

64. *The Structure of the Boron Hydrides.*

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It is suggested that the hydrides of boron contain the hydrogen bridge linkage $>B \begin{array}{c} \text{H} \\ \text{H} \end{array} B <$, which can be formulated as a resonance hybrid between structures containing only normal electron-pair bonds. It is shown that this type of linkage is intrinsically no less probable than the accepted resonance structure containing one-electron bonds, and that boron and gallium are the only elements known to form covalent hydrides which would be expected to contain such a linkage. The borohydrides of beryllium and aluminium are naturally accounted for by the same hypothesis. The experimental data for the electron diffraction, Raman spectrum, infra-red spectrum, and specific heat of diborane are analysed and shown to support a bridge configuration rather than one resembling ethane. Structures are suggested for the higher boron hydrides.

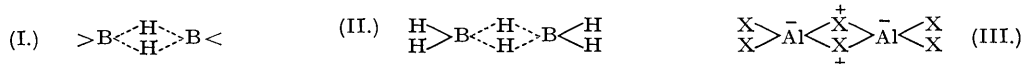
THE molecular formulæ of the hydrides of boron cannot be accounted for in terms of normal electron-pair links, since the total number of electrons present in the outer shells is not sufficient for this purpose. A formulation containing purely ionic links is at variance with the properties of the substances concerned, and it is therefore necessary to postulate some abnormal type of linkage. A number of structures involving one-electron links have been proposed, and the current view is that the boron hydrides can be represented as resonance structures in which each bond is a hybrid between a two-electron link, a one-electron link, and a state in which there is no linkage; for instance, diborane, B_2H_6 , is supposed to have the same configuration as ethane, every link in the molecule having this hybrid character. The interpretation of the chemical and physical properties of the boron hydrides in terms of this type of structure has been summarised in two recent reviews (Schlesinger and Burg, *Chem. Reviews*, 1942, 31, 1; Bauer, *ibid.*, p. 43).

There are, however, a number of difficulties connected with this hypothesis. The one-electron link is not met with elsewhere in chemistry except in the transient species H_2^+ , which, having only one electron, has no alternative. This species can thus hardly be compared with diborane, where the "abnormal" molecule B_2H_6 appears to be more stable than the "normal" (but hypothetical) system $2BH_3$, in which all the electrons are paired. The diamagnetic character of diborane and the fact that every known hydride of boron contains an even number of valency electrons do not follow naturally from the assumption of one-electron links, and suggest rather some structure in which all the electrons are paired. Moreover, it has proved very difficult to account for the observed Raman and infra-red spectra of diborane on the basis of a configuration resembling ethane.

It is the purpose of the present paper to show that another type of resonance linking is intrinsically no less

probable than the usually accepted one, and that it leads to a configuration in better harmony with the experimental facts. We shall deal mainly with the physical evidence, since most of the chemical facts can be explained equally well on either hypothesis. Adequate physical data are available only for diborane, but the problem of the higher hydrides of boron will also be treated briefly.

The Bridge Structure.—The type of structure which we advocate contains linkages which may be written as in (I), there being no direct link between the two boron atoms. Diborane, for example, is written as (II),



where the terminal B-H bonds are normal two-electron links, and the four valencies are arranged tetrahedrally about each boron atom. This structure bears a close resemblance to the accepted one for the dimeric aluminium halides, *viz.*, (III) (where X is a halogen), but differs essentially from that of ethane. It was first proposed by Dilthey (*Z. angew. Chem.*, 1921, **34**, 596; cf. also Core, *Chem. and Ind.*, 1927, **5**, 642), who did not, however, make any suggestion as to the nature of the bridge linkages. More recently, it has been pointed out that the bridge linkage can be formulated as a resonance hybrid between either of the following pairs of equivalent structures, (IVa) and (IVb). Resonance between the covalent structures (IVa) has been suggested by Nekrassov



(*J. Gen. Chem. Russia*, 1940, **10**, 1021, 1156), and the ionic structures (IVb) are favoured by Syrkin and Diatkina (*Acta Physicochim. U.R.S.S.*, 1941, **14**, 547), but no thorough discussion has been given of the theoretical implications or practical consequences of these formulæ.

