STRUCTURES AND PHYSICAL PROPERTIES OF THE HYDRIDES OF BORON AND OF THEIR DERIVATIVES

S. H. BAUER

Department of Chemistry, Cornell University, Ithaca, New York

Received August 23, 1940

CONTENTS

I. INTRODUCTION

Physical methods of investigation have proved very helpful in deducing the configurations of a number of the hydrides of boron and of their derivatives. Where such technics have been successfully applied, the spatial arrangements of the atoms within the molecules as given by the interatomic distances and bond angles are no longer in doubt; for a few compounds the force constants of the molecular vibrations as well as other physical characteristics have also been determined. The immediate problem is the assignment of electronic structures compatible with the available information.

Parallel to the conclusions based on the chemical behavior of the boron compounds, the results of x-ray and electron-diffraction studies and of absorption and Raman-spectral measurements point to interesting similarities as well as to sharp contrasts to the corresponding carbon analogs. The basic dissimilarity between the two elements is the remarkable ability of boron to participate in a large variety of bond types; that this difference becomes evident when one compares the hydrocarbons with the boranes will be indicated below. The structural data will first be presented and discussed; electron configurations for the boranes and some of their derivatives will be suggested. Included also will be a summary of several sets of thermodynamic functions (derived from structural data on the one hand, and directly from specific heats and heats of combustion on the other), as well as the results of measurements of dielectric constant, magnetic susceptibility, and surface tension. Since the subject matter has appeared in the literature after the publication of Stock's monograph (62), it is presented in considerable detail.

II. RESULTS OF ELECTRON-DIFFRACTION MEASUREMENTS

As a tool for determinations of molecular structure the electron-diffraction method needs no justification in this review. It appears to be ideally suited for sufficiently volatile compounds which are available only in small quantities and which are not stable for a matter of days or even hours. The final structures are deduced by means of a stochastic process; to date, all conclusions have been found to be in agreement with chemical intuition, and have been repeatedly confirmed by x-ray and band-spectral investigations.

Experimental details and the various methods of reducing the data are adequately described in the reviews of Brockway (12) and of Maxwell (35). It should be noted that in an electron-diffraction study two items of information are determined,—the atomic configuration and the interatomic distances. Most of the molecules investigated had previously been assigned configurations on the basis of purely chemical data, and these have been unambiguously confirmed by the diffraction experiments; the problem was relatively simple, as it involved only the determination of the distances between atoms in the given model. For compounds in which the question of configuration had not been settled, as was the case for the boranes, the number of models which one had to consider and eliminate at first appeared tremendous. However, by limiting oneself to the known valence numbers of the elements present, and by considering their probable radii and the radial distribution curve (which is obtained directly from the photographs without reference to a particular model), one could eliminate all but a few of the conceivable configurations. The problem was thus resolved to treating in detail a small number of models by varying the interatomic distances and valence angles until (*a*) a particular model was found for which the computed intensity curve agreed with the one observed, both as to the qualitative appearance of the pattern and as to the quantitative positions of the diffraction rings, and (*b*) all the remaining models were proved unsatisfactory in spite of such variations. Only then could one state that a complete structural determination had been made.

It is clear that for the hydrides of boron, where all types of *ad hoc* linkages have been postulated, some specific while others inherently vague, it is not feasible to make a complete structural determination in the sense of (*b*) above. Rather than attempt to study every one of the models that have been or possibly will be proposed, the investigator considered only those atomic arrangements which appeared to him most likely, and rests his case upon the fact that the configuration he selected from among these is in complete agreement not only with the electron-diffraction data, but also with all the available physical and chemical information. Furthermore, extensive experience has shown that when the computed intensity curve for a specific model checks with the observed pattern, it is very unlikely that a totally different model will also agree. However, each compound should be treated individually, and safe predictions may then be made to decide whether two configurations are sufficiently unlike. For example, with the visual method of interpreting electron-diffraction photographs, normal pentane may be distinguished from neopentane, but not readily from isopentane.

A question has often been raised as to whether it is possible to determine the positions of hydrogen atoms in a borane without the use of a rotating sector (17). A simple computation will show that for molecules containing large numbers of *equivalent* hydrogen atoms this is quite possible. Thus, for a hydride of boron represented on the average by n BH_2 groups, the scattered electron intensity is essentially determined by the following terms:

TABLE 1

Results of electron-diffraction studies of hydrides of boron

COMPOUND	REFERENCE	DEFICIENCY*	STRUCTURE CORRESPONDING TO†	B—B	B—H	OTHER DISTANCES
BH............	(27)	0	(Spectroscopic)		1.225	
B_2H_6..........	(3)	2	Ethane	1.86±0.04	1.27±0.03	
B_4H_{10}..........	(6)	4	Butane	1.84±0.04	1.28±0.03	
B_5H_{11}..........	(6)	4	Pentane or isopentane	1.81±0.03	1.26±0.03	
B_5H_9..........	(7)	4	Methylenecyclobutane	1.76±0.02	1.17±0.04	
H_3BCO........	(4)	0	Ketene		1.20±0.03	B—C = 1.57±0.03 C—O = 1.13±0.03
$(CH_3)_3N:BH_3$.	(4)	0	Neopentane			B—N = 1.62±0.15 N—C = 1.53±0.06
B_2NH_7........	(5)	2(?)	(Dimethylamine)		(1.20)	B—N = 1.56±0.03
$B_3H_3H_6$........	(5, 65)	0	Benzene			B—N = 1.44±0.02
$Al(BH_4)_3$......	(9)	6	Trivalent aluminum, planar; boron in trigonal bipyramid		1.27±0.04	Al—B = 2.14±0.02

* This column refers to the "electron deficiency" of the molecule, defined as twice the number of valence bonds minus the number of valence electrons.

† This column gives the structural type.

$$I(s) = 12n\frac{\sin as}{as} + 24(n-1)\frac{\sin bs}{bs} + 25(n-1)\frac{\sin cs}{cs} + 25(n-2)\frac{\sin ds}{ds}$$
$$+ \text{ terms involving distances greater than } d$$

where a = boron–hydrogen distance,
c = boron–boron distance,
$b = \sqrt{a^2 + c^2 + 0.666ac}$ (assuming tetrahedral valence angles), and
$d = 1.633c$ (assuming tetrahedral valence angles).

Clearly, the first two terms which involve the boron–hydrogen distance are almost as important as the subsequent ones, so that it is feasible to fix the positions of the hydrogen atoms in this manner.

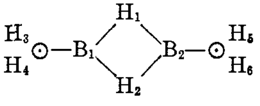
Once the atomic configuration is established, the interatomic distances may be obtained to an accuracy which depends on the complexity of the molecule and the patience of the observer (12, 35, 67). The most recent calibration of the visual method of interpreting electron-diffraction photographs has been undertaken by Schomaker and Stevenson (57); they found that in favorable cases an accuracy of 0.5 per cent is possible (comparison made with values deduced from band-spectra measurements). Because of the low atomic number of the scatterers, considerably larger limits of error have been assigned to the interatomic distances quoted for the boranes; the limits given are, however, on the conservative side.

In table 1 the results of electron-diffraction studies of several hydrides of boron are summarized.

The simplest of the hydrides has only spectroscopic stability. It is analogous in many respects to the diatomic hydrides of carbon and nitrogen; the interatomic distance quoted was deduced from its moment of inertia. Concerning the next three hydrides, it was stated above that many of the structures previously suggested (70) do not correspond to a definite geometric form and hence were not considered in detail. It soon became clear that, for diborane, an ethane-like model with the ratio B—B/B—H = 1.47 was in good agreement with the data[1]; B_4H_{10} and B_5H_{11} presented a similar case. For the latter compound the photographs were not sufficiently good to permit distinguishing between a pentane-like and an isopentane-like configuration. A point of interest with regard to internal rotation may be mentioned here. Although electron-diffraction photographs definitely eliminate rigid configurations for B_4H_{10} and B_5H_{11}, they cannot be used to determine whether a restricting potential of several kilocalories or complete freedom of rotation exists about the B—B bonds. However, the configuration of B_5H_9 is somewhat strange, were one to reason by analogy from the corresponding carbon compounds. Whereas the cyclobutanes are less stable than their aliphatic chain analogs, this pentaborane, as well as hexaborane and decaborane, differ from the other hydrides in that they form a group of relatively greater stability. To provide further confirmation of the structure given in the table for B_5H_9, electron-diffraction photographs of methylenecyclobutane were taken (8). The form of the pattern was found to be identical with the one for the pentaborane except in the shape of one peak,

---

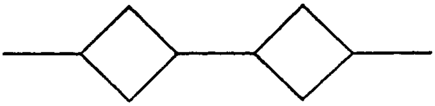
[1] In the original investigation (3) only ethane-like and ethylene-like (70) models were studied. The large B—B/B—H ratio definitely eliminates the latter, for which a value near 1.35 is to be expected. Very recently, interest in the configuration wherein two hydrogen atoms form a bridge between the boron atoms (18, 15) was again revived, with the



($B_1H_1H_2B_2$ in a plane perpendicular to the plane of $H_3H_4B_1B_1H_5H_6$)

hope that it would provide a simple explanation for the rather complex infrared spectrum observed by Stitt (61). The question then arose whether the electron-diffraction data contradicted such an assumption. Intensity curves were computed for this model for various B—B/B—H ratios and boron valence angles. Only by assuming distorted bond directions ($<H_1B_1H_2 = 100°$, $<H_3B_1H_4 = 120°$, and B—B/B—H = 1.79/1.18) could agreement be obtained between the predicted and observed intensity of electron scattering for values of s_0 between 4.5 and 20. However, this bridge model *fails* to predict the appearance of a small inner peak at about $s_0 = 3$, as is observed on both the diborane and the ethane photographs, and hence can be eliminated. The results of several other experiments lead to the same conclusion; these will be discussed in detail below.

just as predicted from the computed curves. It has been suggested (7) that B_6H_{10} has a dimethylcyclobutane-like structure, and that the configuration of $B_{10}H_{14}$ is a double four-membered ring with BH_3 groups at the two ends:



In borine carbonyl the B—C—O atoms are linearly arranged, with boron tetrahedrally bonded to three hydrogens and a carbon. However, the compound B_2NH_7 requires further elucidation; there is still some doubt whether its configuration is $H_3B{:}NH{:}BH_3$, as in dimethylamine, or $H_2B{:}NH_2{:}BH_3$. Schlesinger and coworkers (54) give several arguments, based on the chemical behavior of the substance, which favor the second of the two atomic arrangements; all but one (the fact that only one molecule of ammonia is added with the formation of a B—N link) may be equally well accounted for by the first, assuming resonance between several Lewis structures, as will be discussed below. The electron-diffraction data strongly support the dimethylamine-like configuration, but do not definitely eliminate the second, provided both boron–nitrogen distances are assumed equal. The structure of $B_3N_3H_6$ is analogous to that of benzene.

The structure of AlB_3H_{12} can best be represented diagramatically as shown in figure 1.

