junction between two salt solutions of arbitrary composition. The analysis is restricted to the class of strong electrolytes for which it may be assumed that the relative mobilities of the ions are constant through the system.

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Electron Deficient Molecules. I. The Principles of Hydroboron Structures

BY KENNETH S. PITZER

Atoms such as boron and aluminum with fewer valence electrons than valence shell orbitals do not complete their valence shells by electron sharing of the usual type. While many compounds of such elements are metallic and others are salt-like or ionic, still others consist of essentially non-polar molecules. Such molecules can be termed electron deficient. In some cases the simple molecules predicted by conventional valence theory actually combine further. The most extensive series of this type is the subject of this paper.

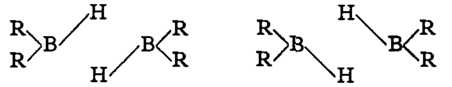
The compounds of hydrogen with boron have long been a puzzle in valence theory. In 1942 Bauer[1] summarized the most fully developed theory of that time, which assumed hydrocarbon-like structures. Since too few electrons are present for electron pair bonds, resonance is assumed among structures with one electron and no electron bonds in various positions. The net results with this point of view are unsatisfying. At many points the natural, expected result is not found and the theory must be strained to fit the facts. One may mention the infrared spectrum[2] of B_2H_6, which is quite unlike that of C_2H_6, and the need of assuming a higher potential barrier to internal rotation[2] in B_2H_6, than in C_2H_6, in spite of larger distances and fewer electrons in the former. Other points will be noted below. However, possibly a more serious failure of the hydrocarbon-like structural theory is its failure to give any adequate reasons for the existence of the particular hydroborons that are found, and for the absence of any others in the lower molecular weight range. For example, why should there be no molecule with three boron atoms?

Very recently Nekrasov,[3] Syrkin and Dyatkina[4] and Longuet-Higgins and Bell[5] have revived and discussed the structure proposed earlier by Dilthey[6] and by Core.[7] This structure places two of the hydrogen atoms of B_2H_6 between the boron atoms, one above and one below the plane of the rest of the molecule. Thus a small, four-membered ring bond or bridge is formed. The evidence as presented by these authors[3,4,5] is most favorable to this point of view. Indeed the theory presented below develops in part from this structure and is entirely consistent with it. However, several additional elements are needed before all hydroboron chemistry is brought into a coherent picture.

The first important addition is the recognition that this ring bond is not inconsistent with the essentials of the Wiberg[8] structure, which so ably explained certain reactions of the hydroborons. The present picture is much more specific than Wiberg's, and differs from it in many ways. Hellriegel[9] proposed somewhat similar structures to those given below, but his postulate of K shell binding is totally different and is not acceptable. Let us now proceed with a logical exposition of the theory.

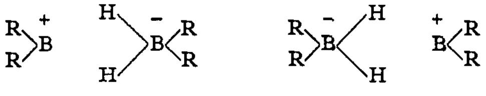
The Protonated Double Bond.—The first element of the theory is the new type of bond. It can form between electron pair bonded groups of the general formula R_nMH where $n + 1$ is less than the number of valence shell orbitals of the atom M. Thus in $(CH_3)_2BH$ or BH_3 all atoms are bonded with electron pair bonds, but the boron atom has one vacant orbital, and there is at least one hydrogen atom bonded to boron. The formation of this bond uses one hydrogen atom and one vacant orbital in each group.

As two such groups come together with a hydrogen of one group near the vacant orbital of the other, the following resonance can occur



I

where we have taken boron with its valence shell of four orbitals as the example. Ionic forms are also possible.



II

These forms will be particularly important if one central atom is more electronegative than the

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(1) S. H. Bauer. *Chem. Rev.*, **31**, 43 (1942).

(2) F. Stitt, *J. Chem. Phys.*, **8**, 981 (1940); and **9**, 780 (1941).

(3) B. V. Nekrasov. *J. Gen. Chem.* (U. R. S. S.). **10**. 1021, 1156 (1940).

(4) Ya. K. Syrkin and M. E. Dyatkina. *Acta Physicochim.* (U. R. S. S.). **14**, 547 (1941); *Compt. rend. acad. sci.* (U. S. R. S.). **35**, 180 (1942).

(5) H. C. Longuet-Higgins and R. P. Bell. *J. Chem. Soc.*, 250 (1943).

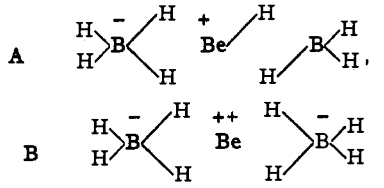
(6) W. Dilthey. *Z. angew. Chem.*, **34**. 596 (1921).

(7) A. F. Core, *Chemistry and Industry*, **5**. 642 (1927).

