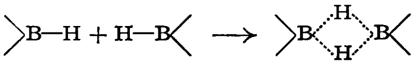
39. *The Structure of Some Electron-deficient Molecules.*

By H. C. LONGUET-HIGGINS.

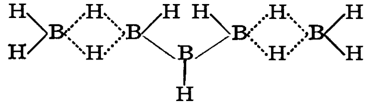
In this paper the hydrogen bridge theory of diborane is extended in detail to the borohydrides and the other covalent hydrides of elements in the first three groups of the Periodic Table. In particular, the theory relates the structure and properties of all the known borohydrides to those of diborane, and accounts for the non-volatility of the newly discovered aluminium hydride $(AlH_3)_n$, for which a hexagonal layer structure is predicted. It is further shown that the theory provides possible mechanisms for the anomalous polymerisation of the alkyls of elements in the first three periodic groups.

PITZER (*J. Amer. Chem. Soc.*, 1945, **67**, 1126) has recently shown how the hydrogen bridge theory of diborane, for which strong evidence has been advanced by the author and Bell (J., 1943, 250; *Proc. Roy. Soc.*, 1945, **183**, *A*, 357), can be extended to account for the formulæ and properties of all the known hydrides of boron, and for the non-existence of any others with six or fewer boron atoms. The main essentials of this theory are: (1) That the hydroborons are all built up of smaller units, conveniently termed "borines," of general formula B_nH_{n+2} and containing tervalent boron, linked together by hydrogen bridges through their free >B—H groups:



(2) That this polymerisation will continue until there are no free >B—H groups left, except those adjacent to two bridges, such as the central >B—H groups in B_5H_{11}, which is formulated as (I). (3) That hydroborons containing rings of fewer than five boron atoms are not stable.

(I.)



The absence of further polymerisation in B_5H_{11} and similar systems is explained by Pitzer in terms of a new conception of the hydrogen-bridge linkage, as a " protonated double bond " between the boron atoms. This may be thought of as a σ bond together with a π bond in whose antinodes two protons are embedded. The π parts of the protonated double bonds in B_5H_{11} can conjugate through the $2p$ orbital of the central boron atom, thereby preventing further polymerisation.

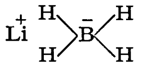
Not only is this theory completely successful in accounting for the formulæ of the known hydroborons, but it also explains their individual properties. In particular, Pitzer shows that the structure predicted for B_5H_9 agrees as well with the evidence from electron diffraction (Bauer and Pauling, *J. Amer. Chem. Soc.*, 1934, **58**, 2403) as that proposed by Bauer and Pauling, with reasonable values for the dimensions of the molecule. It is also noteworthy that the two series of hydroborons, of general formulæ B_nH_{n+4} and B_nH_{n+6}, are simply those consisting of two and three borines respectively; and all the cyclic hydroborons, which would be expected to be more stable, belong to the former series, whereas all those in the latter series are chain molecules. Hence Stock's classification (" Hydrides of Boron and Silicon," Cornell Univ. Press, Ithaca, 1935) relating stability and formula finds a theoretical foundation.

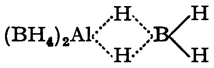
In economy of hypothesis and in the range of experimental evidence which it explains, this theory is considerably superior to any previous theory of the boron hydrides; and since there are at present no experimental facts which conflict with it, we believe that it is substantially correct.

In the present paper we extend the theory to other electron-deficient molecules, *viz.*, the borohydrides (which were discussed briefly in another paper, *loc. cit.*, 1943), the other hydrides of Group III, the non-ionic hydrides of Groups I and II, and the associated alkyls of these three groups. The adjective " electron-deficient " implies the difficulty in formulating these compounds according to classical valency ideas : their molecules have insufficient valency electrons to hold them together entirely by 2-electron covalent links, whereas their properties (apart from those of $LiBH_4$) conflict with the view that they contain pure ionic links.

The Borohydrides.—It has already been suggested elsewhere (*loc. cit.*, 1943) that the borohydrides have structures resembling those of the boron hydrides in containing bridge linkages through hydrogen. It seems reasonable to suppose that in lithium borohydride the ionic structure (II) predominates, whereas in the aluminium compound a larger contribution comes from covalent structures of the type (III). This accords with the physical properties of these compounds, of which the volatility increases enormously from $LiBH_4$ to $Al(BH_4)_3$.