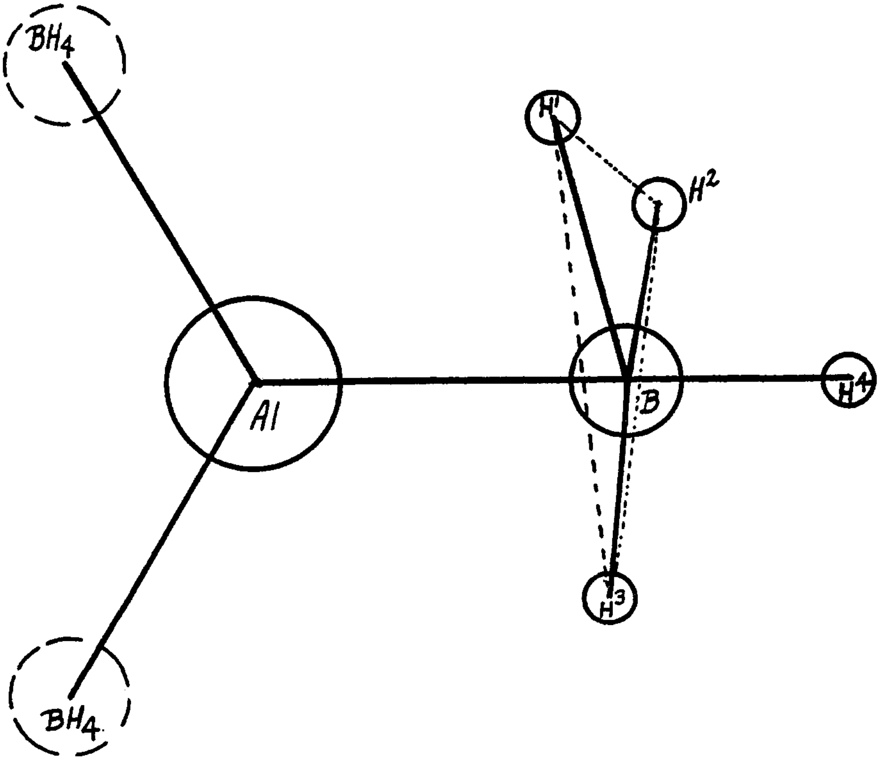


FIG. 1. $Al(BH_4)_3$

$\angle \mathrm{AlBAl} = 120°$ $\angle \mathrm{AlBH}^2$ (or H^1, H^3) $= 85°$ $\angle \mathrm{AlBH}^4 = 180°$

The boron atom is not quite at the center of an asymmetric trigonal bipyramid; the steric requirement that non-bonded hydrogen atoms (H^4 and H^1, H^2, H^3) be approximately 2 Å. apart forces the $\angle \mathrm{AlBH}^1$ to be less than 90°. The available chemical data (55), although meagre, are in harmony with the above arrangement of atoms. The structures of the other metallo borohydrides (BeB_2H_8 and $LiBH_4$) are very likely analogous to that of the aluminum compound (14, 53).

III. RESULTS OF X-RAY STUDIES OF CRYSTAL STRUCTURE

As yet, no complete structure determination has been made of crystals of any boron hydride or of a derivative. Powder photographs of diborane at liquid-air temperatures have been taken by Mark and Pohland (34). These investigators found a complete similarity between the structures of ethane and of diborane. In both cases the crystals are hexagonal; the space group is D_{6h}^4, with four molecules per unit orthohexagonal cell.

TABLE 2

Results of x-ray studies of crystal structure

	B_2H_6	C_2H_6
a	7.89 Å.	7.74 Å.
b	4.54 Å.	4.46 Å.
c	8.69 Å.	8.19 Å.
c/b	1.91 Å.	1.84 Å.
n	4	4
X—X (in molecule)	1.8–1.9 Å.	1.5–1.6 Å.
Distance between axes of adjacent molecules	4.54	4.45
Volume per molecule in lattice	78.0 Å.^{3}	70.6 Å.^{3}

To place the boron (or carbon) atoms, only one parameter had to be determined. The final results of this study are given in table 2. Even though the hydrogen atoms could not be located, the close parallel between the two unit cells strongly indicates a similar disposition of the hydrogen atoms in ethane and in diborane.

Möller (36) worked with single crystals of decaborane. He reported that the crystals are rhombic bipyramidal and that the space group is V_h^{21}, with two molecules per unit cell: a = 14.46 Å., b = 20.85 Å., c = 5.69 Å. He was further able to demonstrate that the molecules must have one of the following symmetries: C_i, C_2, or C_s. Hence he concluded that, if $B_{10}H_{14}$ is a chain, it must be strongly bent or folded; a more reasonable proposal presented by Möller is that the compound has a double-ring structure analogous to that of naphthalene; the structure suggested by Bauer and Pauling (7) is another possibility.

Debye–Scherer photographs of a number of salt-like compounds of alkali metals with these hydrides have been published (10, 63). The crystals thus studied are $Na_2B_2H_6$, $K_2B_2H_6$, CaB_2H_6, $K_2B_4H_{10}$, $Na_2B_4H_{10}$, and $K_2B_5H_9$. Very little data are given in the reports. Since analyses have not yet been offered by the investigators, a number of interesting problems are thus open to those working on crystal structure.

IV. DEDUCTION OF ELECTRONIC CONFIGURATIONS FROM MOLECULAR STRUCTURES

From the above structures and other physical data it is possible to deduce a number of interesting conclusions regarding the electronic configurations of the boranes. However, to establish a common basis for discussion we shall summarize briefly two well-established points.

A. Even when electron configurations are known as well as we may ever hope to know them, as is the case at present for atoms, diatomic molecules, and a few polyatomic molecules, the concept is essentially an approximation. To a greater or lesser extent, the electrons belong to the molecule as a whole and there are continual exchange interactions between them, but the approximation of assigning given numbers of electrons to particular orbitals is a fairly good one for the inner-shell (atomic) electrons, and is a convenient book-keeping scheme, though perhaps not a rigorous one, for the valence (*atomic* or *molecular*,—depending on the point of view) electrons. Clearly, it is not advisable to localize valence electrons too specifically.

B. There are two methods of approach to the problem of the distribution of valence electrons in a molecule (68). In the zero-order approximation of the atomic orbital scheme, all electrons are placed in somewhat modified atomic orbits but every valence electron is permitted to occupy one orbital in each of two adjacent atoms,—these orbitals being so chosen that the density of electricity extends in the direction of the bond. (An *atomic orbital* is defined as a one-electron wave function for an electron moving in the field of only one atom.) To form an electron-pair bond there are needed two electrons with opposed spins and a stable orbital in each of the two bonded atoms. The Lewis electron-pair bond is thus incorporated in quantum-mechanical discussions of valence. However, many molecules, among them the boranes, cannot be simply represented by atoms attached to one another by Lewis bonds. To them it may be possible to assign more than one Lewis structure and, as a consequence, some of the bonds are single in one configuration, double or triple in another, etc. Since the ground state of the molecule is best represented by a linear combination of all the structures which possess the same symmetry, this combination having an energy lower than any of the component terms, it is customary to speak of the individual bonds as being a given fraction single, double, or triple.

In this review we shall refer only occasionally to the alternative point of view of assigning electron configurations by the method of molecular orbitals. The latter emphasizes the fact that the valence electrons occupy orbits which are characteristic of the molecule as a whole; thus, a *molecular orbital* is defined as a wave function which gives the probability density of only one electron and which is a solution of the dynamical problem involving all the nuclei and that electron, corrected for internuclear repulsions. Hence it is highly dependent on the symmetry of the atomic arrangement. A symbolism has evolved as a consequence of group theory considerations of the symmetry properties, but the final assignment of electrons to the various possible orbitals is based on a comprehensive study of the spectra, electric and magnetic susceptibilities, and ionization potentials and on a correlation of the energy levels of the whole ensemble of atoms with those of the smaller units comprising the molecule. Since the wave function for the whole molecule (containing n electrons) is approximated by a product of n molecular orbitals, the assignment of integral numbers to bonds becomes somewhat nebulous; the degree of "bonding," "non-bonding," or "anti-bonding" character exhibited by the electrons in a particular orbital varies with the atoms involved.

In spite of the fact that in some instances (i.e., in the discussion of hyperconjugation in methylacetylene and ethane (45)) the molecular-orbital description appears to be the less artificial of the two, the atomic-orbital method is the more familiar one to chemists. We shall therefore discuss the electron configurations of the hydrides of boron in terms of resonance among several Lewis structures and shall but briefly present the molecular-orbital configuration for diborane. Our approach is based on the assumption that the bond distance is a function of the density of bonding electrons between the atoms. Pauling and coworkers (46) were first to point out that a definite relation existed between *bond order* and the distance between adjacent atoms, the form of which depends on the definition selected for the term "bond order." For instance, one may compute for each bond in a molecule an order number by summing over all the electron pairs contributing to the bond, each weighted by the probability of its being at the bond under consideration. A recently published curve[2] for C—C bonds is reproduced in figure 2 (45). We have extrapolated the curve (dotted portion) towards the left, to bond orders less than unity; clearly, the interatomic distance would be greater when part of the time only one electron or no electrons occupied the orbitals forming the bond between adjacent atoms (46, Chapter VIII). (Compare, for instance, H_2, r_e = 0.749 Å., D_e = 4.454 volts

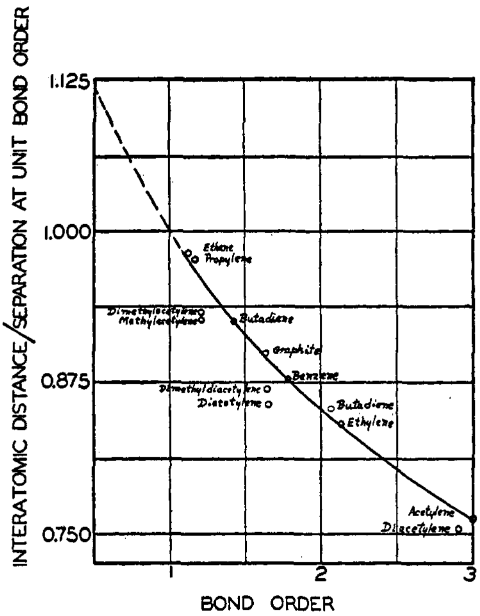


FIG. 2. The interatomic distance, with that for single bond taken as unity, is plotted along the ordinate and the degree of multiple bonding along the abscissa. C—C pure single bond = 1.58 Å., extrapolated. According to Mulliken *et al.*

---

[2] Similar curves have been published by Lennard-Jones and Caulson, Penney, and others. For further discussion and references see 45.

(electron-pair bond), with H_2^+, r_e = 1.070 Å., D_e = 2.62 volts (one-electron bond).) Parallel to the dependence of bond distance on bond order, relationships between the interatomic distance, the force constant for the stretching vibration, and the energy of dissociation of the bond have been proposed (33). It is reasonable to postulate that curves of the general form shown in figure 2 are applicable to pairs of atoms other than C—C. If, for a given pair, a single point on the curve is determined (such as the separation corresponding to unit bond order), one may thenceforth use it either to predict interatomic distances from computed bond orders or to deduce bond orders from observed distances, providing certain small corrections are applied to the distances between atoms, these being due to factors such as the extent of *s-p* hybridization (which is assumed to account for some points falling below the curve, in figure 2), the presence of formal charges, change in coördination number, forces between non-bonded atoms, etc.

