution, leading to formation of the salt-like lithium borohydride: $6LiC_2H_5 + 2Al(BH_4)_3 = 6LiBH_4 + Al_2(C_2H_5)_6$. Lithium borohydride differs from the borohydrides of beryllium and aluminium in being inert towards trimethylamine. The beryllium and the aluminium compound first form addition products [*e.g.*, $Be(BH_4)_2,N(CH_3)_3$], and on further reaction yield trimethylamine–borine, $BH_3,N(CH_3)_3$, one molecule of which is formed per molecule of borohydride. The borine radical is removed more easily from the aluminium than from the beryllium compound, and is not removable from the ionic lithium compound.

Lithium borohydride reacts quantitatively with boron trifluoride [preferably in the form of the ethyl ether complex, $(C_2H_5)_2O,BF_3$] according to the equation $3LiBH_4 + BF_3 = 2B_2H_6 + 3LiF$. This reaction gives a ready way of generating diborane, though, since the borohydride can only be prepared from diborane, it is less convenient than the method already described, using lithium aluminium hydride.

Research so far published on other borohydrides shows that the gallium compound is relatively unstable.[18] On treating trimethylgallium with diborane at room temperature, no reaction took place for a time: then there was a sudden deposition of a film of gallium, accompanied by formation of free hydrogen. It was suggested that gallium borohydride was formed as an intermediate in this reaction: thus,

$$2(CH_3)_3Ga + 9B_2H_6 = 2Ga(BH_4)_3 + 6CH_3{\cdot}B_2H_5$$
$$2Ga(BH_4)_3 = 2Ga + 3B_2H_6 + 3H_2$$

The same reactants at − 45° gave practically pure dimethylgallium boro-

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[17] H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, 1942, **31,** 36.

[18] H. I. Schlesinger, H. C. Brown, and G. W. Schaeffer, *J. Amer. Chem. Soc.*, 1943, **65,** 1786.

hydride (extrapolated b.p. 92°), which decomposed slowly at room temperature : $2(CH_3)_3Ga + 3B_2H_6 = 2(CH_3)_2GaBH_4 + 2CH_3{\cdot}B_2H_5$.

The abnormal electronic structure of the boron hydrides, which is discussed fully below, at once raises the question of whether the remaining Group III elements, which have similar structures, also form hydrides. The first of these compounds, gallium hydride, was prepared by E. Wiberg and T. Johannsen.[19] Hydrogen and trimethylgallium, passed through a glow discharge, gave among other products the comparatively non-volatile compound tetramethylgallium hydride, $Me_4Ga_2H_2$. This reacted with trimethylamine forming the compound $GaMe_3,NMe_3$, which was taken as evidence of the unsymmetrical formula of the substituted hydride. This being so, the other product of the trimethylamine reaction should be the radical $GaH_2{\cdot}CH_3$, which, however, was found to disproportionate into trimethylgallium and digallane. In its final form this preparation of digallane was carried out with triethylamine in order to facilitate the working up of the products. It is represented by the equation :

$$3Ga_2H_2Me_4 + 4NEt_3 = Ga_2H_6 + 4GaMe_3,NEt_3.$$

The extrapolated b.p. of digallane is 139°. It begins to decompose into its elements at 130°.

The preparation of lithium aluminium hydride, aluminium hydride, and lithium gallium hydride, described very recently,[20] marks yet another advance in this fascinating subject. The first of these, as already mentioned, is formed by treating lithium hydride with an ethereal solution of aluminium chloride ($4LiH + AlCl_3 = LiAlH_4 + 3LiCl$). The structure of this compound has not yet been described in detail, but in view of the similar electron configurations of boron and aluminium, it is clearly the aluminium analogue of the borohydrides already described. The latter vary in type from the ionic lithium borohydride to the volatile covalent aluminium borohydride. Lithium borohydride and lithium aluminium hydride appear to be very similar. Both are stable in dry air. The borohydride decomposes at a temperature of 250—275°, whereas the aluminium compound decomposes at 125—150°, forming aluminium, hydrogen, and lithium hydride. Both compounds dissolve in diethyl ether, but lithium hydride is seven or eight times as soluble as, and to judge from the chemical behaviour, rather less polar than, the borohydride.

The most fully described reaction of lithium aluminium hydride is its strong reducing action. The conversion of boron trichloride into diborane in almost quantitative yield has already been mentioned. A similar reaction occurs with the tetrahalides of silicon, germanium, and tin and with alkyl silicon and tin halides. This has led, not only to a convenient method of preparing substances such as monogermane and monostannane, but also to the isolation of new alkyl-substituted hydrides[21]

$$(e.g., Me_2SnCl_2 + LiAlH_4 \longrightarrow LiCl + AlCl_3 + 2Me_2SnH_2).$$

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[19] *Angew. Chem.*, 1942, **55**, 38.