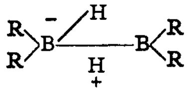
(8) E. Wiberg, *Ber.*, **69B**. 2816 (1936), and earlier papers there cited. See also B. Eistert. *Z. physik Chem.*, **B52**, 202 (1942); and M. L. Huggins, *J. Phys. Chem.*, **26**. 833 (1922).

(9) W. Hellriegel, *Z. anorg. allgem. Chem.*, **185**, 65 (1930).

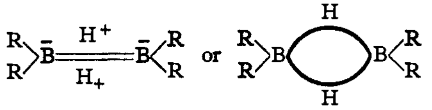
other. Thus in $Be(BH_4)_2$ the four forms of type A will be very important and even B will contribute markedly. Probably $LiBH_4$ is almost fully ionic.



However, at the distances involved, direct bonding between the two central atoms is also possible. As Bauer[1] pointed out, forms such as



involve too small a bond angle. However, the structure involving a double bond is not subject to this objection.


III

The second form under III is written to remind one that the electron cloud of a normal double bond spreads out in the plane perpendicular to that of the R's. Thus the electron density (probability) implied by III is not much different from that of a resonance of the various forms in I and II. The difference is primarily a moderate increase in electron density around the protons in I and II. Numerous structures involving one-electron bonds can also be written.

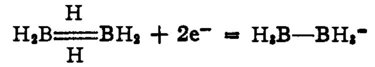
This new bonding unit, although geometrically similar to the chlorine ring or bridge in $Cl_2AlCl_2AlCl_2$, is intrinsically different in electronic arrangement. Let us call it a proton containing double bond or, shorter, a *protonated double bond*. The left form III, less the charges, will be used as a shorthand expression of it.

The essential orbital characteristics of the atoms are that M has two bonding orbitals available (at bond angles not greatly exceeding, say 100°) and that the atom called H has an *s* orbital available. Silver ion has an *s* orbital vacant and does form complexes with olefins. Except for the presence of only one silver per double bond (because of electrical repulsion) this "argentated double bond" is quite similar to the protonated double bond. The structures written by Winstein and Lucas[10] are consistent with this picture. This theory does not predict[5] a ring molecule, H_4, because the H atoms in the M positions would not have two bonding orbitals available.

The molecular orbital picture of this bond is easily derived by breaking two protons off the carbon nuclei in ethylene and moving them to the indicated positions. It is readily seen that the same molecular orbitals are still appropriate, though now concentrated more around the protons.

The general properties of this structural unit are just those expected of a double bond with two protons imbedded in it.

1. The protons increase the X–X bond distance several tenths Å. above the double bond value to roughly a single bond value. This is easily understood on the basis of electrical repulsions.
2. The bond resists twisting as a double bond.
3. Two additional electrons can be added. However, the two groups to use these new single bonds are already present in the form of the double bond hydrogens. Thus

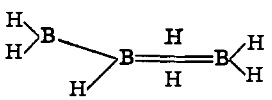


$$H_2B\overset{H}{\underset{H}{=\!=}}BH_2 + 2e^- = H_3B{-}BH_3^-$$

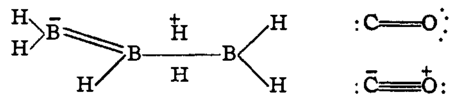
4. The double bond protons can be removed by strong bases.
5. The presence of the two protons capable of forming separate single bonds makes it much easier to break this double bond than an ordinary one.
6. The electronic energy levels and hence the electronic spectra are very similar to those of ordinary double bonds. This follows because the protons cannot move appreciably in the time of an electronic transition. However, an excited state, which is stable in an ordinary double bond, might lead to eventual dissociation of a protonated double bond.
7. The usual conjugation or resonance phenomena of double bonds can occur.

It is not to be inferred that the one electron bond resonance structure[1,11] for an ethane-like diborane is unstable. Probably it is stable, but the protonated double bond structure is more stable and therefore is the form observed.

Conjugation with Protonated Double Bonds.—The next essential element of the theory is the interaction of protonated double bonds with adjacent unsaturated groups. If a B_2H_4 group combines with one BH_3 the structure



is formed. Here the first boron atom has a vacant orbital. Consequently, we would expect the double bond to conjugate or resonate with it in a fashion somewhat analogous to carbon monoxide.



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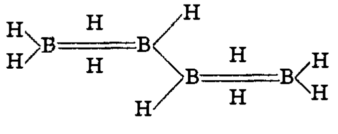
[10] S. Winstein and H. J. Lucas, This Journal, 60, 836 (1938).