After a study of many compounds, Pauling and Huggins (48) proposed a table of atomic radii; the sum of these radii for a given pair of atoms was the separation expected when they were held together by a single bond. According to this first approximation, the extent of the ionic contributions to the ground state of the molecule did not exert an observable influence on the interatomic distances. Recently a more successful procedure for predicting the interatomic distance for a given pair of atoms at unit bond order was proposed by Schomaker and Stevenson (56), in which the difference in electronegativity between the two atoms and thus the ionic character of the bond were taken into consideration. Their equation is

$$d_{AB} = r_A + r_B + \alpha \mid x_A - x_B \mid$$

where $\alpha = -0.09$, r_A and r_B are the tabulated radii (which differ somewhat from the values of Pauling and Huggins), and x_A and x_B are the positions of the atoms in Pauling's electronegativity table (46). Still better approximations may be proposed; in fact, R. S. Mulliken suggested that an expansion of the form

$$d_{AB} = r_A + r_B + \alpha_1(x_A - x_B)^2 + \beta_1(x_A - x_B)^4$$

has a more valid theoretical basis than the one given above. Regardless of the equation used, however, it is clear that, given an appropriate table of radii and values for the constants α and β, one can deduce from figure 2 the bond orders of various interatomic linkages when the corresponding interatomic distances are known. From these bond orders, a fair notion of the electronic configuration of the molecule can be obtained.

V. THE INTERATOMIC DISTANCES EXPECTED IN THE HYDRIDES OF BORON

As was pointed out in the introduction, one finds that boron enters into a wide variety of bonds, showing coördinations of 3, 4, and 5, with 4 as the most usual number. Previous to the suggestion of Schomaker and Stevenson (56), the observed interatomic distances for compounds of boron appeared to fall into two groups, those leading to a covalent radius of 0.88 Å., and those which could be satisfactorily accounted for only by assuming a radius close to 0.80 Å. Bauer and Beach have discussed this question (8) and have found that the difficulty is almost completely removed when the electronegativity difference between the atoms is taken into consideration. It is, therefore, instructive to compare table 1 with table 3.

The particularly large values observed for B—B *and* B—H *in* B_2H_6, B_4H_{10}, B_5H_{11}, B_5H_9, *and* $Al(BH_4)_3$ *lead to the supposition that in these molecules the bonds are of order less than unity; i.e., these bonds are weaker than single covalent ones,* as may be deduced from the upper extrapolated region of figure 2.

TABLE 3

Interatomic distances expected in boron compounds

ELEMENT	RADIUS	BOND	INTERATOMIC DISTANCE EXPECTED*
			Å.
B	0.85	B—B	1.70
H	0.37	B—H	1.21
C	0.77	B—C	1.57
N	0.74	B—N	1.50
Al	1.28	B—Al	2.08

* Schomaker and Stevenson.

VI. ELECTRONIC STRUCTURES OF THE HYDRIDES

A. Boron hydride, BH

The electron configuration of the diatomic hydride has been given by Mulliken (37) in terms of molecular orbitals; the ground state is best represented by

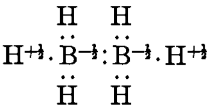
$$\text{BH:}\quad (1s_B^2)(2s\sigma)^2(2p\sigma)^2, \qquad {}^1\Sigma^+$$

Three excited states are known—$^3\Pi$, $^1\Pi$, and $^3\Sigma^+$—produced by raising the $(2p\sigma)$ electron to the higher $(2p\pi)$ state, but the equilibrium interatomic distances change little in going from one to the other. Values of the exchange integrals by means of which the energy of the hydride molecule may be expressed have been discussed and summarized by King (27).

B. Diborane, B_2H_6

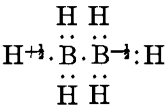
That both the B—B and B—H bonds in diborane would be of order less than unity was to be expected on the basis of the electronic structures suggested by Sidgwick (58) and Lewis (32); the proposed configurations have been discussed by Pauling (47) and Mulliken (42). Sidgwick's structure (formula I, below) gives each B—H two-thirds single-bond and one-third one-electron-bond character; hence the large B—H separation. A slight extension of this configuration considering resonance to structures such as II would further account for the observed increase in the boron-boron distance. The electron-diffraction data are equally compatible with Lewis' electron configuration, representing resonance among the seven structures III and IV, giving each bond six-sevenths single-bond character and one-seventh no-bond character (i.e., each bond orbital is unoccupied, on the average, one-seventh of the time).

In the language of atomic orbitals, the electron configuration of diborane should therefore be described as follows: The allowed orbitals for boron are four in number, of the hybridized sp^3 type, directed toward the corners of a tetrahedron. Each of these may be occupied by a shared electron pair or by a single electron, or may be left empty. Thus the valence-bond configurations which contribute to the ground state are (formal charges indicated):



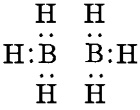
$$\mathrm{H^{+\frac{1}{2}}\cdot\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}{}^{-\frac{1}{2}}:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}{}^{-\frac{1}{2}}\cdot H^{+\frac{1}{2}}}$$

(9)
Type I



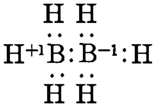
$$\mathrm{H^{+\frac{1}{2}}\cdot\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}\cdot\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}{}^{-\frac{1}{2}}:H}$$

(6)
Type II



$$\mathrm{H:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}\quad\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}:H}$$

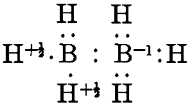
(1)
Type III



$$\mathrm{H^{+1}\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}:\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}{}^{-1}:H}$$

(6)
Type IV

and



$$\mathrm{H^{+\frac{1}{2}}\cdot\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H^{+\frac{1}{2}}}{\cdot}}{B}}\;:\;\overset{\overset{H}{\cdot\cdot}}{\underset{\underset{H}{\cdot\cdot}}{B}}{}^{-1}:H}$$

(6)
Type V

so that the wave function of diborane may be represented approximately by a linear combination of the wave functions of the above structures.[3] Although the individual members of the types II, IV, and V do not have the symmetry which we associate with diborane (D_{3d}), symmetric and antisymmetric linear combinations of the various components of each type (given in parentheses below the structures) will result in two configurations of equal energy, one of which (the symmetric) may be used in further combinations with I and III. The latter interaction will cause the energy of the over-all symmetric combination to be lowered, and of the remaining antisymmetric one to be raised,

---

[3] Justification for writing the configurations involving a one-electron bond between B_2H_5 and H, as in structure I, has been presented by Pauling (47); a similar argument may be given in favor of structures involving a one-electron bond between two BH_3 groups (3).

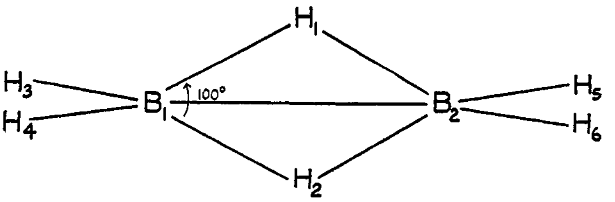
It is clear that the total of twenty-eight structures suggested for diborane are not independent; however, the selection of a suitable independent set should await an attempt at a quantitative discussion.

so that the ground state of diborane will be of the A_1 type. To deduce the multiplicity of the ground state consider the following: Structures III and IV are in singlet states; structures I, II, and V may have the spins of the electrons participating in the one-electron bonds either parallel or antiparallel, but only when in the latter configuration are the structures permitted to combine with III and IV. Since such an interaction will lead to a lowering of the energy of the ground state, we may conclude that the latter is singlet, i.e., that diborane has a ground state which is diamagnetic ($^1A_1$), as observed, and a low-lying paramagnetic state ($^3A_2$), the existence of which has not yet been verified.[4]

Mulliken (42) has presented a discussion of diborane and related molecules in terms of molecular orbitals. He has listed the possible electron configurations which combine to form the various states of diborane, and a rough correspondence between these and the atomic-orbital representations given above has been indicated (3). Of particular interest is the tentative energy-level scheme proposed by him, showing how the various electronic states of two BH_3 radicals correlate with those of diborane. These estimates are based in part on an analogy with the states of molecular oxygen, which is isoelectronic with diborane, and were intended to indicate orders of magnitude only. In figure 3 the levels on the right are those of two BH_3 groups, with the electron configurations of the various states indicated. Those on the left are the lower ones of diborane; five levels ($^3A_{2g}$, ^1E_g, $^1A_{1u}$, ^3E_u, and $^3A_{2u}$, in order of increasing energy) are represented by the bracket. Only $^1A_1$ states contribute to the ground level, and the two participating to the greatest extent are shown. The dotted horizontal lines are the estimated positions of these $^1A_{1g}$ states had they not interacted; mutual perturbations pushed them apart, as shown by the arrows. Dissociation correlations are indicated by the sloping lines, assuming that the symmetry D_{3d} is preserved during the dissociation. In considering the possible electronic transitions, Mulliken concluded that, since the transitions which are permitted for selected angles of orientation of the two BH_3 groups will probably

---

[4] Were one to overlook the discrepancy between the intensity curve predicted on the basis of the bridge model[1] and the pattern observed, comparison of the dimensions required for such a configuration (B—B = 1.79 Å.; B—H = 1.18 Å.) with table 3 will call attention to an inherent structural difficulty. Since the separation expected for a B—B single bond (1.70 Å.) is only slightly less than that required for the bridge model, one would have to use the following valence-bond structure



in order to represent the structural data even partially. Not only is a high electron deficiency thus introduced, but one must also postulate a pentavalent boron atom with three of its bonds coplanar and making an angle of 50° with one another, an absurd conclusion.

be weak, whereas the ones between singlet and triplet states are forbidden in light molecules, the transition which would be fairly intense and easily observed is $^1A_{1g} \rightarrow {}^1E_u$; it should be found in the near infrared. Also, the paramagnetic $^3A_{2g}$ state should make its presence evident by introducing a paramagnetic con-

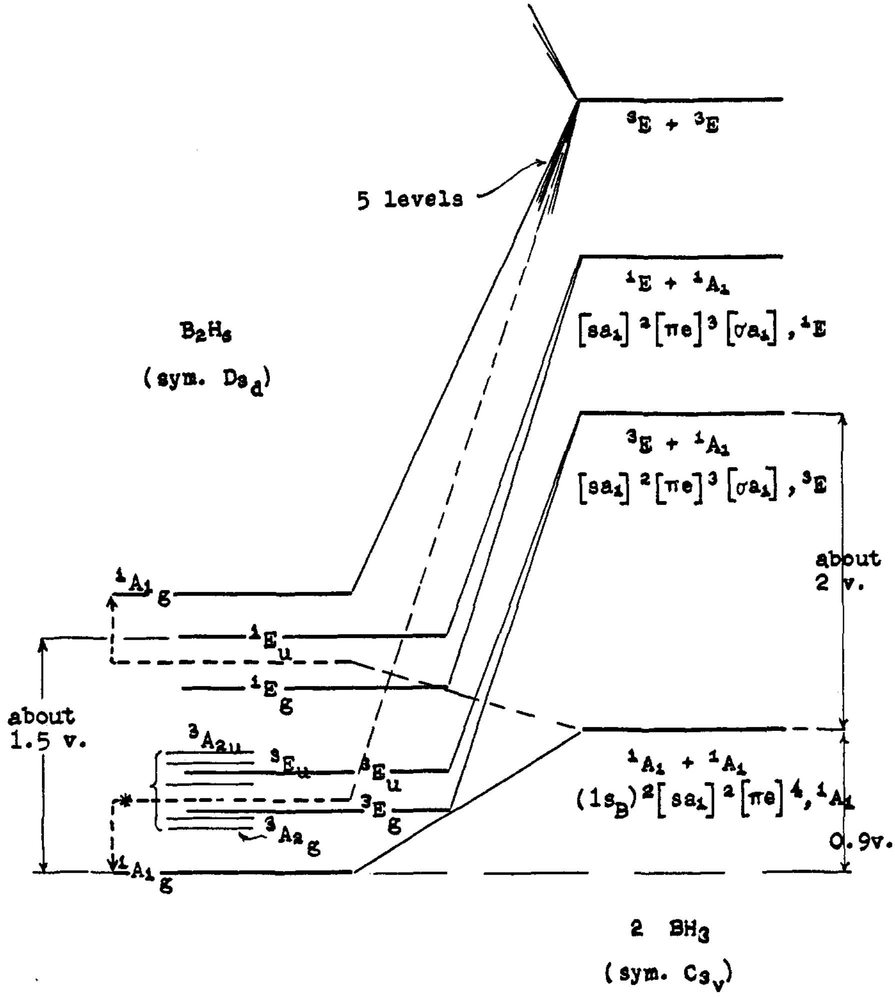


FIG. 3. Diagram showing how the energy levels of diborane may be correlated with those of two BH_3 groups (according to Mulliken).

tribution to the susceptibility as the temperature is raised. The data regarding these predictions will be presented below.