Since all the resonance forms suggested contain only paired electrons, the bridge linkage provides a ready explanation of the diamagnetic character of diborane, and of the fact that every known hydride of boron contains an even number of electrons. The absence of a direct link between the boron atoms accounts for the ease with which the various hydrides are interconverted, and the facility of reactions like $B_2H_6 + 2CO \longrightarrow 2\bar{B}H_3^+CO$, $B_2H_6 + 2NMe_3 \longrightarrow 2\bar{B}H_3^+NMe_3$, $B_2H_6 + 2NH_3 \longrightarrow NH_4^+[BH_3^-\cdot NH_2^-\cdot BH_3^-]$, etc. It is also significant that mono-, di-, tri-, and tetra-methyldiborane are all known, but that attempts to prepare the penta- and hexa-methyl compound have failed; moreover, hydrolysis shows that neither the tri- nor the tetra-methyl compound has more than two methyl groups attached to the same boron atom. The one-electron link hypothesis provides no reason for this behaviour, but it is explained by the bridge structure, which requires at least one hydrogen on each boron atom. Similarly, trimethylboron is known, but not the di- or the mono-methyl derivative, which presumably dimerise through their hydrogen atoms to give tetra- and di-methyldiborane, respectively.

The Nature and Occurrence of the Resonance Link.—The linking of two boron atoms through a bridge of two apparently bivalent hydrogen atoms can be formally described as a pair of "hydrogen bonds," but it differs essentially from the linkage which occurs, *e.g.*, in the association of compounds containing hydroxyl or imino-groups. The latter classes of hydrogen bonds were at one time attributed to resonance of the type $\{X-H \cdot Y, X \cdot H-Y\}$ (see, *e.g.*, Sidgwick, *Ann. Reports*, 1933, **30**, 112) but are now believed to depend on electrostatic attraction between a dipole $\overset{+}{X}-\overset{-}{H}$ and an unshared pair of electrons on the atom Y (cf. Pauling, "The Nature of the Chemical Bond," Chap. 9, 1940). This kind of linkage is very unlikely to occur in the boron hydrides, since the link $>B-H$ will have a much smaller dipole moment than $-OH$ or $>NH$, and there are no unshared electrons on the (hypothetical) molecule BH_3 . We shall therefore use the term "resonance link" for the bridge linkage in the boron hydrides, in order to distinguish it from the more usual type of hydrogen bond.

There is a considerable amount of both theoretical and experimental evidence that resonance between equivalent bond assignments can contribute greatly to the stability of a system, though it is not usually considered that two parts of a molecule can be held together solely by such resonance stabilisation. Thus, from the fact that the reaction $H + H_2$ (para-hydrogen \longrightarrow ortho-hydrogen) has an activation energy of only about 9 kg.-cals./mole, we can conclude that the lowest energy for the symmetrical configuration $H \cdots H \cdots H$ is 90 kg.-cals./mole lower than that of three hydrogen atoms, though it is still slightly higher than that of the system $H + H_2$, and therefore constitutes an activated state rather than a stable molecule. The formation of a stable molecule by resonance will be opposed by the energy needed to stretch the links of the constituent parts and to bring these parts close together, but there is no theoretical reason why this expenditure of energy should always exceed the resonance stabilisation. Theoretical calculations of the energy are subject to many uncertainties. Even in the simple case $H \cdots H \cdots H$ the calculated values differ considerably from the observed one, and in other cases the usual simplified treatment predicts the existence of stable molecules $H \cdots H \cdots CH_3$ and $Cl \cdots Cl \cdots Cl$, for which there is no experimental evidence (Gorin, *Acta Physicochim. U.R.S.S.*, 1938, **9**, 691; Gorin, Kauzmann, Walter, and Eyring, *J. Chem. Physics*, 1939, **87**, 633; Rollefson and Eyring, *J. Amer. Chem. Soc.*, 1932, **54**, 2661). We are therefore unable to attach much weight to the calculations given by Syrkin

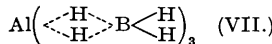
and Diatkina (*loc. cit.*) for the resonance link in the boron hydrides, since they depend on similar simplifying assumptions and do not take into account the repulsion between electrons attached to different atoms. In particular, we do not believe that there is yet sufficient evidence to prefer either the covalent structures (IVa) or the ionic structures (IVb) as representing the state of the resonance link. Either set represents an equivalent pair of bond assignments and will lead to a resonance stabilisation : on the other hand, appreciable resonance between the two sets will only occur if their energies happen to be close enough together. The ionic structures do not conflict with the high volatility of the boron hydrides, since the resonance hybrid will have no dipole moment.