[11] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

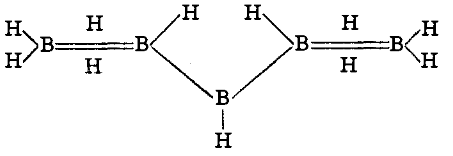
The effect in the boron system will be weaker because charge separations are greater there. Nevertheless, we would expect this B_3H_7 structure to be more stable than BH_3 with its completely vacant orbital.

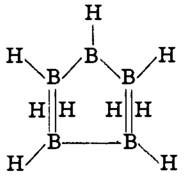
Actually this stabilization of B_3H_7 is not enough for it to exist as a stable molecule. This B_3H_7 group adds another BH_3 to form tetraborane, for which we assume the structure



This molecule is less stable[12,13] than B_2H_6, possibly because the dissociation $B_4H_{10} = BH_3 + B_3H_7$ is assisted by conjugation whereas $B_2H_6 = 2BH_3$ is not.

However, if the boron atom with the nominally vacant orbital is adjacent to two protonated double bonds, it is not only conjugated to both but is also the avenue of interaction between the two double bonds. Now this orbital is so occupied that combination with another BH_3 to form a protonated double bond at this point does not occur. Thus we find as stable molecules B_5H_9 and B_5H_{11} with structures as follows





The names pentaborane (or normal pentaborane) and cyclopentaborane would seem to be appropriate.

Strictly, it cannot be said that these molecules will not add BH_3; rather, that the reactions in which B_2H_6 would furnish BH_3 do not proceed.

$$2B_5H_{11} + B_2H_6 \longleftarrow 2B_6H_{14}$$

The type of conjugation that exists between the two double bonds of 1,3-butadiene no doubt also exists in tetraborane and cyclopentaborane, as we shall see later. However, it is an effect of a weaker order than the one considered above.

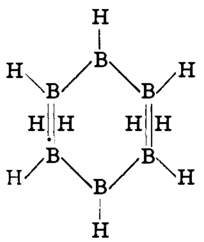
Summary of Principles and Hydroboron Structures.—If we add the expected rule that rings of fewer than five heavy atoms (borons) are excessively strained, we have completed the discussion of the primary principles of hydroboron structures. Let us tabulate them.

1. In addition to the usual B–B and B–H single bonds, protonated double bonds can form between two boron atoms, if each has both a vacant orbital and a singly bonded hydrogen atom.
2. These protonated double bonds will form until all vacant orbitals are occupied, except that nominally vacant orbitals conjugated with (adjacent to) two or more protonated double bonds are regarded as occupied.
3. Rings of less than five boron atoms are too strained to be stable.

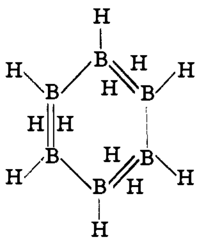
In order to show just what hydroborons are expected, let us take the lighter groups, sometimes called borines, which involve only B–B and B–H bonds, and see how they can be linked together. No ordinary boron–boron double bonds are assumed, nor would they be expected to form.

a. $2BH_3 \longrightarrow B_2H_6$
b. $H_2B—BH_2 + 2BH_3 \longrightarrow B_4H_{10}$
c. $2H_2B—BH_2$ = a four-membered ring which is not stable
d. $3H_2B—BH_2 \longrightarrow B_6H_{12}$, a six-membered ring
e. $xH_2B—BH_2 \longrightarrow$ an infinite chain or larger ring
f. $nH_2B—BH_2 + 2BH_3 \longrightarrow$ a long chain with BH_3 completing each end
g. $H_2B—BH—BH_2 + 2BH_3 \longrightarrow B_5H_{11}$
h. $H_2B—BH—BH_2 + H_2B—BH_2 \longrightarrow B_5H_9$
i. $2H_2B—BH—BH_2 \longrightarrow B_6H_{10}$, a six-membered ring
j. Reactions of B_3H_5 of the type e and f

The structures of most of these molecules have been given above; the two hexaboranes have the following structures



B_6H_{10}



B_6H_{12}

We have now accounted for all known boranes of six or less boron atoms and have predicted no unknown compounds in this range. Stock[12] considers that B_6H_{12} probably exists, but has not yet characterized it as well as the others.

Structures involving the next "borine" $H_2B—BH—BH—BH_2$ are not too clear cut. The end borons can easily form protonated double bonds with $2BH_3$ to give a chain, or with B_2H_4 to give a ring, but this leaves the two middle boron atoms only singly conjugated. Thus any stable molecules must contain more than six borons. Probably several forms are of comparable stability, making it difficult to isolate any one.