As an example of the electron configurations describing the left-hand set of levels, we quote

$$[s + s, a_{1g}]^2[s - s, a_{2u}]^2[\sigma + \sigma, a_{1g}]^2[\pi e]^3[\pi e]^3, {}^1A_{1g}, \text{ etc.}$$

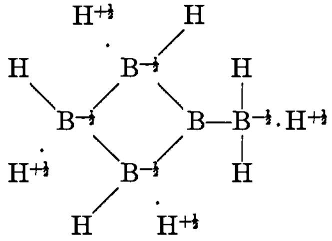
for the state marked by *; it corresponds to structure I, above. One should note that whole-molecule orbitals are written for the $[sa_1]$ electrons, but not for the $[\pi e]$ electrons.

The use of whole-molecule orbitals $[\pi + \pi, e_u]$, $[\pi - \pi, e_g]$ would indicate strong resonance between the $[\pi e]$ electrons of the two BH_3 groups. This would necessitate that the $[\pi]$ bonding be strong, and that there be considerable overlapping of their wave functions in the region between the boron atoms, introducing effectively a double-bond contribution. Each of the BH_3 groups would then have a tendency to be planar. The observed spatial structure is in contradiction to such an hypothesis. The boron–hydrogen and the boron–boron distances are larger than might have been expected even for pure single bonds, and the BH_3 groups are pyramidal. (Wiber's structure (70) is therefore eliminated.) Indeed, this state of affairs was anticipated by Mulliken on the basis of the fact that diborane does not have an absorption region in the visible. The possibility of a slight double-bond contribution, both in diborane and in ethane, should be retained, however (estimated at roughly 12 per cent for the latter). In the former, the shortening thus introduced would be more than counterbalanced by the Sidgwick and Lewis structures. It has been estimated (44) that the magnitude of this effect (hyperconjugation) is too low to account for the observed barrier height restricting freedom of rotation about the C—C and B—B single bonds.

Professor Mulliken also called attention to the theorem discovered by Jahn and Teller (24), namely, that the degenerate states of most symmetric polyatomic molecules are unstable, in such a way as to cause the molecules to become less symmetric, with the consequent splitting of these states into non-degenerate ones. These forces which would tend to introduce into diborane a symmetry lower than D_{3d} are strongest for levels with orbital degeneracy (such as ${}^1E$), particularly when the degenerate electrons participate in the bonding. However, the final configuration of the two components of the split ${}^1E_u$ state may not differ appreciably from the normal-state configuration.

C. *Extension of the theory to* B_4H_{10} *and* B_5H_{11}

The extension of the hypothesis of resonance beween various electronic structures, involving electron-pair, one-electron, and no-electron bonds, to B_4H_{10} and B_5H_{11} is based on the assumption that a structure involving a one-electron-bond or no bond between two boron atoms has a somewhat higher energy than one with those bonds between a boron and hydrogen atoms (owing to the slightly greater electronegativity of boron with respect to hydrogen); hence it contributes less to the ground state. As the number of atoms in the molecule increases, the B—B links tend to be more fully covalent at the expense of the B—H bonds, resulting in a boron–boron separation closer to that expected for a pure single bond. It appears likely that the configuration of B_5H_9 may be represented by a linear combination (7) of



and the structures resulting from the permutation of the four one-electron bonds (and possible no bonds) among all the linkages in the molecule. The distances between the boron atoms are approximately 0.05 Å. less in B_5H_9 than in B_5H_{11}, in spite of the fact that both molecules have the same four-electron deficiency; this may be associated with the relatively greater stability of the hydride, though it is not clear why a four-membered ring should be particularly stable.

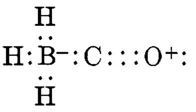
D. Borine carbonyl, H_3BCO

Let us now consider the electron configurations of the derivatives in terms of their interatomic distances. In borine carbonyl the B—C—O atoms are linearly arranged, with the carbon–oxygen separation very near to that in carbon monoxide. The fact that the compound readily dissociates into carbon monoxide and diborane at room temperature further supports the assumption that the characteristic resonance of the carbon monoxide molecule (39)

$$:C^-:::O^+: \qquad :C::O:: \qquad :C^+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{}^-:$$

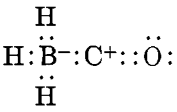
has not been quenched in the association of the latter with the BH_3 group. The substance is gaseous at fairly low temperatures (vapor pressure 314 mm. at −78.8°C.) and thus probably has a low dipole moment. Finally, one should note that in borine carbonyl, conjugation of the type found in methylacetylene is possible (first-order hyperconjugation), as contrasted with $(CH_3)_3B$ and $(CH_3BO)_3$, wherein second-order hyperconjugation is permissible (45).

In terms of electron-pair-bond structures, the ground state resonates among the following (4),



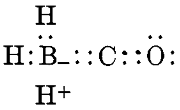
$$\begin{array}{c} H \\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{B}}{}^-:C:::O^+: \\ H \end{array}$$

I



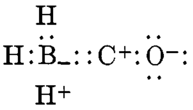
$$\begin{array}{c} H \\ H:\overset{\cdot\cdot}{\underset{\cdot\cdot}{B}}{}^-:C^+::\overset{\cdot\cdot}{O}: \\ H \end{array}$$

II



$$\begin{array}{c} H \\ H:\overset{\cdot\cdot}{B}_-::C::\overset{\cdot\cdot}{O}: \\ H^+ \end{array}$$

III



$$\begin{array}{c} H \\ H:\overset{\cdot\cdot}{B}_-::C^+:\overset{\cdot\cdot}{\underset{\cdot\cdot}{O}}{}^-: \\ H^+ \end{array}$$

IV

(There are three of these, and three more involving one-electron bonds between the boron and two of the hydrogen atoms)

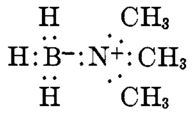
(There are three of these, and three more involving one-electron bonds. . .)

Structures III and IV represent the atomic-orbital formulation of the hyperconjugation effect, and serve to introduce dipole moments opposed to the large ones of I and II. The extent of the contribution of III and IV cannot be readily estimated; apparently neither in H_3BCO, nor in $(H_3C)_3B$ and $(H_3CBO)_3$, are the effects of sufficient importance to shorten the boron–carbon distance below that expected (8, Tables I and II) for a pure single bond.

E. Trimethylamine-borine, $(CH_3)_2N:BH_3$

The experimental error is large in the case of trimethylamine-borine, owing to the fact that the molecule contains many atoms symmetrically arranged.

Hence no conclusions regarding its electron configuration can be drawn from the observed boron–nitrogen distance. For the ground state only one electron-pair-bond structure need be written:



$$\begin{array}{ccccc} & H & & CH_3 \\ H: & \ddot{\underset{\cdot\cdot}{B}}{}^-: & \ddot{\underset{\cdot\cdot}{N}}{}^+: & CH_3 \\ & H & & CH_3 \end{array}$$

It indicates a fairly high dipole moment, as would be expected from the observed high boiling point of the substance (171°C.).

F. Comparison of borine carbonyl with trimethylamine-borine

Superficially, borine carbonyl and trimethylamine-borine should show similarities in chemical behavior, since the association linkages are analogous from a valence-bond point of view; i.e., the empty fourth orbital of boron is occupied by the unshared electron pair of the nitrogen or carbon. However, an extraordinary difference in the stabilities of the two compounds exists (13). Evidently the situation is a complicated one, and it is not certain that strictly similar rôles are played by the unshared electron pairs in carbon monoxide and nitrogen trimethyl. Were this possibility excluded, one might undertake to explain the difference in stability as being due to the fact that nitrogen is twice as far removed from boron on the electronegativity map as is carbon; consequently, the B—N bond may be as much as 17 kilocalories stronger than the B—C bond. (Some deduction, of the order of 3 kilocalories, should be made from this value for the possible double-bond character (hyperconjugation) of the latter linkage.) Since in the *association* of borine with carbon monoxide or trimethylamine no bonds are broken and one covalent bond of the "donor" type is formed per compound, the activation energy is probably the same for these two reactions. But we have argued above that the resultant bond in the carbonyl is weaker to the extent of approximately 14 kilocalories than in trimethylamine-borine; hence the activation energy for the *dissociation* is expected to be smaller for the borine carbonyl by the same amount, leading to the

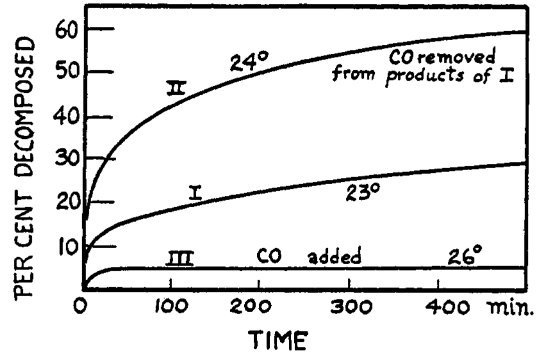


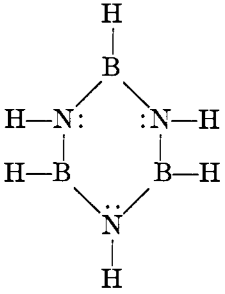
FIG. 4. Rate of decomposition of borine carbonyl (Burg and Schlesinger)

possibility that the rate constant for $H_3BCO \rightarrow H_3B + CO$ is greater by a factor of 10^{10} than for the analogous reaction for trimethylamine-borine.[5]

From the molecular-orbital point of view there is no formal analogy between the bonds formed in these two association reactions. In the discussion of the structure of carbon monoxide, Mulliken (37, 38) has described the slightly antibonding (unshared) pair of electrons as occupying an orbital which is essentially an s-orbital of carbon. On the other hand, in his discussion of ammonia and its methyl derivatives (40), it is principally the $2p_z$-orbital of nitrogen, nonbonding in character, which is occupied by the unshared electron pair. We would accordingly expect a difference in the bonds formed between borine and carbon monoxide or trimethylamine and, indeed, that the latter would form a stronger bond than the former, inasmuch as the bonding power of a p-orbital (with greater concentration of the wave function in the bond direction) is known to be greater than of an s-orbital. The problem is well worth further consideration. The compounds CO_2, H_2CCO, and H_3BCO are isosteric, and would possess similarities in electron configuration, spectra, etc. The first of these has already been discussed by Mulliken (43) and the analogy with borine carbonyl has been indicated.