An apparent difficulty connected with the bridge configuration is the close approach of the two boron atoms. If the B...H links are not to be much longer than the normal B-H distance, the distance between the two borons cannot exceed about 2 Å., and electron-diffraction measurements do in fact give a value of 1.8 Å. for this distance in diborane (see below). The closest distance of approach of two unlinked atoms is usually taken as 3.0—3.5 Å., and the energy expended against repulsive forces in reducing this distance to 1.8 Å. would be so great as to out-weigh the resonance stabilisation. We believe, however, that this difficulty is only an apparent one. The experimental evidence on the repulsion of unlinked atoms relates mainly to atoms having unshared electrons in their outer shells (*e.g.*, -Cl, >O, >N) and to directions of approach far removed from the bonds attached to these atoms. Under these conditions the repulsion is chiefly due to the unshared electrons. On the other hand, in every resonating structure proposed for the boron hydrides the boron atoms have no unshared electrons in their outer shells, and the electron density in the line joining the two borons will be low : hence the repulsion between them will be much lower than in the general case of unlinked atoms. There will, of course, be repulsion between the nuclei and between the *K*-shells of electrons, but the radius of the latter in boron is only about 0.12 Å. (*cf.* Bartlett and Dunn, *Physical Rev.*, 1933, **44**, 296). It is therefore quite reasonable to suppose that the two unlinked boron atoms in the bridge can approach to a distance of 1.8 Å. without any great expenditure of energy.

The same kind of consideration explains why the resonance bridge link is not formed by other hydrides, notably ammonia, water, and hydrogen fluoride. If a hypothetical dimeric bridge structure is written for any of these compounds, *e.g.*, (V), it will be found that every resonance form contains one or more pairs of unshared electrons on the central atoms. The resulting repulsion renders the bridge structure impossible, and the polymerisation of these hydrides therefore takes place only by the familiar "hydrogen bond," giving chain polymers of indefinite length. In other cases, *e.g.*, methane and hydrogen sulphide and chloride, there is no appreciable polymerisation by either mechanism.

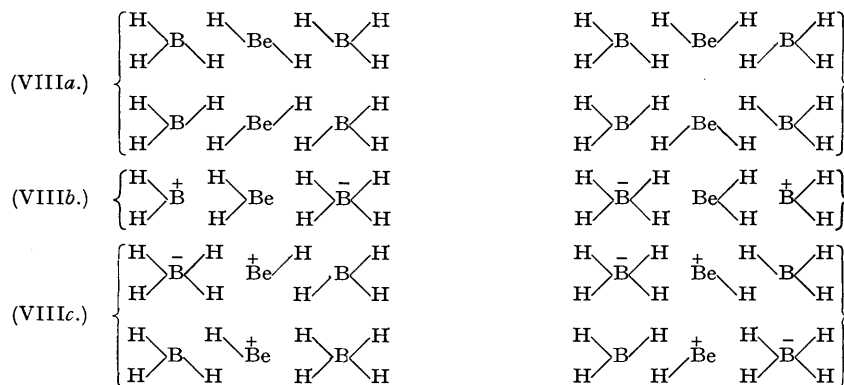
In general, we should expect to find polymerisation by the resonance bridge mechanism in any covalent hydrides XH, XH₂, or XH₃ having no unshared electrons in the outer shell. These hydrides would occur in the first three groups of the periodic table, or among the transition and rare-earth elements. Until recently, boron was the only element known to form covalent hydrides fulfilling the necessary conditions, but a volatile gallium hydride, Ga₂H₆, has now been reported having properties very similar to those of diborane (Wiberg and Johansen, *Angew. Chem.*, 1942, **55**, 38). The only other well-defined hydrides formed in the appropriate part of the periodic table are salt-like in character (*e.g.*, Li⁺H⁻), so the resonance bridge hypothesis thus accounts satisfactorily for the unique position occupied by the boron and gallium hydrides. Some indications of hydride formation have been observed in the action of atomic hydrogen on the elements silver, copper, gold, beryllium, indium, and thallium (Pietsch, *Z. Elektrochem.*, 1933, **39**, 577), the products being non-volatile (except in the last two cases) and stable at fairly high temperatures. They are decomposed by water with the evolution of hydrogen and were regarded by Pietsch as salts containing the anion H⁻. However, it seems unlikely that these relatively noble metals should form stable hydrides of a type so far known only for the strongly electro-positive alkali and alkaline-earth metals, and it is possible that the products obtained are covalent hydrides polymerised through a bridge linkage. It may be noted that a hydride XH₂ containing no unshared outer electrons can polymerise by resonance bridges to form long-chains polymers of indefinite length, while XH and XH₃ are limited to dimerisation.