(II.)

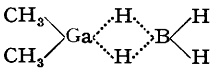




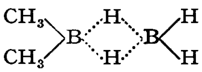
(III.)

Moreover, there is chemical evidence to support this formulation. Schlesinger and Brown in their discussion (*J. Amer. Chem. Soc.*, 1940, **62**, 3429) of the borohydrides draw attention to the series of compounds $LiBH_4$, $Be(BH_4)_2$, $Al(BH_4)_3$, B_2H_6. Along this series there is a progressive decrease in stability towards air and water, and a progressive ease of reaction with trimethylamine to form BH_3NMe_3. They describe this change as an " increase of BH_3 character " and a " decrease of BH_4^- character." This progressive change in chemical properties is obscured if we suppose (see Beach and Bauer, *ibid.*, p. 3440) beryllium and aluminium borohydrides to contain quinquevalent boron, and lithium borohydride and diborane to contain quadrivalent boron.

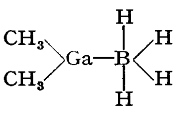
Another piece of evidence pointing to a continuity between the borohydrides and boranes is the recent discovery of dimethylgallium borohydride (Schlesinger, Brown, and Schaeffer, *ibid.*, 1943, **65**, 1838). According to the present theory this compound is formulated as (IV), in close relationship to the formula for 1 : 1-dimethyldiborane (V). One may contrast this scheme with that put forward by Pauling and others (see Beach and Bauer, *loc. cit.*), in which the borohydrides are supposed to contain quinquevalent boron, each link being partly ionic, partly covalent, and partly a one-electron bond. In the latter theory the borohydrides are regarded as essentially different in structure from the boranes; for instance, dimethylgallium borohydride and 1 : 1-dimethyldiborane are assigned the structures (IV*a*) and (V*a*) respectively.



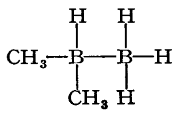
(IV.)



(V.)



(IV*a*).



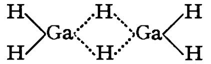
(V*a*.)

The Covalent Hydrides of the Metals.—For the existence of these there is now much evidence. In 1933 Pietsch (*Z. Elektrochem.*, **39**, 577) reported the formation of hydrides of Cu, Ag, Au, Be, Ga, In, Tl and Ta by the action of atomic hydrogen on the elements. The hydrides of In and Tl were volatile, but the others were white solid films of uncertain composition, decomposing water with evolution of hydrogen. In recent years a volatile hydride of gallium (Wiberg and Johansen, *Angew. Chem.*, 1942, **55**, 38) and a non-volatile hydride of aluminium (Stecher and Wiberg, *Ber.*, 1942, **75**, 2003) have been discovered, and also methylaluminium hydrides (*idem, ibid.*) of general formula $Al_2Me_nH_{6-n}$.

Pietsch regarded his " atomic hydrides " as containing metallic cations and hydrogen anions, but in view of the relative electronegativities of these metals and hydrogen this description is inacceptable. However, the non-volatility of the hydrides of Cu, Ag, Au, Be and Ta indicates that they are not covalent separate molecules but polymers. In aluminium hydride, where there are definitely three hydrogen atoms to each aluminium atom, it is therefore impossible to formulate the molecule according to classical valency ideas.

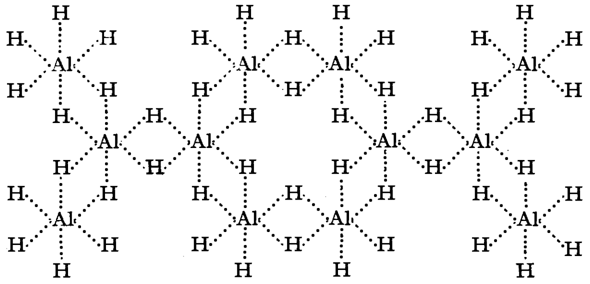
The present theory provides a satisfactory solution to the problem. It has already been suggested (*loc. cit.*, 1943) that the volatile Ga_2H_6 has the structure (VI) analogous to that of B_2H_6, and it seems likely that the