G. *Triborine triamine* (*borazole*), $B_3N_3H_6$

Triborine triamine appears to be analogous to benzene in atomic configuration, interatomic distances, and intramolecular force constants (see below); that there is a correspondence between the electron configurations of the two compounds is therefore strongly indicated. In this respect the analogy is not complete. Whereas in benzene there are three double bonds in every structure which contributes to the ground state, whence the reduction in carbon–carbon distance from the single-bond value of 1.54 Å. to 1.39 Å., in triborine triamine the most important structure is the completely single-bonded one,



---

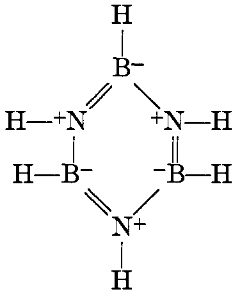
[5] A few preliminary experiments on the kinetics of the dissociation of borine carbonyl have been reported by Burg and Schlesinger (13). At 100°C., the equilibrium constant for the reaction

$$2H_3BCO = 2CO + B_2H_6$$

was estimated to be

$$K = \frac{p^2(CO) + p(B_2H_6)}{p(H_3BCO)} = 2.9 \times 10^4$$

Owing to the presence of side reactions and other complicating factors, this value is only an approximate one. At room temperature the reaction is very slow; carbon monoxide while the double-bonded configurations



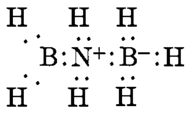
(Two of these and three Dewar structures, etc.)

play a lesser rôle, owing to the fact that the formal charge thus introduced implies an electron distribution which is contrary to the relative electronegativities of the boron and nitrogen atoms. As a consequence, the boron–nitrogen distance is only 0.06 Å. less than that expected for a single bond.

In treating this compound, we should note that the symmetry of the various orbitals used in the discussion of benzene will have to be reduced from sixfold to threefold, and the number of degeneracies, selection rules, etc. changed accordingly.

H. B_2NH_7

The electronic structure of B_2NH_7 cannot be specified until a decision is reached regarding its atomic configuration. If it is H_2B—NH_2—BH_3 (54), only one Lewis structure can be written:



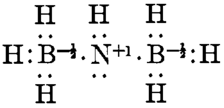
$$\begin{array}{cccc} \mathrm{H} & \mathrm{H} & \mathrm{H} & \\ \mathrm{B}: & \mathrm{N}^+: & \mathrm{B}^-: & \mathrm{H} \\ \mathrm{H} & \mathrm{H} & \mathrm{H} & \end{array}$$

(the formal charges indicate the presence of an appreciable dipole moment), but then it is difficult to account for the observed boron–nitrogen separations (both equal to 1.56 ± 0.03 Å.). From table 2, the single-bond distance should be 1.50 Å. On the other hand, the configuration H_3B—NH—BH_3 is much more symmetric and hence would have a smaller moment.[6] The ground state might be represented by a linear combination of a large variety of one-electron and no-bond structures, some of which are shown below.

---

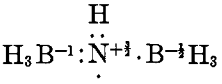
appears to inhibit the attainment of equilibrium, as may be seen from the pressure *versus* time curves of figure 4.

[6] The dipole moment of $NH(BH_3)_2$ would nevertheless be considerably larger than that of $NH(CH_3)_2$, owing to the greater electronegativity difference between nitrogen and boron (one unit) as compared with that between nitrogen and carbon (0.5 unit). The higher boiling point of B_2NH_7 (76.2°C. *versus* 7.2°C.) can therefore be readily explained.



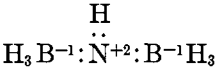
$$H:\overset{H}{\underset{H}{\ddot{B}}}{}^{-\frac{1}{2}}\cdot\overset{H}{\ddot{N}}{}^{+1}\cdot\overset{H}{\underset{H}{\ddot{B}}}{}^{-\frac{1}{2}}:H$$

(1)
Type I



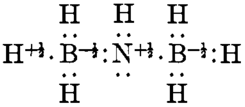
$$H_3B^{-1}:\overset{H}{\ddot{N}}{}^{+\frac{3}{2}}\cdot B^{-\frac{1}{2}}H_3$$

(2)
Type II



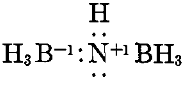
$$H_3B^{-1}:\overset{H}{\ddot{N}}{}^{+2}:B^{-1}H_3$$

(1)
Type III



$$H^{+\frac{1}{2}}\cdot\overset{H}{\underset{H}{\ddot{B}}}{}^{-\frac{1}{2}}:\overset{H}{\ddot{N}}{}^{+\frac{1}{2}}\cdot\overset{H}{\underset{H}{\ddot{B}}}{}^{-\frac{1}{2}}:H$$

(6)
Type IV



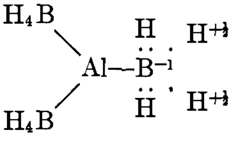
$$H_3B^{-1}:\overset{H}{\ddot{N}}{}^{+1}BH_3 \quad \text{etc.}$$

(2)
Type V

The importance of the contributions made by configurations such as I, IV, and V determines firstly, the extent to which B_2NH_7 possesses the characteristics generally associated with a free electron pair on a nitrogen atom, and secondly, the electron deficiency of the B—N and B—H bonds. The larger than expected boron–nitrogen distances are therefore reasonable. Resonance with types similar to II and III serves to quench the base-like character of the nitrogen atom, as the somewhat similar type of resonance does in pyrrole. A possible, but entirely hypothetical, way of accounting for both the chemical and the physical data is to assume this latter atomic configuration plus a tautomerism, as suggested by Burg.

I. $Al(BH_4)_3$

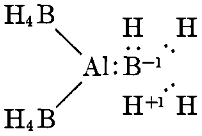
The Al—B bonds in $Al(BH_4)_3$ appear to be single covalent ones of the sp^2 type; the interatomic distance observed is but slightly greater than the sum of the single bond radii (table 2). The boron–hydrogen distances, however, are large, being the same as in B_2H_6, B_4H_{10}, and B_5H_{11}, and this would be expected in view of the six-electron deficiency present in the molecule. Therefore, the ground state could be represented by a linear combination of



$$(H_4B)_2Al{-}\overset{H}{\underset{H}{\ddot{B}}}{}^{-1}\begin{matrix}H^{+\frac{1}{2}}\\ H^{+\frac{1}{2}}\end{matrix}$$

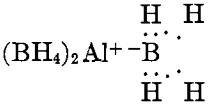
(There are six such configurations per BH_4 group)

in which each BH orbital is occupied by an electron pair half of the time and by one electron the other half, and numerous excited structures, such as



$$(H_4B)_2Al:\overset{H\ \ H}{\underset{H^{+1}\ H}{\ddot{B}}}{}^{-1}$$

(four per BH_4 group);



$$(BH_4)_2Al^{+}\,{-}\overset{H\ \ H}{\underset{H\ \ H}{\ddot{B}}}$$

; etc.

The contribution from ionic structures probably is not appreciable. First, the large boron-hydrogen distances indicate that the electron deficiency resides primarily in the BH_4 groups, and second, the aluminum–boron distances are close to that expected for electron-pair bonding. The extent of such ionic contributions must increase, however, as one goes down the series,

$$Al(BH_4)_3 \qquad Be(BH_4)_2 \qquad LiBH_4$$

in harmony with the observed decrease in volatility. The electron configuration of the latter compounds could be represented in a fashion similar to that given for $Al(BH_4)_3$. In view of the conclusions reached by Kimball (26) regarding the configurations which could lead to a bipyramidal arrangement of the atoms (dsp^3, d^3sp), it is interesting to note that in these compounds four electrons are as effective as the five needed, provided the molecule permits structures involving one-electron bonds to contribute to the ground state.

TABLE 4

Constants for boron hydride (BH)

		FORCE CONSTANT	D_0	r_e
	$cm.^{-1}$	*megadynes*	*volts*	*Å.*
Ground state $A^1\Sigma^+$	$\omega_e = 2366$	0.302	3.60	1.225
Configuration $D^3\Pi$				1.198
Configuration $C^1\Pi$	$\omega_e = 2344$	0.297	0.73	1.219
Configuration $B^3\Sigma^+$				1.220

VII. SPECTROSCOPIC DATA

A. Boron hydride

Fitting in with and extending beyond the structural measurements are conclusions regarding internal symmetry and bond force constants derived from spectroscopic investigations. A number of bands have been observed for boron hydride, BH; these proved the existence of the three excited states enumerated above. The constants of chemical interest deduced from them (27) are shown in table 4.

B. Diborane

The ultraviolet, visible, and infrared spectra of diborane have been mapped. Blum and Herzberg (11) studied the two bands in the ultraviolet which start at about 2200 Å., with no sharp long-wave-length limit, and extend to as short wave lengths as were permitted by the apparatus (1550 Å.). They made the tentative suggestion that the absorption region on the short-wave-length side may be due to a transition from the ground state, the configuration of which is to be roughly approximated by the molecular-orbital description given above (page 49), to one of the many states resulting when a [πe] electron is excited to a [$3sa_1$] orbital; the band with the maximum at 1820 Å. may be produced by a transition to a somewhat lower state resulting from such an excitation. In both of these upper states, the number of bonding electrons remains the same as in the ground level, and hence both would be stable. However, there would be the tendency for predissociation, which accounts for the continuum observed.

Plumley (49) found no absorption by diborane in the region from 2500 to 12,000 Å.; on the basis of the energy-level diagram given above, the transition $^1A_{1g} \rightarrow {}^1E_u$ (indicated by ↑ in figure 3) should result in a band at about λ 8000. A tentative explanation of this discrepancy might be that the estimated spread between the ground $^1A_{1g}$ and the excited ^1E_u is approximately five times that actually present. Thus one might expect that the above transition would result in an absorption band between 4 and $5\,\mu$. In his infrared studies of diborane, Stitt (61) found indications that fairly strong bands do occur in that region, and some of these may be electronic in origin. Indeed, it appears that the thermocouple infrared absorption spectrum of diborane has too many bands to permit a simple analysis. Stitt carefully explored the region from 400 to 4000 cm.$^{-1}$ under low dispersion. His tentative conclusions are summarized below.

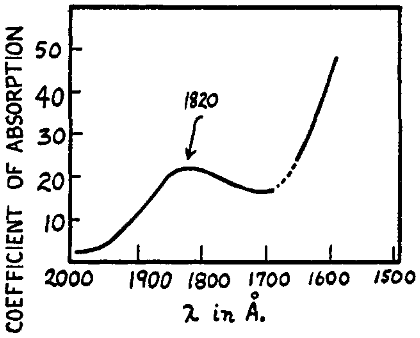


FIG. 5. Absorption of diborane in the ultraviolet (Blum and Herzberg)

The first attack on the problem was undertaken by Anderson and Burg (1), who obtained the Raman spectrum of liquid diborane. They were able to make a preliminary assignment of some of the frequencies and thus obtained an estimate of the stretching and bending force constants through the use of Howard's (23) formulas for the normal modes of vibration of an ethane-like molecule. The results of their assignment are given in table 5. As in the case of ethane and disilane, the constant for the stretching vibration of the bond between the two heavy atoms thus obtained is considerably greater than the one deduced from Badger's rule (2), using the electron-diffraction interatomic distances. Anderson and Burg suggest that in all three cases the apparent compression of the bond, leading to tighter binding, is probably related to the potential hindering freedom of rotation. It should be noted, however, that the discrepancy between the computed and observed distances becomes less, although it is not entirely eliminated, if a potential function including interaction terms is used (59).