Aluminium hydride has not been prepared in a pure state, although according to Wiberg and Stecher (*Angew. Chem.*, 1939, **52**, 372) there is little doubt that it is dimeric. Moreover, both beryllium and aluminium form well-defined volatile mixed hydrides with boron, BeB₂H₈ and AlB₃H₁₂ (Schlesinger *et al.*, *J. Amer. Chem. Soc.*, 1940, **62**, 3421, 3425, 3429). Hitherto, two types of structure have been proposed for these compounds, first, the ionic structures Be⁺⁺(BH₄⁻)₂ and Al⁺⁺⁺(BH₄⁻)₃, and secondly, resonance covalent structures involving single-electron links in which boron has a covalency of five. Although the salt-like compound LiBH₄ undoubtedly has an ionic structure, such a structure seems inappropriate for the most volatile beryllium and aluminium compounds known, and a covalency of five is not met with in other boron compounds, or elsewhere in the first short period. In terms of the bridge linkage these compounds appear naturally as (VI) and (VII),



the valencies being arranged tetrahedrally round beryllium and boron, and octahedrally round aluminium. This disposition of valencies predicts that the three boron atoms in AlB₃H₁₂ will be at the vertices of an equilateral triangle with the aluminium at the centre, as is found by electron diffraction (Beach and Bauer, *J. Amer. Chem. Soc.*, 1940, **62**, 3440). The bridges in these compounds can be interpreted in terms of resonance

structures analogous to those for diborane : for example, in BeB_2H_8 we have the possibilities (VIII, *a*, *b*, and *c*). [The four covalent bond assignments in (VIIIa) are actually all equivalent, and the apparent difference between



the first and second pairs is due to the planar representation employed.] The unstable compound $\text{CH}_3 \cdot \text{BeBH}_4$ can be similarly formulated as (IX).



There is only one case in which the resonance bridge link fails to appear in apparently favourable circumstances, and that is in hydrogen itself, where the structure (X) might be expected. (The formation of H_4 from 2H_2 must actually be considerably endothermic, since the conversion of para- into ortho-hydrogen does not take place appreciably by direct interchange between two hydrogen molecules.) We have already seen that $\text{H} \cdots \text{H} \cdots \text{H}$ only just fails to be a stable molecule, and the distinction between the existence of B_2H_6 and the non-existence of H_4 may depend only on the relative magnitude of exchange and repulsion energies. On the other hand, H_4 can only be formulated in terms of covalent bond assignments, since the analogous resonance structure to $\text{BH}_2^+ \text{BH}_4^-$ would be $\text{H}^+ \text{H}_3^-$, which cannot exist. This suggests that a resonance link may only be stable when it is formed partly or entirely from ionic structures, which can be achieved by the simple and mixed boron hydrides, but not by hydrogen itself.

Physical Evidence for the Structure of Diborane.—The evidence discussed in this section relates chiefly to the disposition of the boron and hydrogen atoms in space, and is largely independent of particular assumptions about the nature of the links involved. We consider that, as a whole, it favours the bridge configuration rather than one resembling ethane.

Electron diffraction. Electron diffraction by gaseous diborane has been studied by Bauer (*J. Amer. Chem. Soc.*, 1937, 59, 1096), who originally interpreted his observations on the basis of the ethane model and obtained 1.86 Å. and 1.27 Å. for the B-B and the B-H distance respectively. These distances are larger than the expected single-bond values, which lent support to the idea of one-electron or "no electron" bonds. More recently, Bauer has compared his results with the bridge structure (*Chem. Reviews*, 1942, 31, 43, and private communication from the author; cf. also Diatkina and Syrkin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1942, 35, 180). The qualitative features of the observed curve are predicted equally well by the ethane structure and by the bridge structure, except that the latter fails to predict the faint inner peak observed at small scattering angles. When the calculated positions of maxima and minima are compared with the observed ones, agreement is good for both models, except that the unresolved maximum observed at $s = 11.9$ is predicted more correctly by the bridge model ($s = 12.1$) than by the ethane model ($s = 13.2$). For the remaining maxima and minima the mean deviations are 1.7% and 1.9% for the bridge and for the ethane structure, respectively. The results of electron diffraction thus do not lead to any clear-cut decision between the two structures. Bauer considers that the bridge structure can be eliminated on account of its failure to predict the faint inner peak, but in view of the other arguments advanced in this paper we shall not regard this objection as final.