[20] A. E. Finholt, A. C. Bond, junr., and H. I. Schlesinger, *loc. cit.*

[21] A. E. Finholt, A. C. Bond, junr., K. E. Wilzbach, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 2692.

Lithium aluminium hydride also shows great promise as a reducing agent in organic chemistry. Reductions are carried out in ethereal solution at room temperature. The examples given below [22] illustrate the possibilities, the reagent being especially valuable for preparing unsaturated alcohols since it does not reduce double bonds.

Compound reduced.	Product.	Yield, %
n-Heptaldehyde	*n*-Heptyl alcohol	86
Crotonaldehyde	Crotyl alcohol	70
*cyclo*Pentanone	*cyclo*Pentanol	62
Ethyl adipate	Hexane-1 : 6-diol	83
Ethyl benzoate	Benzyl alcohol	90
Benzoyl chloride	Benzyl alcohol	72
*iso*Hexoyl chloride	*iso*Hexyl alcohol	95
Phthalic anhydride	Phthalyl alcohol	87

Lithium gallium hydride, $LiGaH_4$, has been prepared by the method used for the aluminium compound (*i.e.*, from lithium hydride and gallium chloride in ethereal solution). Indirect evidence has also been obtained of the existence of sodium and calcium aluminium hydrides.

An aluminium hydride, AlH_3, is formed when either lithium aluminium hydride or lithium hydride reacts with aluminium chloride in presence of ether: $3LiAlH_4 + AlCl_3 \rightarrow 4AlH_3 + 3LiCl$; $3LiH + AlCl_3 \rightarrow AlH_3 + 3LiCl$. The aluminium hydride remains in solution, but the latter is unstable and deposits a white solid with an H : Al ratio of 3 : 1 ; but ether cannot be completely removed from this without loss of hydrogen. O. Stecher and E. Wiberg [23] have also described a solid aluminium hydride formed by passing trimethylaluminium with a large excess of hydrogen through a glow discharge. From the complex mixture of products the volatile compounds $Al_2H_2Me_4$ and $Al_2H_3Me_3$ were isolated. Treatment of the non-volatile material with trimethylamine gave the compound AlH_3,NMe_3 which, when heated to 100—135°, formed a non-volatile aluminium hydride with the empirical formula AlH_3.

Structural Problems

The boron hydrides and related compounds offer a challenge to accepted theories of valency, since they are all *electron-deficient*, *i.e.*, they do not contain enough electrons in the valency shells of the constituent atoms to provide the minimum number of two-electron bonds needed to hold the molecule together. For the same reason the usual stereochemical analogues give little clue to the probable configurations of these molecules. No notable progress could be made until modern methods of structure determination were available, and even here the lack of a firm basis of comparison has caused some difficulty. It is therefore particularly important in dealing with these molecules to distinguish clearly between experimental evidence

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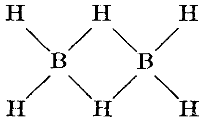
[22] R. F. Nystrom and W. G. Brown, *J. Amer. Chem. Soc.*, 1947, **69**, 1197.

[23] *Ber.*, 1942, **75**, 2003.

about nuclear configuration, and theoretical interpretation of the nature of the bonds involved.

The Configuration of Diborane and its Simple Derivatives.—The numerous structures which have been proposed for diborane can be reduced to three essential types, as follows : (*a*) Structures analogous to *ethane*, which may be written $H_3B{\cdot}BH_3$; a large proportion of investigators have assumed this type of structure as a starting point. (*b*) Structures in which two of the hydrogen atoms form a *bridge* uniting the two boron atoms, leading to a configuration resembling that of Al_2Cl_6, *i.e.*, (I), which we shall write as $H_2B(H_2)BH_2$. This kind of structure was originally suggested about twenty years ago [1], [2] and has recently been revived by several authors.[3–6]. (*c*) *Ionic* structures, *e.g.* $[H_2\bar{B}{=}\bar{B}H_2][H^+]_2$; when this type of structure was originally proposed [27] the configuration of the molecule was left unspecified, but we shall see later that it is most reasonable to assume that the two protons lie between the two boron atoms, like the hydrogen atoms in the bridge structure, and for the present we shall consider ionic structures together with bridge structures.[7]



(I.)

There are two essential differences between the ethane and the bridge model of diborane, which are independent of the exact nature of the links involved. (i) In the ethane model all the six hydrogen atoms are equivalent, while in the bridge model two of them differ from the other four in geometrical situation, and presumably also in binding. (ii) In the ethane model there should be effectively free rotation between the two ends of the molecule, while in the bridge model free rotation is not possible.

We shall now see how far different lines of evidence are able to discriminate between these possibilities for diborane and its simple derivatives.