Stitt (61) found that a complete analysis of the infrared and Raman spectra of diborane and a satisfactory assignment of all the frequencies observed must await further work. As in the case of ethane, it is not possible to decide, on the basis of the spectroscopic data alone, whether the molecular symmetry is D_{3h} or D_{3d}. He pointed out that there are two factors which may contribute to the extra complexity of the diborane spectrum: firstly, the occurrence of two abundant isotopes of boron, so that three types of diborane molecules, B^{11}—B^{11}, B^{11}—B^{10}, and B^{10}—B^{10} of the relative concentrations 16:8:1, respectively, must be considered; secondly, the possibility that some of the observed infrared and Raman transitions involve low-lying electronic states.

If the potential function of diborane is not very different from that of ethane, comparison of the spectra of the two molecules emphasizes several striking features: (*1*) The separation of 421 cm.$^{-1}$ between the two strong Raman lines in the neighborhood of 2300 cm.$^{-1}$ (ν_3, table 5) seems too large to permit their assignment to a resonance degenerate pair; (*2*) the two very strong infrared bands at 1608 and 1863 cm.$^{-1}$ are apparently not assignable to fundamental vibrations; and (*3*) a strong infrared band appears at 400 cm.$^{-1}$, the origin of which is somewhat perplexing. Stitt found that there are several ways in which these may be accounted for. Accordingly, he presented the following alternate analyses of the main features of the spectrum, both of which are in accord with the heat capacity of gaseous diborane over the temperature interval 100° to 300°K., and both are based on the ethane-like model.

TABLE 5

Assignment of frequencies to diborane

	FORCE CONSTANT
B—B stretching (symmetric)	
B^{11}—B^{10} 793 cm.$^{-1}$	3.57×10^5 dynes per centimeter
B^{11}—B^{10} ν_1......... 806	
B^{10}—B^{10} 821	
B—H stretching (symmetric)	
ν_3......... 2102 cm.$^{-1}$ 2523	3.0×10^5 dynes per centimeter. One line expected; splitting interpreted as a coincidence resonance with one of the overtones, as in ethane
B—H bending (symmetric)	
ν_2......... 1180 cm.$^{-1}$	0.26×10^5 dyne per centimeter

(*a*) One may assume a singlet low-lying electronic state at 412 cm.$^{-1}$ and another at 1863 cm.$^{-1}$, to which transitions from the ground state are permitted. The strong absorption region at 1608 cm.$^{-1}$ would then be due to an electronic-vibrational transition (a combination of the 412 cm.$^{-1}$ and one of the parallel deformation frequencies), as would also the Raman line at 2102 cm.$^{-1}$ A potential barrier of approximately 15 kilocalories hindering free rotation about the B—B bond (corresponding to a torsional frequency of 605 cm.$^{-1}$) must be assumed in order that the heat-capacity data may be accounted for. The band at 1863 cm.$^{-1}$ has two peaks and hence, if due to an electronic transition, may be one of the components of the complex of bands resulting from the transition $^1A_{1g} \rightarrow {}^1E_u$. In Mulliken's energy-level diagram there appears no allowed transition from the ground level which could give rise to the band at 412 cm.$^{-1}$, even if one assumes that his scale is considerably overextended. Also, the very large potential barrier hindering internal rotation is difficult to accept for an ethane-like model, particularly when the observed boron–boron distance is considerably greater than expected for a single bond.

(*b*) One may assume that the bands at 1608 cm.$^{-1}$ and 1863 cm.$^{-1}$ are due to electronic transitions from the ground state to two low-lying levels; the 412 cm.$^{-1}$ absorption is assumed to be an electronic-vibration difference band and the Raman line at 2102 cm.$^{-1}$ is assigned as above. Then the more reasonable restricting potential of 5 kilocalories (corresponding to a tortional frequency of 350 cm.$^{-1}$) is satisfactory for the interpretation of the specific-heat data. (In computing the heat capacities for both (*a*) and (*b*), the electronic state at 1608 cm.$^{-1}$ was assumed to be triply degenerate.) A difficulty remains, however, since the band at 1608 cm.$^{-1}$ is the strongest one of the infrared bands observed for diborane, and appears to be of the *parallel* type. Assuming that the symmetry D_{3d} (hydrogen atoms staggered) is retained during transitions from the ground state, one might expect (42)

$$^1A_{1g} \rightarrow {}^3E_u,\ {}^3A_{2u},\ {}^3E_u,\ {}^1E_u$$

of which the singlet-triplet transitions are known to be weak for molecules as light as diborane, while the $^1A_{1g} \rightarrow {}^1E_u$ should be the most intense, resulting in a *perpendicular*-type band, as indeed the one at 1863 cm.$^{-1}$ appears to be. Of course, it is quite possible that the *excited* states have a lower symmetry than D_{3d} (for instance, the splitting of the ^1E_u state into two non-degenerate singlet ones, according to the Jahn–Teller theorem), so that the estimated relative intensities based on the above selection rules may be quite inaccurate.

R. S. Mulliken has suggested two other possible causes for the complexity of the diborane spectrum. Firstly, owing to the probable changes in the equilibrium positions of the atoms during the electronic transition, vibrational excitation in the upper state should be considered (Franck–Condon principle). Hence $^1A_{1g} \rightarrow {}^1E$ may result in several strong electronic-vibrational bands. Secondly (and much less probably), there still exists the possibility that the *ground* state does not have the symmetry D_{3d}, as it may be one of the components of the split ^1E state. The discussion of the electron configuration of diborane, selection rules, etc. given above would then have to be revised.

No extensive normal coördinate treatment such as was carried through by Stitt for ethane (59) was undertaken for diborane, since the frequency assignment is considerably in doubt.

C. Triborine triamine (borazole)

Triborine triamine has been carefully studied as to both infrared and Raman spectra by Crawford and Edsall (16). The data are best interpreted by assuming the symmetry D_{3h}, as given by the electron-diffraction measurements. The normal modes of vibration were obtained in a manner similar to that proposed for benzene by Wilson (71), and the observed frequencies assigned. Throughout, the similarity to the latter molecule is rather striking. Indeed, Crawford and Edsall found discrepancies between the calculated (from Raman spectra) and observed (infrared) frequencies of the non-planar bending B—H and N—H modes in triborine triamine, corresponding to the similar discrepancy observed for the non-planar bending C—H frequency in benzene. For comparison, they tabulated the various force constants (see table 6) for the two molecules; the approximate characters of the corresponding vibrations are indicated. Note the general correspondence between the B—H stretching and bending frequencies in triborine triamine and in benzene.

TABLE 6

Force constants for triborine triamine and for benzene

$B_3N_3H_6$			C_6H_6		
Planar:			*Planar*:		
K	(B—N stretching)	6.300×10^5 dynes per cm.	K	(C—C stretching)	7.58×10^5 dynes per cm.
k	(B—N—B or N—B—N bending)	0.525	k	(C—C—C bending)	0.65
H_B	(B—H bending)	0.35	H	(C—H bending)	0.76
H_N	(N—H bending)	0.65			
q_B	(B—H stretching)	3.423 $\nu = 2535$	q	(C—H stretching)	5.05
q_N	(N—H stretching)	6.524 $\nu = 3450$			
Non-planar:			*Non-planar*:		
κ	(B—N torsion)	0.10	κ	(C—C torsion)	0.23
h_B	(B—H bending)	0.23	h	(H—CH bending)	0.34
h_N	(N—H bending)	0.42			

Crawford and Edsall found four intense Raman lines with the shifts 851, 938, 2535, and 3450 cm.$^{-1}$; these were the only lines found to be polarized. They were therefore assigned to the non-degenerate symmetric class (A_1'). The last two frequencies are readily identified with the B—H and N—H stretching, respectively.

VIII. THERMODYNAMIC FUNCTIONS FROM SPECTRAL AND STRUCTURAL DATA

Upon combining the spectroscopic and diffraction data, a number of thermodynamic functions may be computed. This has been done for diborane (1) and for triborine triamine (16). Anderson and Burg assumed an entropy contribution due to internal "torsional" vibration of 2.4 E.U., and obtained, for the entropy of the ideal gas at 25°C., $S^*_{298} = 55.3 \pm 1.5$ calories per mole per degree and for the entropy of formation, $\Delta S^0_{298} = -50.4 \pm 3.5$ calories per mole per degree. The assumption regarding the torsional vibration is now justified by the specific-heat data on diborane (60). Such a vibration would contribute 2.0 E.U. to the entropy, while for completely free rotation the contribution is 3.3 E.U. Further, by combining the experimentally determined heat of formation of diborane (51, 52) (44 ± 3 kilocalories) with their computed entropy, Anderson and Burg were able to estimate the free energy of formation of diborane (from the elements): $\Delta F^0_{298} = -30 \pm 4$ kilocalories. In this computation they had to assume that the entropy of solid boron is 4 ± 1 calories per mole per degree at 298°K.

The results of statistical computations made for triborine triamine (16) are given in table 7. Values in calories per mole per degree are tabulated for various temperatures for the perfect gas at 1 atm.

TABLE 7

Results of statistical computations made for triborine triamine

T	S^0	$-(F^0 - E^0_0)/T$	C^0_p
°K.			
298.1	73.7	60.4	23.3
326†	75.8	61.5	25.3
350	77.7	62.6	27.1
400	81.5	64.8	30.4
500	88.9	68.7	36.0
600	95.9	72.6	40.5
700	102.5	76.6	44.2
800	108.5	80.2	47.2
900	114.2	83.6	49.6
1000	119.6	87.0	51.8

From vapor pressure data, and these values:
$S^0_{298}(l) = 51.0$
$S^0_{326}(l) = 53.4$ (boiling point)
$[(F^0 - E^0_0)/T]_{298}(l) = 62.5$ calories per mole-degree

† Boiling point.

IX. THERMOCHEMICAL MEASUREMENTS AND SPECIFIC HEAT OF DIBORANE

The heats of vaporization and sublimation of many of the hydrides and of their derivatives have been obtained from their vapor-pressure curves. The heats of formation of several boron compounds have been deduced indirectly. Thus Kelley (25) gives

$$\text{for B(s):} \qquad C_p = 1.54 + 4.40 \times 10^{-3}T \quad \text{for } T < 1{,}173°$$

and

$$\text{for BN(s):} \qquad C_p = 3.22 + 8.00 \times 10^{-3}T \quad \text{for } T < 1{,}173°$$

Then, from equilibria measurements on the thermal decomposition of boron nitride, he computed for the reaction $BN = B + \frac{1}{2}N_2$,

$$\Delta H_{298} = 31.5 \text{ kilocalories}$$

$$\Delta F_{298} = 27.7 \text{ kilocalories}$$

The work of Roth and Börger (51) and of Roth, Börger, and Bertram (52) appears to be the only direct calorimetric measurements on the compounds of boron. Their final results may be summarized by the following equations:

$$2B(s) + 1.5O_2(g) = B_2O_3(s) + 349 \pm 2 \text{ kilocalories}$$

$$B_2H_6(g) + 3H_2O(1) = B_2O_3(s) + 6H_2(g) + 100.2 \pm 2.1 \text{ kilocalories}$$

$$2B(s) + 3H_2(g) = B_2H_6(g) + 44 \pm 3 \text{ kilocalories}$$

These investigators call attention to the fact that the heat of formation of ethane (20.96 kilocalories) is about half that of diborane.