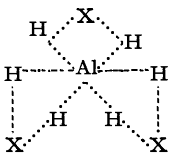
(VI.)



volatile hydrides of In and Tl have similar structures. As regards aluminium hydride $(AlH_3)_n$, we suppose that the unit $>Al—H$ can polymerise like $>B—H$, but that whereas the polymerisation of the latter stops when the boron atom has its four valency shell orbitals occupied, the polymerisation of the former will continue until six of its valency orbitals are occupied. This is an extension of the idea of a " covalency maximum " to these anomalous compounds, and has already been tacitly assumed in our formulation of $Al(BH_4)_3$. The monomeric AlH_3 could then polymerise in two dimensions by the continued formation of bridge linkages as in (VII).

(VII.)

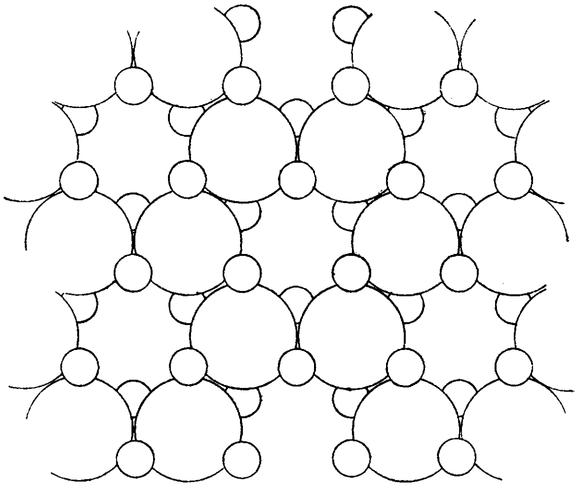




(VIII.)

In fact, if we assume that (*a*) the hydrogen atoms form bridges in pairs between the Al atoms, every Al atom being joined octahedrally to six H atoms, and (*b*) all the Al····H bonds in the giant molecule are crystallographically equivalent, then it follows that the Al atoms must be arranged in two-dimensional layers, with the Al atoms in each layer at the vertices of a hexagonal tessellation. One such layer is illustrated in Fig. 1, where the large circles represent Al atoms and the small circles H atoms. However, if we accept Pitzer's view (*loc. cit.*) of the hydrogen bridge as a " protonated double bond," it seems likely that the hydrogen atoms in the group (VIII) may be arranged, not at the vertices of an octahedron, but at the vertices of a trigonal prism with the aluminium atom at the centre. The Al–X σ orbitals can be constructed from a linear combination of 3*s*, $3p_x$, and $3p_y$ orbitals (*z* axis perpendicular to the plane of the heavy atoms); and of the remaining orbitals, $3p_z$, $3d_{xy}$, and $3d_{xz}$ can be combined linearly to give three π orbitals directed towards the three X atoms and having nodal planes $z = 0$. The protons would be situated near the antinodes of these π bonds, that is, at the vertices of a trigonal prism (Fig. 2). This configuration leads to the same arrangement of the heavy atoms in $(AlH_3)_n$ and $Al(BH_4)_3$ as the octahedral configuration (Fig. 3), so it would be difficult to distinguish the two possibilities by electron-diffraction or *X*-ray analysis; a more hopeful line might be to investigate some property depending on the symmetry of the borohydride, since with the prismatic arrangement this molecule has the symmetry D_{3h} with reflexive summetry, whereas with the octahedral configuration it belongs to the group D_3 with no reflexive symmetry.

Fig. 1.



As for the methyl derivatives of aluminium hydride, one can formulate many plausible polymers derived from the units AlH_3, AlH_2Me, $AlHMe_2$, and $AlMe_3$. Moreover, the monomeric $AlMe_3$ can polymerise on its own (see next section), which shows that the presence of Al–H bonds is not necessary for polymerisation;

this greatly increases the number of possible polymers, and makes less certain the formulation of any particular one. Generally speaking, however, this scheme is in excellent agreement with experiment : it appears (Stecher and Wiberg, *loc. cit.*) that the interconversion of the polymers takes place through the intermediate formation of such monomeric units, and the more hydrogen a polymer contains the greater its degree of polymerisation, as estimated from the volatility and viscosity.