Chemical evidence. Diborane itself is too versatile in its chemical reactions to provide much evidence as to its structure. In its reactions with electron-donors it shows a strong tendency to pass over into molecules with normal electron-pair bonds, but this does not point to any particular configuration in the original molecule. On the other hand, it is significant that it is possible to substitute not more than four hydrogen atoms in diborane by alkyl groups, giving products with not more than two alkyl groups on each boron atom. Similarly, trimethylboron is known, but not the di- or the mono-methyl derivative, which presumably dimerise to give tetra- and di-methylborane, respectively. This evidence strongly suggests that diborane and its alkyl derivatives contain two hydrogen atoms which play a special part in holding the molecule together. It may be pointed

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[1] W. Dilthey, *Z. angew. Chem.*, 1921, **34**, 596.

[2] A. F. Core, *Chem. and Ind.*, 1927, **5**, 642.

[3] B. V. Nekrassov, *J. Gen. Chem. U.R.S.S.*, 1940, **10**, 1021, 1156.

[4] J. K. Sirkin and M. E. Diatkina, *Acta Physicochim. U.R.S.S.*, 1941, **14**, 547.

[5] H. C. Longuet-Higgins and R. P. Bell, *J.*, 1943, 250.

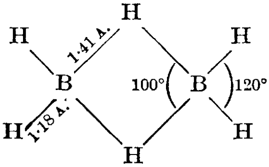
[6] F. Seel, *Z. Naturforsch.*, 1946, **1**, 146.

[7] K. S. Pitzer, *J. Amer. Chem. Soc.*, 1945, **67**, 1126.

out that the bridge structure predicts *cis-trans*-isomerism for some of the substituted diboranes, though this may be difficult to establish in view of the labile nature of these compounds.

Crystal structure. The work of H. Mark and E. Pohland [8] on solid diborane has often been quoted as evidence for the ethane structure. Actually, the *X*-ray observations give information only about the position of the boron atoms in the lattice, and the further data given are derived by assuming an ethane configuration. The crystal evidence thus provides no criterion for deciding between the two structures.

Electron diffraction. The diffraction of electrons by gaseous diborane has been studied by S. H. Bauer.[9] In principle these measurements should distinguish between the two models, but this is not so in practice, since they differ chiefly in the hydrogen–hydrogen distances, which make only a small contribution to the observed scattering. Bauer originally interpreted his data in terms of the ethane model, and derived the distances B–B = 1·86 A., B–H = 1·27 A. However, it was shown later [10, 11, 5] that the observed data are equally well represented by a bridge model with approximately the following dimensions:



where the four terminal hydrogen atoms are in a plane at right angles to the plane of the central ring. The electron-diffraction data for diborane itself are thus inconclusive, but it should be possible to obtain much more definite evidence by investigating alkyl-substituted diboranes. It has been recently reported [9a] that measurements on tetramethyldiborane show that the four methyl groups and the two boron atoms are coplanar, thus supporting the bridge model.

Vibrational spectrum. The Raman spectrum of liquid diborane has been studied by T. F. Anderson and A. B. Burg,[12] and the infra-red spectrum of the gas by F. Stitt [13] and by W. C. Price.[14] Their results provide strong evidence in favour of the bridge structure. The detailed arguments have been given by R. P. Bell and H. C. Longuet-Higgins,[15] and only the main points will be mentioned here. The observed spectrum is much more complex than that of ethane, and in particular there are too many strong lines in the region corresponding to B–H bond-stretching (1500—3000 cm.$^{-1}$). This difficulty appears in a simple form in the Raman spectrum, where the two most intense frequencies, 2102 and 2523 A., must both be attributed

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[8] *Z. Kryst.*, 1925, **62**, 103.

[9] *J. Amer. Chem. Soc.*, 1937, **59**, 1096.

[9a] L. Pauling, *Ind. Eng. Chem.*, 1947, **25**, 2970, 3045.

[10] S. H. Bauer, *Chem. Rev.*, 1942, **35**, 180.

[11] M. E. Diatkina and J. K. Sirkin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **35**, 180.

[12] *J. Chem. Physics*, 1938, **6**, 586.

[13] *Ibid.*, 1941, **9**, 780.

[14] *Ibid.*, 1947, **15**, 614.

[15] *Proc. Roy. Soc.*, 1945, **183**, *A*, 357.

to symmetrical stretching vibrations, though the ethane model admits only one fundamental vibration of this type. Moreover, the infra-red spectrum contains eight bands which appear to be strong enough for fundamentals, compared with the five predicted by the ethane model, and of these the one at 412 cm.$^{-1}$ is much too low to be readily accounted for. Attempts (*e.g.*, by Stitt [13]) to interpret the spectrum on the basis of the ethane model have been forced to adopt *ad hoc* assumptions about low-lying electronic levels and resonance splitting, and even then the proposed assignments are not very satisfactory.