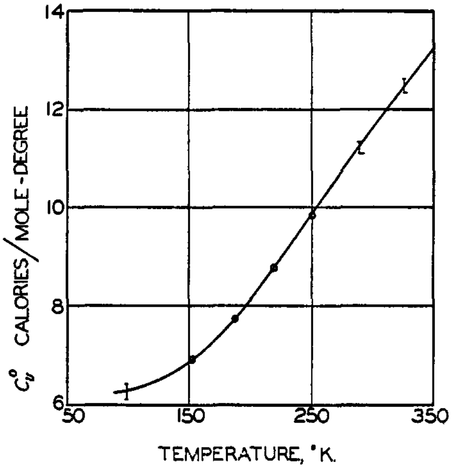


FIG. 6. The gaseous heat capacity of diborane, as a function of the temperature (Stitt)

Stitt measured the heat capacity of gaseous diborane over the temperature range 95° to 324°K. (60) by means of the low-pressure thermal conductivity apparatus first used for ethane (28). His results are presented graphically in figure 6. The heat capacity (C_v) at the lowest temperature is particularly interesting, since the translational and over-all rotational contribution is $3R$ = 5.96 calories per mole, while the observed value is 6.35 ± 0.2 calories per mole. The small difference 0.4 ± 0.2 calorie per mole is all that is left for the internal rotational degree of freedom. This indicates an appreciable barrier restricting rotation about the B—B bond; indeed, Stitt computed a height between 3300 and 6000 calories per mole, assuming that the barrier is of a cosine form. From the heat capacity at 142°K., he deduced that the lower limit is 4 kilocalories per mole. On the other hand, the estimate of the upper limit is valid provided the vibrational and electronic contributions to the specific heat at 100–150°K. are negligible. The barrier will be considerably higher if a very low lying electronic state is postulated, as was discussed above. Whichever assignment is selected [(*a*) → 15 kilocalories; (*b*) → 5 kilocalories], the specific-heat curve may be reproduced accurately over the entire range. For comparison, the barrier in ethane is considered to be of the order of 3 kilocalories per mole.

X. DIELECTRIC POLARIZATIONS

Ramaswamy (50) made dielectric-constant measurements on the vapors of two of the hydrides. The dipole moments deduced for diborane and triborine triamine from his data are zero and 0.67 D, respectively. The first value is that which would be predicted both by the Sidgwick–Lewis and the Mulliken electron configurations; in both schemes the over-all symmetry of diborane is D_{3d}, owing to the linear combination of the individual structures contributing to the ground state. The small but non-vanishing moment for triborine triamine is in disagreement with both the diffraction and the spectroscopic data, which assign to the molecule the symmetry D_{3h}. However, Ramaswamy admits that the data on the latter compound are doubtful, as the presence of impurities in the sample used was later established.

TABLE 8

Values for the molecular polarizations of some compounds

COMPOUND	P_T	P_E	P_A
C_2H_6	11.16	11.07	0.09
B_2H_6	14.46	12.91	1.55
Si_2H_6	28.10	23.72	4.38
C_6H_6	27.01		
$B_3N_3H_6$	23.76 (?)	20.18 (?)	3.58 (?)

Values for the molecular polarizations of the two hydrides are given in table 8. For comparison, data on several analogous compounds are included (69).

XI. MAGNETIC SUSCEPTIBILITIES

Since paramagnetic molecules or ions were found to catalyze the conversion of para- to ortho-hydrogen, Farkas and Sachsse (19) tested diborane for paramagnetism by studying its effectiveness in the conversion. They obtained no reaction at 195°K. and concluded that the ground state is diamagnetic. They set a lower limit for the first paramagnetic level at 3000 calories above the lowest energy state, and suggested that it is undoubtedly higher. To explain the small amount of conversion which was obtained at 293° and 373°K., they postulated the *exchange* reaction

$$H_2(p) + B_2H_6 = B_2H_6 + H_2(o)$$

and estimated the heat of activation to be about 15 kilocalories. Freed and Thode (20) measured directly the diamagnetic susceptibility of diborane (Gouy method); they found no evidence for the presence of a low-lying paramagnetic state ($^3A_{2g}$) at room temperature.

$$\chi_{B_2H_6} = -17 \times 10^{-6} \text{ per mole}$$

For comparison, $\chi_{C_2H_6} = -30 \times 10^{-6}$, and the value expected for $B_2H_6^{--}$ from the atomic susceptibilities (30, 66) is

$$\chi_{B_2H_6^{--}} = -31 \times 10^{-6}$$

In contrasting the value for diborane with that of ethane, one would conclude that of the two opposing factors, one which tends to give a larger χ, owing to the greater interatomic distances ($\overline{r^2}$ larger), and the other which serves to decrease χ, owing to a lower electron density (twelve instead of fourteen electrons, spread over a larger volume), the latter seems to predominate. At any rate it is clear from these measurements that the ground state of diborane is singlet.

The magnetic susceptibilities of two of the potassium salts were determined by Klemm and Klemm (29); both were found to be diamagnetic (see table 9). The data prove that $K_2B_2H_6$ and $K_2B_2O_2H_6$ are the correct formulas, whereas KBH_3 and $K(OBH_3)$, respectively, (these would be paramagnetic) are incorrect. The slight paramagnetic contribution which appears in $K_2B_2H_6$ as the temperature is raised has no clear explanation. The magnetic behavior of $B_2H_6^{--}$ should parallel that of ethane. The lowest excited state of the latter compound results from the excitation of one of the C—C bonding electrons (41); i.e., ethane assumes the configuration $[\sigma + \sigma, a_1]^{-1}(3sa_1)$, ${}^3A_1$, ${}^1A_1$. The position of the paramagnetic level is unknown, owing to the fact that transitions from the ground state to it are forbidden. Because of the lower nuclear charge, the ${}^3A_1$ state in $B_2H_6^{--}$ should be considerably below that of ethane. Assuming that the observed paramagnetic effect was not due to an impurity,[7] the position of that level was estimated to be about 6.2 kT (at T = 300°C.) above the ground state, much lower than would have been expected.

TABLE 9

Magnetic susceptibilities of $K_2B_2H_6$ *and* $K_2B_2O_2H_6$

T	χ(gm) $K_2B_2H_6$	χ(gm) $K_2B_2O_2H_6$
°*K.*		
90	-0.60×10^{-6}	
195	-0.57	
293	-0.42	-0.5 to -0.3×10^{-6}
353	-0.34	

XII. SURFACE-TENSION DATA

Stock, Wiberg, and Mathing (64) measured the (liquid-vapor) interfacial tension of diborane at various temperatures. Over the temperature range −110° to −90°C., the equation for the density of the liquid is

---

[7] The diamagnetic susceptibility expected for $K_2B_2H_6$ is -58.1×10^{-6} per mole (30, 66), somewhat less than the value observed at the lowest temperature (-63.5×10^{-6} per mole). This might be used to argue against the possible presence of a paramagnetic impurity in the sample.

$$D = 0.4371 + 1.0115 \times 10^{-3}(180.6 - t)$$

Values for the surface tension are given in table 10 and plotted in figure 7. The mean value for the parachor deduced through the equation

$$P = \frac{M}{D_l - D_v}\gamma^{1/4}$$

TABLE 10

Surface-tension data for diborane

T	γ	T	γ	T	γ
°C.		°C.		°C.	
−119.0	17.16	−112.3	16.30	−102.8	14.84
−118.6	17.26	−111.8	16.36	−94.8	13.78
−117.2	16.98	−108.3	15.82	−94.5	13.70
−116.0	16.88	−108.1	15.67	−92.1	14.41
		−105.9	15.48		

$$\text{Slope } \frac{\partial\gamma}{\partial T} = -0.146$$

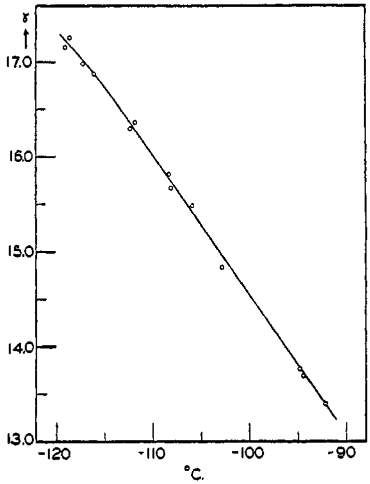


FIG. 7. The surface tension of diborane (Stock *et al.*)

is reported by them to be 121.9. This measurement was recently confirmed by Laubengayer and coworkers (31). By making some rather arbitrary assignments for the contribution of the H^+ (a value of zero) and the one-electron bonds, Stock, Wiberg, and Mathing sought to prove that the parachor computed on the basis of Wiberg's structure of diborane was in agreement with the one obtained experimentally, whereas the ones computed for other structures were in definite disagreement. These conclusions are highly questionable (3, 31). Data on the surface tensions of the other hydrides are not yet available.

XIII. IONIZATION BY ELECTRON IMPACT

Very recently J. A. Hipple has studied the ionization and dissociation of diborane through electron impact by means of a mass spectrograph (22). Relative intensities of the ions observed (90 volt electrons) are given in table 11, and are compared with the relative intensities of the corresponding ions formed in ethane, under comparable conditions. It is particularly interesting to note that (*a*) $B_2H_6^+$ does not appear; presumably, an electron deficiency of three makes the ion unstable. (*b*) BH_3^+ and BH_2^+ and BH^+ do not appear, whereas the $B_2H_n^+$ ions are prominent. Since the dissociation process takes place at low pressures, the ions formed are primary collision products. Hence the prominence of B_2H^+ and the definite presence of B_2^+ appear to be strong evidence against the bridge structure. Dr. Hipple is continuing with his very interesting investigations, and is planning to determine the appearance potentials of the above ions. Eventually, an analysis similar to the one that he made for ethane may be possible (21).

TABLE 11

Relative intensities of ions formed by electron impact

ION	RELATIVE INTENSITIES		ION	RELATIVE INTENSITIES		ION	RELATIVE INTENSITIES	
	Boron	Carbon		Boron	Carbon		Boron	Carbon
$X_2H_6^+$	0	100	$X_2H_2^+$	63.7	62	XH_3^+		9
$X_2H_5^+$	100	76	X_2H^+	29	12	XH_2^+		6
$X_2H_4^+$	44.8	360	X_2^+	2.2	2.5	XH^+		2.5
$X_2H_3^+$	21.7	105	X^+	40	1	H^+		50
$X_2H_5^{++}$		1				H_2^+		5
$X_2H_3^{++}$		0.1				H_3^+		0.5

XIV. CONCLUSIONS

Boron was found to be either tri-, tetra-, or penta-coördinated in the compounds the structures of which have been determined. The interatomic distances observed can be readily interpreted in terms of resonance among several Lewis structures, provided R_B is assigned a value close to 0.85 Å., and the formula proposed by Schomaker and Stevenson (56), in which the electronegativity difference between the bonded atoms is considered, is employed. The observed boron–hydrogen and boron–boron separations in B_2H_6, B_4H_{10}, B_5H_{11}, B_5H_9, and $Al(BH_4)_3$ are considerably larger than those predicted in this manner. A resonating system of structures involving one-electron bonds and no bonds, as well as electron-pair bonds, is therefore postulated.