FIG. 2.

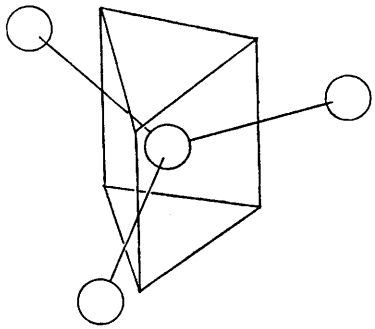
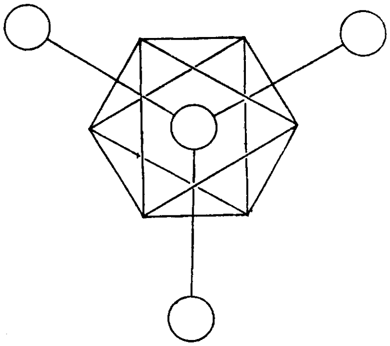
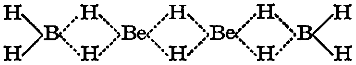


FIG. 3.

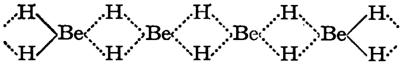


As for the other hydrides of Group III, the absence of further polymerisation in gallium, indium, and thallium hydrides is probably connected with the general reluctance of these sub-group B elements to attain a co-ordination number of six; the atomic orbitals involved would be the same.

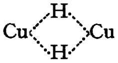
No beryllium hydride of definite composition has yet been prepared, but even apart from Pietsch's work there are indications that one exists. Burg and Schlesinger (*J. Amer. Chem. Soc.*, 1940, **62**, 3425) describe the preparation of a compound $BeBH_5$ which was left as a solid after BeB_2H_8 had been distilled away. This may be written as (IX). If this is correct one would naturally expect there to exist a beryllium hydride $(BeH_2)_n$ of structure (X).



(IX.)



(X.)



(XI.)

At present there is little evidence about the hydrides of Group IB. According to the present ideas a univalent hydride can polymerise only two-fold, to give a structure of the type (XI). The copper hydride formed by the action of sodium hypophosphite on cupric salts is probably not of this type, however, according to the crystal evidence (Huttig and Brodkorb, *Z. anorg. Chem.*, 1926, **153**, 242).

The Alkyls of Elements of Groups I, II, *and* III.—These include LiR, NaR; BeR_2, MgR_2, ZnR_2, CdR_2, HgR_2; BR_3, AlR_3, GaR_3, InR_3, TlR_3. Of these, the alkyls of Li, Na, Be, Mg and Al have the properties of associated substances. Thus LiEt is roughly tetrameric in concentrated benzene solution, $MgEt_2$ is a viscous, non-volatile, insoluble liquid (Krause and v. Grosse, " Die Chemie der metall-organischen Verbindungen," Berlin, 1937), and $AlMe_3$ is found from vapour-density measurements (Laubengayer and Gilliam, *J. Amer. Chem. Soc.*, 1941, **63**, 477) to have a mean degree of polymerisation of 2 at 70°. The alkyls of Zn, Cd, Hg, B (Stock and Zeidler, *Ber.*, 1921, **54**, 531), Ga and In (Laubengayer and Gilliam, *loc. cit.*) are all monomeric in the vapour and in solution. The degree of polymerisation of TlR_3 does not appear to have been investigated.

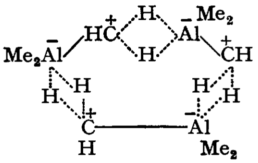
It is impossible to formulate such polymerisation in terms of normal valency bonds between the units in the polymer, since in each monomer all the valency electrons are engaged in covalent linkages. A possible explanation of the polymerisation is that it is due to dipole association; but this explanation will hardly account for the magnitude of the effect, which is greater than the association by hydrogen bonding of ammonia, water, and hydrogen fluoride.