These difficulties largely disappear if the bridge model is adopted for diborane. The molecule now has the symmetry of ethylene rather than of ethane, and the observed spectrum does in fact resemble that of ethylene. The absence of degeneracy in the bridge model allows eight distinct fundamental frequencies to appear in the infra-red, and the low frequency 412 cm.$^{-1}$ is naturally interpreted as a bending of the molecule about the line joining the two bridge hydrogens. Moreover, there are now two different kinds of B–H bond, and hence there will be two symmetrical stretching vibrations to be allotted the Raman frequencies 2102 and 2523 cm.$^{-1}$. Using these and other more detailed considerations, it is possible to identify 15 out of the expected 17 active vibrations of the bridge model, and also to predict their frequencies within 5% by using a potential-energy function with five constants. Further, Price [14] has examined some of the bands under higher resolution, and finds that the band contours, the alternating intensities of the rotational lines, and the calculated moments of inertia are in excellent accord with the symmetry properties of the bridge model and its dimensions derived from electron-diffraction data, and are quite incompatible with the ethane model.

Thermodynamic properties. These properties depend upon the dimensions and modes of motion of the molecule, and may thus provide evidence as to its structure. The only relevant experimental data for diborane are the specific-heat measurements from 100° to 300° K. carried out by Stitt,[16, 13] who compared his data with the vibrational assignment arrived at on the basis of the ethane model. The discrepancy was attributed to the hindered rotation of the two BH_3 groups, and calculation led to a value of either 5 or 15 kg.-cals./mole for the height of the barrier to rotation, depending on the assumptions made about the supposed low-lying electronic states. The corresponding value for ethane is 3 kg.-cals./mole, and it is surprising that a higher value should be obtained for diborane, where the two groups are farther apart and there is a deficiency of electrons. For the bridge molecule, internal rotation is replaced by a torsional oscillation, which is not active in either the Raman or the infra-red spectrum. However, this frequency (together with the two unidentified active frequencies) can be calculated approximately from the potential-energy function derived by Bell and Longuet-Higgins,[15] and the vibrational specific heat then calculated. The results agree with experiment except at the highest temperature, where the calculated value is a little too low, possibly on account of neglect of

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[16] *J. Chem. Physics*, 1940, **8**, 981.

anharmonicity, or because of error in the calculated frequencies. The specific-heat data thus favour the bridge structure on the whole, though they do not decide definitely between the two models.

Although no measurements have yet been made of the entropy of diborane, it might be hoped that such measurements would distinguish between the two models in virtue of their differences in moments of inertia, and hence in rotational entropy. However, it has been shown by K. S. Pitzer [17] that these differences are almost exactly cancelled by differences in the symmetry numbers of the two structures, so no decision is possible.

Electron impact. The fragments produced from diborane by electron impact have been examined in the mass spectrograph by J. A. Hipple.[18] It has been claimed [10] that the occurrence of ions like B_2^+ and B_2H^+ constitutes evidence against the bridge structure, since they contain less than two hydrogen atoms. However, each of these ions contains enough electrons to form normal electron-pair links, and their formation gives no information about the structure of the original electron-deficient molecule.

The Electronic Structure of Diborane.—The electron-deficiency of diborane implies at once that it cannot be represented by any of the ordinary valency formulæ involving electron-pair bonds. Purely ionic structures are unsatisfactory, since the physical properties of diborane are not at all those expected of such a structure. The various formulations of the electronic structure of diborane are therefore in some measure attempts to force the problem into a framework which is ill adapted to receive it. Since none of these formulations is sufficiently precise to produce quantitative predictions, the choice between them is at present largely a matter of taste, and we shall therefore devote less space to this question than has been usual in recent literature on the subject.

Earlier views have been summarised by Bauer.[10] They are all based upon the ethane configuration, which now appears very unlikely in view of the evidence reviewed in the last section. The most recent formulation along these lines involved resonance between a large number of structures, each containing either two one-electron links or one "no-electron" link. Apart from other difficulties, there is no obvious reason why the presence of one-electron links should not lead to paramagnetism, whereas experiment shows diborane to be diamagnetic.[19]

If we turn to the bridge structure, some information about the site of the electron-deficiency can be obtained from the electron-diffraction and spectrum data. The dimensions derived from the former give 1·18 A. for the length of the terminal B–H links, compared with 1·41 A. for the distance between the boron and the central hydrogen atoms. The former is close to the length 1·20 A. found experimentally by S. H. Bauer [20] in the compound $H_3\overset{-}{B}\cdot\overset{+}{C}O$ (which has no electron-deficiency), and also to the value 1·21 A.