The apparent lack of a fixed coördination number for boron suggests that several opposing factors of comparable importance are to be considered; the observed behavior is the result of a balance between various tendencies, summarized by the following set of empirical statements:

(*a*) 5.35 electron volts are required to promote the configuration of boron from the ground state (s^2p, ^2P) to that required for the formation of three planar bonds (sp^2, ^2D). This excitational energy must be less, but not much less, than the stabilizing energy due to bond formation. The boron trialkyls are the only known examples of this case. The tendency of these compounds to associate with other molecules indicates that type (*d*) below is a more stable coördination.

(*b*) In all other stable compounds boron assumes a formal charge, varying in value from 0 to −1, in order that it may participate in the sharing of more than three electron-pair bonds. The electron affinity of boron is very little (estimated at a tenth of a volt), but the promotional energy for B^{-1} (s^2p^2, $^3P \rightarrow sp^3$, ^5S) is probably also low (in the order of 4.7 volts); stabilization due to an increase in the number of bonds may therefore take place. Three types of bindings may result.

(*c*) In the first of these, boron remains tricoördinated, but at times shares an extra electron pair belonging alternately to one of its neighbors (chlorine, oxygen, and nitrogen are examples). A resonating system like that present either in graphite or in benzene results. Generally, this separation of formal charge ($>B^- = {}^+X$) is opposed by the relative electronegativities of the atoms, so that such contributions are not extensive.

(*d*) In the second group, boron is tetracoördinated, and either shares an electron pair of the donor type, thus assuming a formal charge of −1 (H_3BCO, $(C_2H_5)_2O:BF_3$, and $H_3N:B(CH_3)_3$ are examples), or where there is an insufficiency of electrons to give the boron a full formal charge of −1, a resonating system of the type present in diborane results, provided the boron atom is attached to hydrogen or to other boron atoms, for which linkages one-electron bonds are permissible (presumably owing to the fact that the electronegativities of boron and hydrogen are almost equal).

(*e*) In the last group boron is pentacoördinated. It appears quite reasonable that a formal charge greater than −1 requires more excitational energy than could be counterbalanced by the stabilizing effect of the five bonds; hence, pentacoördinated boron occurs only when most of its bonds are to hydrogen or other boron atoms, for which linkages one-electron bonds are possible. A resonating system involving electron-pair-bond, one-electron-bond, and no-bond structures results in a set of directed valences such as would be due to dsp^3 or d^2sp^2 ($Al(BH_4)_3$ or CaB_6, respectively) or equivalent configurations with a formal charge of only −1 on the central boron atom.

(*f*) Where there is an electron deficiency, it is always even; if odd, the ground state would be at least doublet, and there would probably be several low-lying excited states, a condition usually associated with high energy or particular reactivity in the case of polyatomic molecules. Favorable circumstances are required for the deficiency to be greater than four; a deficiency of six present in $Al(BH_4)_3$ appears to be the largest found to date; CaB_6 may have a deficiency of ten per B_6 group, but such an assignment is arbitrary and depends on how the electrons are distributed in the crystal.

The spectra of the hydrides of boron and derivatives which have been studied show strong similarities to those of the corresponding carbon compounds. In general, the observed physical and chemical properties are in agreement with the assigned electron configurations.

I wish to thank Professors Mulliken, Schlesinger, and Burg for their interest in this paper. They read the manuscript prior to publication and offered several helpful suggestions.

REFERENCES

(1) Anderson, T. F., and Burg, A. B.: J. Chem. Phys. **6,** 586 (1938).
(2) Badger, R. M.: J. Chem. Phys. **2,** 128 (1934); **3,** 710 (1935).
(3) Bauer, S. H.: J. Am. Chem. Soc. **59,** 1096 (1937).
(4) Bauer, S. H.: J. Am. Chem. Soc. **59,** 1804 (1937).
(5) Bauer, S. H.: J. Am. Chem. Soc. **60,** 524 (1938).
(6) Bauer, S. H.: J. Am. Chem. Soc. **60,** 805 (1938).
(7) Bauer, S. H., and Pauling, L.: J. Am. Chem. Soc. **58,** 2403 (1936).
(8) Bauer, S. H., and Beach, J. Y.: J. Am. Chem. Soc. **63,** 1394 (1941).
(9) Beach, J. Y., and Bauer, S. H.: J. Am. Chem. Soc. **62,** 3440 (1940).
(10) Bergkampf, E. S. v.: Z. anorg. allgem. Chem. **225,** 254 (1935).
(11) Blum, E., and Herzberg, G.: J. Phys. Chem. **41,** 91 (1937).
(12) Brockway, L. O.: Rev. Modern Phys. **8,** 231 (1936).
(13) Burg, A. B., and Schlesinger, H. I.: J. Am. Chem. Soc. **59,** 780 (1937).
(14) Burg, A. B., and Schlesinger, H. I.: J. Am. Chem. Soc. **62,** 3425 (1940).
(15) Core, A. F.: J. Soc. Chem. Ind. **46,** 642 (1927).
(16) Crawford, B. L., and Edsall, J. T.: J. Chem. Phys. **7,** 223 (1939).
(17) Debye, P. P.: Physik. Z. **40,** 66, 404 (1939).
(18) Dielthey, W.: Z. angew. Chem. **34,** 596 (1921).
(19) Farkas, L., and Sachsse, H.: Trans. Faraday Soc. **30,** 331 (1934).
(20) Freed, S., and Thode, H. G.: Unpublished.
(21) Hipple, J. A., Jr.: Phys. Rev. **53,** 530 (1938).
(22) Hipple, J. A., Jr.: Phys. Rev. **57,** 350 (1940).
(23) Howard, J. B.: J. Chem. Phys. **5,** 442 (1937).
(24) Jahn, H. A., and Teller, E.: Proc. Roy. Soc. (London) **A161,** 220 (1937).
(25) Kelley, K. K.: U. S. Bur. Mines, Bull. No. 407 (1937).
(26) Kimball, G. E.: J. Chem. Phys. **8,** 188 (1940).
(27) King, G. W.: J. Chem. Phys. **6,** 378 (1938).
(28) Kistiakowsky, G. B., Locker, J. R., and Stitt, F.: J. Chem. Phys. **7,** 289 (1939).
(29) Klemm, L., and Klemm, W.: Z. anorg. allgem. Chem. **225,** 258 (1935).
(30) Klemm, L.: Z. Elektrochem. **45,** 354 (1939).
(31) Laubengayer, A. W., Ferguson, R. P., and Newkirk, A. E.: J. Am. Chem. Soc. **63,** 559 (1941).
(32) Lewis, G. N.: J. Chem. Phys. **1,** 17 (1935).
(33) Linnett, J. W.: Trans. Faraday Soc. **36,** 1123 (1940) for brief review of subject.
(34) Mark, H., and Pohland, E.: Z. Krist. **62,** 103 (1925).
(35) Maxwell, L. R.: J. Optical Soc. Am. **30,** 374 (1940).
(36) Möller, H.: Z. Krist. **76,** 500 (1931).
(37) Mulliken, R. S.: Rev. Modern Phys. **4,** 1 (1932).
(38) Mulliken, R. S.: Phys. Rev. **46,** 549 (1934).
(39) Mulliken, R. S.: J. Chem. Phys. **2,** 400 (1934).
(40) Mulliken, R. S.: J. Chem. Phys. **3,** 506 (1935).
(41) Mulliken, R. S.: J. Chem. Phys. **3,** 517 (1935).
(42) Mulliken, R. S.: J. Chem. Phys. **3,** 635 (1935).
(43) Mulliken, R. S.: J. Chem. Phys. **3,** 720 (1935).
(44) Mulliken, R. S.: J. Chem. Phys. **7,** 339 (1939).

(45) MULLIKEN, R. S., RIEKE, C. A., AND BROWN, W. G.: J. Am. Chem. Soc. **63,** 41 (1941) and references given therein.
(46) PAULING, L.: *The Nature of the Chemical Bond.* Cornell University Press, Ithaca, New York (1939).
(47) PAULING, L.: J. Am. Chem. Soc. **53,** 3225 (1931).
(48) PAULING, L., AND HUGGINS, M. L.: Z. Krist. **A87,** 205 (1934).
(49) PLUMLEY, H. J. (reported by Mulliken): J. Phys. Chem. **41,** 305 (1937).
(50) RAMASWAMY, K. L.: Proc. Indian Acad. Sci. **2A,** 364, 630 (1935).
(51) ROTH, W. A., AND BÖRGER, E.: Ber. **70,** 48 (1937).
(52) ROTH, W. A., BÖRGER, E., AND BERTRAM, A.: Ber. **70,** 971 (1937).
(53) SCHLESINGER, H. I., AND BROWN, H. C.: J. Am. Chem. Soc. **62,** 3429 (1940).
(54) SCHLESINGER, H. I., RITTER, D., AND BURG, A. B.: J. Am. Chem. Soc. **60,** 2297 (1938).
(55) SCHLESINGER, H. I., SANDERSON, R. T., AND BURG, A. B.: J. Am. Chem. Soc. **61,** 536 (1939); **62,** 3421 (1940).
(56) SCHOMAKER, V., AND STEVENSON, D. P.: J. Am. Chem. Soc. **63,** 37 (1941).
(57) SCHOMAKER, V., AND STEVENSON, D. P.: Private communication.
(58) SIDGWICK, N. V.: *The Electronic Theory of Valence,* p. 103. Oxford University Press, London (1929).
(59) STITT, F.: J. Chem. Phys. **7,** 297 (1939).
(60) STITT, F.: J. Chem. Phys. **8,** 981 (1940).
(61) STITT, F.: J. Chem. Phys. **9,** 780 (1941) and private communications.
(62) STOCK, A.: *Hydrides of Boron and Silicon.* Cornell University Press, Ithaca, New York (1932).
(63) STOCK, A., AND LAUDENKLOS, H.: Z. anorg. allgem. Chem. **228,** 178 (1936).
(64) STOCK, A., WIBERG, E., AND MATHING, W.: Ber. **69,** 2811 (1936).
(65) STOCK, A., AND WIERL, R.: Z. anorg. allgem. Chem. **203,** 228 (1931).
(66) STONER, E. C.: *Magnetism and Matter,* p. 470. Methuen and Co., London (1934).
(67) SUTHERLAND, G. B. B. M.: J. Chem. Phys. **7,** 1066 (1939).
(68) VAN VLECK, J. H., AND SHERMAN, A.: Rev. Modern Phys. **7,** 168 (1935).
(69) WATSON, H. E., AND RAMASWAMY, K. L.: Proc. Roy. Soc. (London) **A156,** 144 (1936).
(70) WIBERG, E.: Ber. **69,** 2816 (1936).
(71) WILSON, E. B., JR.: Phys. Rev. **45,** 706 (1934).