The dimensions derived by Bauer for the bridge structure accord well with its formulation as a resonance linkage. He finds 1.79 Å. for the distance between the two boron atoms, terminal B-H = 1.18 Å., ring B \cdots H = 1.39 Å., terminal angle H-B-H = 120°, ring angle H \cdots B \cdots H = 100°. The terminal B-H distance agrees within the experimental error with the value 1.21 Å. given by Bauer and Beach (*J. Amer. Chem. Soc.*, 1941, 63, 1394) and with 1.20 Å. found experimentally in the compound $\text{H}_3\text{B}^-\text{CO}^+$ (Bauer, *ibid.*, 1937, 59, 1804). On the other hand, the B \cdots H distance in the ring is greater than this, as would be expected for a resonance link having only one-half single-bond character. The repulsion between the boron atoms has lowered the ring angle to somewhat less than the normal tetrahedral angle, and there is a corresponding increase in the terminal angle. Bauer (*Chem. Reviews*, 1942, 31, 46) has used these dimensions as an argument against the bridge structure, but he assumes that the boron atoms are connected directly by a link as well as indirectly through the hydrogens which leads to an unacceptable orientation of five valencies round each boron.

Electron bombardment. Hipple (*Physical Rev.*, 1940, 57, 350) has found that when diborane is bombarded with electrons, the ions formed include B_2^+ and B_2H^+ , and the formation of these two species has been quoted

as strong evidence against the bridge structure (Bauer, *loc. cit.*, p. 72). However, it should be noted that each of the ions $B_2H_3^+$, $B_2H_2^+$, B_2H^+ and B_2^+ contains enough electrons to form normal electron-pair links throughout. Either type of resonance link (one-electron or bridge) would be replaced by normal links as soon as enough hydrogen atoms had been removed from the diborane molecule, and the formation of the observed ions thus gives no information about the structure of diborane itself.

Vibrational spectrum. Both the Raman and the infra-red spectrum of diborane have been observed (Anderson and Burg, *J. Chem. Physics*, 1938, **6**, 586; Stitt, *ibid.*, 1941, **9**, 780) and their interpretation in terms of the ethane model has been attempted, though with little success. The infra-red spectrum is far more complicated than that of ethane, and in particular, there are too many strong lines of low frequency which cannot be regarded as overtones or combination tones and will not fit into any theoretical scheme. In order to meet this difficulty, Stitt (*loc. cit.*) has postulated the existence of one or more low-lying electronic levels, and gives two tentative assignments of frequencies on this basis. However, there is no independent evidence for the existence of these levels in diborane or in any similar molecules, so the explanation is hardly convincing. The same difficulty appears in a simple form in the Raman spectrum, where the two most intense lines are at 2102 and 2523 cm^{-1} . From their intensity they must be fundamental vibrations of a completely symmetrical type, and their frequencies both lie in the range expected for stretching vibrations of the B-H link. However, the ethane-like structure predicts only *one* symmetrical type of B-H stretching vibration, and Anderson and Burg (*loc. cit.*) could only suggest that this pair of lines might be due to a resonance splitting, although the difference of 421 cm^{-1} is about 10 times as great as the normal separation of a resonance pair.

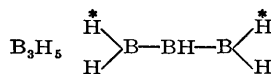
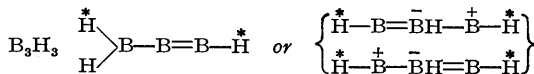
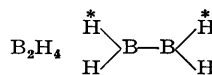
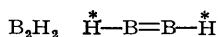
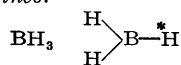
The vibrational spectrum can be explained without difficulty on the basis of the bridge structure for diborane. (This fact is mentioned by Stitt, *loc. cit.*, but dismissed without further consideration.) We shall publish elsewhere a complete vibrational analysis, but the main points can be stated briefly. The bridge molecule has the same symmetry characteristics as ethylene (three perpendicular planes of symmetry), and none of its vibrational modes is degenerate. There are hence 18 distinct vibrational frequencies (compared with 12 for ethane), of which 9 can appear in the Raman spectrum, 8 in the infra-red, and one is inactive. Moreover, since there are two different kinds of B-H binding, the number of frequencies in the range corresponding to bond-stretching is twice as great as for ethane. This increase in the number of fundamental frequencies clears away the difficulties encountered with the ethane model, and in particular, the two intense Raman lines 2523 and 2102 cm^{-1} can be pictured (somewhat crudely) as due to symmetrical stretching vibrations of the terminal B-H groups and the ring respectively. The observed vibrational spectrum thus lends strong support to the bridge configuration, and constitutes probably the strongest single piece of evidence in its favour.