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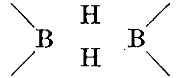
[17] *J. Amer. Chem. Soc.*, 1947, **69**, 184.

[18] *Physical Rev.*, 1940, **57**, 350.

[19] S. Freed and H. G. Thode, quoted by S. H. Bauer, ref. 10.

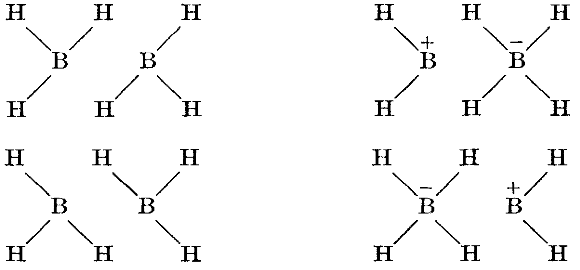
[20] *J. Amer. Chem. Soc.*, 1937, **59**, 1804.

expected for a normal covalent link between boron and hydrogen,[21] while the latter is considerably longer. Similarly, in the vibrational analysis of the diborane spectrum carried out by Bell and Longuet-Higgins [15] good agreement was found by giving the terminal B–H links a force constant equal to that derived for the "normal" molecule borazole ($B_3N_3H_6$),[22] while the force constant for the central B–H bonds was only half as great. It therefore seems reasonable to suppose that the terminal B–H bonds are normal electron-pair links, and that the electron-deficiency is concentrated in the system  , which is held together by four electrons.

The electronic structure of this system has been given a number of theoretical interpretations, briefly as follows:

(i) In many other hydrogen compounds association is brought about by *hydrogen bonding,* which is now believed to be mainly electrostatic in nature. A similar explanation for the dimeric nature of diborane has been suggested by A. Burawoy,[23] who points out that, although polar character decreases in the series FH, OH_2, NH_3, CH_4, yet it may increase again in BH_3 with the hydrogen atom now constituting the negative end of the dipole. However, this interpretation implies that the bridge hydrogen atoms are not symmetrically placed with respect to the two borons, thus lowering the symmetry of the whole molecule. The vibrational spectrum accords very well with a symmetrical placing, and in particular the rotational structures obtained by Price [14] seem to exclude any lower symmetry: hence the hydrogen-bonding interpretation must be regarded as very unlikely.

(ii) Several authors [3–5] have suggested a *resonance* formulation for the bridge linkage, the separate structures being



Each of these structures contains only paired electrons, so the resulting molecules is diamagnetic. In each case there is some distortion of valency angles to reach the observed shape of the molecule, since BH_3 would naturally be planar, and H_2B^+ linear. Although there is much evidence that molecules with alternative bond assignments can be considerably stabilised by resonance, it is not usually considered that two parts of a molecule can be held together solely by such stabilisation. For example, in the reaction

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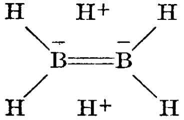
[21] V. Schomaker and D. P. Stevenson, *ibid.*, 1941, **63**, 37.
[22] B. L. Crawford and J. T. Edsall, *J. Chem. Physics*, 1939, **7**, 223.
[23] *Nature*, 1945, **155**, 328.

$H + H_2$ the symmetrical transition state H---H---H has an energy some 9 kg.-cals./mole higher than $H + H_2$ although it is 90 kg.-cals./mole lower than that of three hydrogen atoms. However, there is no reason in principle why in such cases the energy gained by resonance should not exceed that required to stretch and deform the bonds, and approximate calculations [24–26] suggest that H---H---CH_3 and Cl---Cl---Cl may be stable molecules rather than activated complexes, though there is no experimental evidence for this. Unfortunately, such calculations are very uncertain even in the simplest cases, and little weight can be attached to the calculations of Sirkin and Diatkina [4] on the resonance link in the boron hydrides.

The resonance formulation produces plausible reasons for the restricted occurrence of the bridge linkage. In the hydrides of the 5th, 6th, and 7th Groups of the Periodic Table bridge formation will be opposed by repulsion between unshared electrons on the two atoms. On the other hand, polymerisation is expected to occur with any covalent hydrides in the first three groups of that table, which accords with the facts so far as they are known.

(iii) The idea of a *protonated double bond* has been advanced by Pitzer [7] to represent the bridge linkage in diborane and similar molecules. It may be written schematically as in (II), where the proton is embedded in the π-electrons of the double bond, which spread out at right angles to the plane of the rest of the molecule. The formulation bears some resemblance to the ionic structures of E. Wiberg,[27] but differs in giving a specific location to the protons. This model gives the correct shape to the diborane molecule and accounts for the resistance to internal rotation, but the B–B distance is greater and the stretching-force constant much lower than would be anticipated for a double bond, even allowing for some weakening by the protons. The considerable charge displacements account for the high intensity of infra-red bands associated with the central part of the molecule, and also for the high atomic polarisation reported by K. L. Ramaswamy.[28] The shielding of the protons by the π-electrons would account for the absence of ionic properties, but it is surprising that the diborane molecule appears to be devoid of acidic properties, not even showing any deuterium exchange with ND_3.[28a]



(II.)