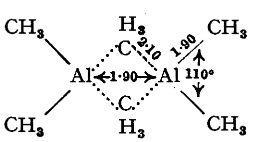
An attempt at solution of the problem has been made with $AlMe_3$ whose vapour density corresponds to the dimeric form at 70° (*idem, ibid.*). It is found (Davidson, Hugill, Skinner, and Sutton, *Trans. Faraday Soc.*, 1940, **26**, 1212; Brockway and Davidson, *J. Amer. Chem. Soc.*, 1941, **63**, 3287) that the electron-scattering curve fits that calculated for an ethane-like dimer in which the aluminium atoms are linked together. It is therefore supposed that some or all of the links have partial single-electron-link character and partial no-link character. Several difficulties at once present themselves. (*a*) The covalent radius of aluminium exceeds that of silicon; hence an Al–Al bond would be expected to be longer than an Si–Si bond, and an electron-deficient bond to be longer still. In fact, the Al–Al distance calculated according to the ethane-like model is considerably shorter (2·20A.) than the Si–Si distance (2·34A.) in Si_2Me_6. (*b*) The Raman spectrum of methylaluminium (Kohlrausch and Wagner, *Z. physikal. Chem.*, 1942, *B*, **52**, 185) resembles those of the aluminium halides much more than that of C_2Cl_6. (*c*) If the polymerisation is due to the formation of electron-deficient links between the central atoms in pairs, it seems strange that BMe_3 does not polymerise at all, whereas LiEt polymerises much more than two-fold.

Unfortunately, the experimental data on the alkyls are scanty, but those available can be satisfactorily interpreted in terms of the present theory, as will now be shown.

Methylaluminium has been studied in the most detail. The formula Al_2Me_6 has been proposed for the polymer on the basis of vapour-density determinations by Laubengayer and Gilliam (*loc. cit.*), and is consistent with the tensimetric measurements by Davidson and Brown (*J. Amer. Chem. Soc.*, 1942, **64**, 318) on mixtures of $AlMe_3$ and BMe_3. However, the evidence as published by no means excludes the possibility that methylaluminium is a mixture of polymers. The hypothetical trimer (XII), for instance, gives as good agreement with the electron-diffraction evidence as the ethane-like dimer (the calculations were carried out by H. A. Skinner, and are to be published shortly); and whereas the latter raises extreme difficulties of formulation, the former is easily understood in terms of the protonated double bond. (The + and − signs indicate a formal displacement of an electron from the carbon to the aluminium atom.) Supposing, however, that the dimeric formula is correct, the ethane-like structure is not the only one compatible with the electron-diffraction evidence. As already mentioned, the low-frequency end of the Raman spectrum of Al_2Me_6 (Kohlrausch and Wagner, *loc. cit.*) is much more closely similar in structure to those of the aluminium halides than that of C_2Cl_6, which suggests a bridged structure for the dimer. Brockway and Davidson (*loc. cit.*) found that moderate agreement with the observed electron-diffraction curve was given by a bridged structure with the dimensions shown in (XIII). They rejected such a structure on the ground that the Al–Al distance was much too short for non-bonded atoms; but this objection is not final, for reasons that will now be given.

(XII.)

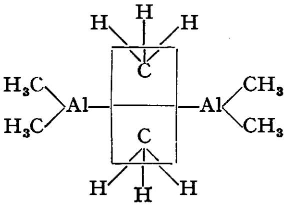




(XIII.)

If we suppose that the central ring in Al_2Me_6 (XIII) is similar in electronic structure to that in B_2H_6, then we may write the structure of the former as in (XIV). Here a line between atoms denotes an ordinary σ bond, and the rectangle represents a π bond between the aluminium atoms, its lobes overlapping the fourth valency orbitals of the central carbon atoms. We may thus emulate Pitzer (*loc. cit.*) and speak of a " methylated double bond " between the aluminium atoms. According to this interpretation, one would expect the Al–Al distance to be between that of a single bond and that of a double bond, and this is what is observed. The other dimensions found for the molecule are quite consistent with this idea. However, further speculation on the structure of the alkyls in general must await more definite information on the molecular complexity of aluminium alkyl or other alkyls.

(XIV.)



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