Specific heat. The specific heat of diborane has been measured between 95° and 324° K., and gives evidence of hindered rotation about the B-B axis (Stitt, *J. Chem. Physics*, 1930, **8**, 981). Assuming an ethane-like structure and a sinusoidal potential barrier, Stitt calculated the height of this barrier to be 4000—6000 cal./mole, compared with 3000 cal. for ethane itself. Later calculations taking into account the supposed low electronic levels gave still higher values for the height of the barrier (*idem, loc. cit.*, 1941). Hindered rotation in ethane and similar molecules has been attributed either to interaction between the hydrogen atoms or to partial double-bond character in the central link. If ethane and diborane are similar molecules, it is remarkable on either hypothesis that there should be greater hindrance to rotation in diborane, since the hydrogens are further apart than in ethane, and double-bond formation between the borons is much less probable. On the other hand, the bridge structure automatically explains the resistance to rotation, and although the torsional oscillation cannot appear directly in the infra-red or Raman spectra, it should be possible to calculate its frequency from those of the other bending vibrations.

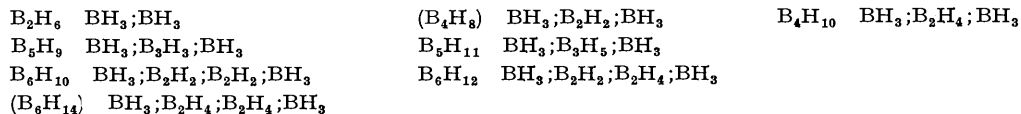
Crystal structure. The work of Mark and Pohland (*Z. Kryst.*, 1925, **62**, 103) on the structure of solid diborane is sometimes quoted as demonstrating its similarity to ethane. Actually, the X-ray observations give information only about the positions of the boron atoms in the lattice, and the further data given are deduced by assuming that the hydrogen atoms have the same arrangement as in ethane. Hence, although the crystal evidence is consistent with the ethane model, it provides no criterion for deciding between this and the bridge structure.

The Higher Hydrides of Boron.—There is little detailed physical information about these compounds, and we shall only show how far the bridge structure is able to predict or account for the formulæ of the hydrides so far known. There are many possibilities, and the structures given are intended only as suggestions. All the hydrides can be built up from "borines," which have normal electronic structures with tervalent boron but contain >B-H groups which can unite two borines by means of a bridge. The first few borines can be formulated as follows, an asterisk indicating a free >B-H. It should be noted that a given BH_3 or $-BH_2$ group can only take part in one resonance bridge, and we have also supposed that the group $>B-BH-B<$ in B_3H_5 shows no tendency to polymerise.

Borines.



This leads to the following formulæ for possible boranes containing six or fewer boron atoms, a semicolon being used to indicate a bridge linkage between two borines. The structures proposed contain no groups capable of further polymerisation, and are the only ones which can be constructed from borines containing up to three boron atoms.

Boranes.

This list includes all the known hydrides of boron except $B_{10}H_{14}$, and only two (B_4H_8 and B_6H_{14}) which do not correspond to known compounds. The bridge structure is thus reasonably successful in predicting the formulæ of the simpler boranes, and it may be particularly noted that no hydrides containing three boron atoms can exist on this hypothesis. If the list of borines is extended it is possible to write alternative structures for the last three hydrides, but not to formulate any new ones containing 6 or fewer boron atoms. Many higher boranes can be formulated, including $B_{10}H_{14}$, the only hydride with more than 6 boron atoms yet isolated.

Electron-diffraction studies have been carried out with B_4H_{10} , B_5H_9 and B_5H_{11} (Bauer and Pauling, *J. Amer. Chem. Soc.*, 1936, **58**, 2403; Bauer, *ibid.*, 1938, **60**, 805), and the results interpreted in terms of the one-electron resonance hypothesis. However, other possibilities are not excluded, and it would be of interest to compare the experimental curves with those derived from the bridge formulæ given above.

Our thanks are due to Professor S. H. Bauer for sending us details of his electron-diffraction calculations for diborane, and to Dr. L. E. Sutton for helpful discussion.

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