The protonated double-bond picture suggests a close analogy with ethylene (rather than with ethane). This similarity is very close in the infra-red spectrum of diborane, and also appears in the ultra-violet.[14] Its diamagnetic susceptibility is also close to that of ethylene, and much lower than that of ethane.[19]

This formulation also accounts well for the range of occurrence of electron-

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[24] G. K. Rollefson and H. Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 2661.

[25] E. Gorin, *Acta Physicochim. U.R.S.S.*, 1938, **9**, 691.

[26] E. Gorin, W. Kauzmann, J. Waller, and H. Eyring, *J. Chem. Physics*, 1939, **87**, 633.

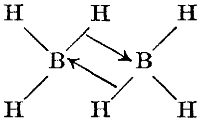
[27] *Ber.*, 1936, **69**, 2816, and earlier papers.

[28] *Proc. Indian Acad. Sci.*, 1935, **2**, *A*, 364, 630.

[28a] A. B. Burg, *J. Amer. Chem. Soc.*, 1947, **69**, 747.

deficient molecules, since it predicts that boron can be replaced by other atoms having two bonding orbitals available, and hydrogen by other atoms with an *s*-orbital vacant. The former prediction fits in with the molecules discussed in the last section of this review, and the latter with the complexes formed between olefins and silver ions,[29] and with the "π-complexes" which have been recently suggested by M. J. S. Dewar [30] as intermediates in various organic reactions.

A. D. Walsh [31] has recently given a treatment of the bridge linkage which has something in common with the two last interpretations. He supposes that the bonding electrons in a normal B–H link can also be used to fill the vacant orbitals on the other boron atom, giving a structure which can be written as in (III). This treatment predicts that the terminal hydrogen atoms should not be exactly coplanar, which conflicts with the spectrum evidence : otherwise it may be regarded as an alternative to the resonance or protonated double bond formulations.



(III.)

(iv) The method of *molecular orbitals* has also been applied to the structure of diborane. Early discussions were based on the ethane model, and predicted properties (including paramagnetism) analogous to those of the isoelectronic oxygen molecule.[32] It was pointed out by Pitzer [7] that the structure for diborane containing a protonated double bond could be derived from ethylene by imagining the removal of a proton from each carbon nucleus : hence it would be expected that the molecular orbitals of ethylene would be applicable to diborane with little alteration. This idea has been worked out in more detail by R. S. Mulliken [33] who has enumerated the orbitals. They are closely similar to those of ethylene, except that the π-orbitals now embrace the protons as well as the boron nuclei. Mulliken has also made some calculations on the $2p$ atomic orbitals of boron, and finds that they will have a considerable overlap even at single-bond distances, thus supporting the idea that diborane contains a double bond.

It will be seen from the above survey that there are a number of different theoretical formulations which lead essentially to the same result. The choice between them must await a refinement of theory which will enable quantitative calculations of stability, etc., to be made, or a refinement of experiment by which the actual electron densities in the centre of the molecule can be observed. The protonated double bond differs from the other formulations in that it predicts a high electron density (due to the σ-bond) directly between the boron atoms, but at present there is no means of testing this.

Most of the simple derivatives of diborane are either covered by the discussion of diborane itself, or can be assigned ordinary electron-pair

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[29] S. Winstein and H. J. Lucas, *ibid.*, 1938, **60**, 836.

[30] *J.*, 1946, 406.

[31] *J.*, 1947, 89.

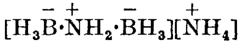
[32] R. S. Mulliken, *J. Chem. Physics*, 1935, **3**, 635.

[33] *Chem. Rev.*, 1947, **41**, 207.

structures: for example, among the nitrogen derivatives we have the trimethylamine compound (IV), the diammoniate (V), and borazole (VI or

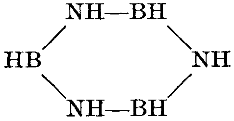
$\overset{-}{H_3B}\cdot\overset{+}{N}Me_3$

(IV.)

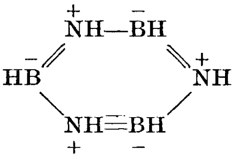


$[\overset{-}{H_3B}\cdot\overset{+}{N}H_2\cdot\overset{-}{B}H_3][\overset{+}{N}H_4]$

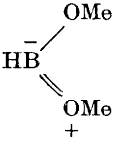
(V.)



(VI.)



(VII.)



(VIII.)

$\overset{-}{H_2B}=\overset{+}{N}Me_2$

(IX.)

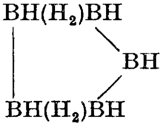
VII), the last structure showing some analogy with benzene.[34] On the other hand, there is still doubt as to the structure of the monoammoniate.[10] The only outstanding anomalies among these simple derivatives are the compounds $BH(OMe)_2$, BH_2NMe_2, and $BH(NMe_2)_2$, which would be expected to dimerise. It may be suggested that the electron deficiency on the boron atom is relieved by the tendency to structures such as (VIII) or (IX).[35]

The Structure of the Higher Boron Hydrides.—There is little direct evidence as to the configuration of these hydrides, but they are all electron-deficient and presumably contain the same kind of link as diborane, which they resemble in general chemical behaviour. It is therefore satisfactory to find that Pitzer [7] has been able to account successfully for all the known boron hydrides with six or less boron atoms using a simple set of principles based on the bridge structure for diborane as follows: (*a*) The hydroborons are built up by the combination through hydrogen bridges of hypothetical "borines", of which the simplest are BH_3, $H_2B\cdot BH_2$ and $H_2B\cdot BH\cdot BH_2$. (*b*) This combination will continue until every boron atom is associated with one bridge linkage, except that a BH group between two boron atoms which are both bridge-linked will not itself take part in a bridge link. (*c*) Rings containing fewer than five boron atoms are not stable. These principles lead to the following possible structures, where (H_2) is a hydrogen bridge:

(1) $2BH_3 = B_2H_6$ $H_2B(H_2)BH_2$

(2) $H_2B\cdot BH_2 + 2BH_3 = B_4H_{10}$ $H_2B(H_2)BH\cdot BH(H_2)BH_2$

(3) $H_2B\cdot BH\cdot BH_2 + H_2B\cdot BH_2 = B_5H_9$



(4) $H_2B\cdot BH\cdot BH_2 + 2BH_3 = B_5H_{11}$ $H_2B(H_2)BH\cdot BH\cdot BH(H_2)BH_2$

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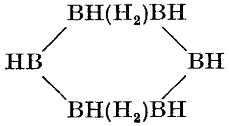
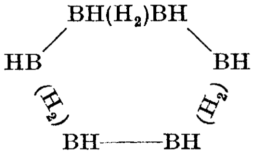
[34] E. Wiberg and A. Boltz, *Ber.*, 1940, **73**, 209.

[35] H. C. Longuet-Higgins, private communication.

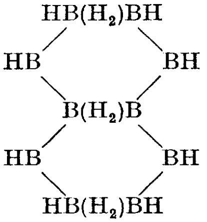
(5) $2H_2B\cdot BH\cdot BH_2 = B_6H_{10}$



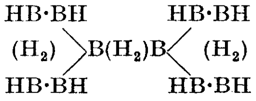
(6) $3H_2B\cdot BH_2 = B_6H_{12}$



This list includes all the well-characterised hydrides of boron except $B_{10}H_{14}$, which can be written as (X) or (XI), of which the second is said by Pitzer



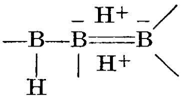
(X.)



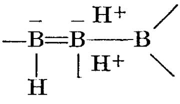
(XI.)

to agree better with H. Möller's crystal data.[36] B_6H_{12} is not well characterised, but Stock[37] considered its existence probable: hence the above principles predict no unknown hydrides with six or fewer boron atoms. There should, of course, be many other hydrides with seven or more boron atoms. They have not yet been isolated, but the experimental evidence does not preclude their existence.

Of the three principles given above, the exception noted under (*b*) needs justification. Pitzer[7] attributed it to a type of conjugation which can be represented by the resonance structures (XII) and (XIII). In the second of these the left-hand boron atom has a complete octet, and if the effect is strengthened by conjugation with a second bridge linkage on the other side it is reasonable to suppose that the BH group will lose its tendency to polymerise. This explanation in terms of conjugation is supported by Mulliken's calculation on the large spread of the $2p$ orbital of boron.[33]



(XII.)



(XIII.)

Although the above principles are strikingly successful in predicting the formulæ of the known hydroborons, it must be admitted that there is no direct evidence in favour of the proposed structures. In fact, electron-diffraction data for B_4H_{10}, B_5H_9, and B_5H_{11} have been interpreted in terms

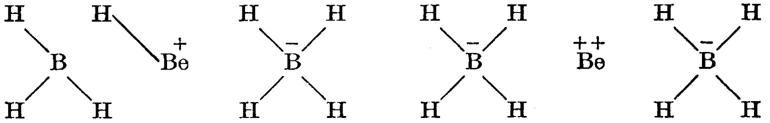
[36] *Z. Krist.*, 1931, **76**, 500.

[37] *Op. cit.*, p. 14.

of quite different configurations based on the ethane model for diborane.[38] In the case of B_4H_{10} and B_5H_{11} the structures proposed by Pitzer have not been tested, and the differences are likely to be small, as for diborane. On the other hand, Bauer and Pauling did test and reject a symmetrical five-membered ring structure for B_5H_9, but Pitzer claims that an unsymmetrical ring of reasonable dimensions represents the electron-diffraction data as well as the structure favoured by Bauer and Pauling. However, this claim has recently been contested by G. Silbiger and S. H. Bauer,[39] who also reject the proposed $B_{10}H_{14}$ structures. The distinction between the different structures rests largely on a visual estimate of intensities, and the question must be regarded as still open.

The Structure of Related Compounds.—Digallane and its alkyl derivatives clearly fit into the same framework as diborane, and the same is true of compounds such as $Al_2H_2Me_4$. There is still some doubt as to the nature of aluminium hydride itself. The ethereal solution prepared from lithium aluminium hydride may contain Al_2H_6, but the solid deposited from this solution is certainly a higher polymer. H. C. Longuet-Higgins [40] has suggested a two-dimensional layer structure for this polymer, in which each aluminium atom is attached to three others through hydrogen bridges, but experimental confirmation is lacking. The non-volatile hydrides of Cu, Ag, Au, Be, and Ta, which E. Pietsch [41] claimed to have obtained by the action of atomic hydrogen on the metal, may be similar chain polymers.

A slightly different problem is presented by the borohydrides and lithium aluminium hydride. They can all be written formally with bridge linkages, *e.g.*, BeB_2H_8 can be regarded as $2BH_3 + BeH_2 = H_2B(H_2)Be(H_2)BH_2$. The physical properties of BeB_2H_8 and AlB_3H_{12} are in reasonable accord with this formulation, but the borohydrides of the alkali metals are salt-like in nature, and it has been recently shown that $NaBH_4$ is an ionic crystal with a face-centred cubic structure : [42] hence the formulation $[X^+][BH_4^-]$ is clearly correct for these compounds. It is therefore likely that in the other borohydrides the hydrogen atoms in the bridge are not symmetrically placed, but are displaced towards the boron atom. If we use the resonance formulation of the bridge structure this amounts to saying that structures such as



become increasingly important as we pass along the series B_2H_6, AlB_3H_{12}, BeB_2H_8, $LiBH_4$, $NaBH_4$. This gradation is shown in decreasing volatility, and it also appears in chemical properties, since there is an increase in

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[38] S. H. Bauer, *J. Amer. Chem. Soc.*, 1938, **60**, 805 ; S. H. Bauer and L. Pauling *ibid.*, 1936, **58**, 2403.

[39] *Ibid.*, 1948, **70**, 115.

[40] *J.*, 1946, 139.

[41] *Z. Elektrochem.*, 1933, **39**, 577.

[42] A. M. Soldate, *J. Amer. Chem. Soc.*, 1947, **69**, 987.

stability towards air, water, and trimethylamine as we pass along the series. It has also been recently shown by W. C. Price[43] that the terminal BH_2 infra-red frequency gradually decreases from 2600 to 2200 $cm.^{-1}$ along the same series, suggesting an increase in the negativity of the boron.

The direct structural evidence is not sufficient to decide between the above structures and those suggested by Beach and Bauer,[44] which involve penta-co-ordinated boron and thus seem inherently less probable. Electron-diffraction measurements with AlB_3H_{12} show that the three boron atoms are arranged symmetrically in a plane round the aluminium atom, but the position of the hydrogen atoms cannot be fixed with certainty. It has been maintained[45] that the electron-diffraction data for BeB_2H_8 eliminate the bridge structure, but this view is based on a visual judgment of relative intensities, and cannot be regarded as final.

A number of less well characterised compounds can be represented by the bridge formulation, *e.g.*, $MeBe(H_2)BH_2$ and $Me_2Ga(H_2)BH_2$. If the compounds described as $(BeBH_5)_n$ and $(ZnBH_5)_n$ are actually dimeric, they can be written as $H_2B(H_2)Be(H_2)Be(H_2)BH_2$.[40] Finally, it should be mentioned that the polymerisation of many metallic alkyls also involves the problem of electron deficiency, and can probably be explained along the same lines as the boron hydrides, though here both experiment and theory are less well founded.[40, 46]

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[43] Private communication.

[44] J. Y. Beach and S. H. Bauer, *J. Amer. Chem. Soc.*, 1940, **62**, 3440.

[45] G. Silbiger and S. H. Bauer, *ibid.*, 1946, **68**, 312.

[46] K S.. Pitzer and H. S. Gutowsky, *ibid.*, p. 2204.