The branched borine, $B(BH_2)_3$, should add three BH_3 to give B_7H_{15} or BH_3 and B_2H_4 to give B_7H_{13}. These would have the structures

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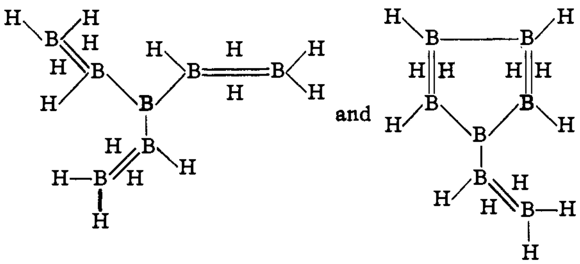
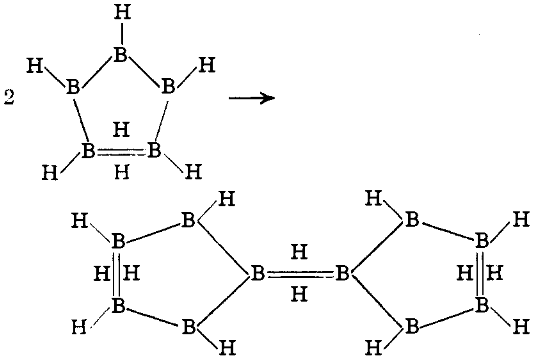
(12) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1933.

(13) H. L. Schlesinger and A. B. Burg, *Chem. Rev.*, **31**, 1 (1942). References 12 and 13 contain general information on hydroboron chemistry and references to the original literature.



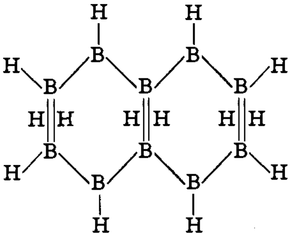
Neither has been prepared, but it is doubtful if present methods produce any considerable quantities of the branched borine.

The normal borine B_5H_7 presents the first case where the borine can complete a ring by itself. Two of these rings then join to give the most stable known volatile borane, $B_{10}H_{14}$.



A

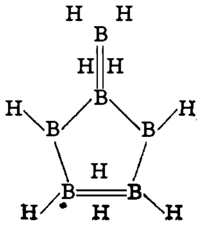
Nekrasov[3] proposed a naphthalene-like structure for decaborane, which is also formally possible under these principles.



B

However, the probability of the B_5H_7 groups remaining open chains until this structure forms is very small. Furthermore, the freedom of vibrational motion in form A is certainly greater than in B, giving A the larger entropy. Therefore, unless some unexpected energy difference arises, form A should be thermodynamically stable. Additional evidence will be mentioned below.

The borine B_5H_7 might also combine with BH_3 to give an isomer of B_6H_{10} of the structure



However, since decaborane is produced and is stable in the presence of diborane, this molecule probably disproportionates according to the equation

$$2B_6H_{10} = B_2H_6 + B_{10}H_{14}$$

This completes the list of definitely characterized hydroborons. Many boranes are possible with seven or more boron atoms. Also it is easy to see that a variety of long or infinite chain "polymers" are possible. Such substances are known to form[12] and can be correlated with this theory. However, it does not seem worth while to discuss them in detail at present.

Physical Properties of the Hydroborons

Let us now see if the physical properties of the hydroborons are consistent with these structures.

Electron Diffraction.—The evidence which, *prima facie*, opposes these structures is that of electron diffraction.[14,15] However, we may immediately say that the structures expected on the present theory were not tested in the original researches. Longuet-Higgins and Bell[5] report that for diborane both the ethane-like and the "bridge" or protonated double bond models give reasonably satisfactory but not perfect agreement with the observed pattern. Thus either is acceptable so far as this criterion is concerned.

When one considers the essential principle of electron diffraction, this lack of differentiation is not surprising. The electron diffraction pattern depends essentially on the boron–boron and the boron–hydrogen distances without regard to their relative positions. Hydrogen–hydrogen scattering is practically negligible. Thus the boron–boron, six short boron–hydrogen and four long boron–hydrogen terms are the same for both models of diborane. The difference is that the two remaining boron–hydrogen terms are for the short distance on the present model, but for the longer distance in the ethane-like model. It is therefore not surprising that small changes in the exact distances can counteract this small change.

On this basis it seems certain that the electron diffraction patterns of B_4H_{10} and B_5H_{11} can also be explained on the present model since equally small differences are involved. For B_5H_9, however, there is more justification for doubt, since five-membered rings were discarded by Bauer and Pauling[15] in favor of a methylcyclobutane-like structure. However, these authors did not test unsymmetrical rings. Consequently, the electron diffraction pattern was calculated for the present model and after a few adjustments an acceptable pattern was obtained as shown in Table I. Because of the labor involved and the writer's present circumstances, no attempt was made to test small changes in all parameters in order to improve the agreement.

[14] S. H. Bauer, THIS JOURNAL, 59, 1096 (1937); 60, 805 (1938).

[15] S. H. Bauer and L. Pauling, *ibid.*, 58, 2403 (1936).

TABLE I

RING DIAMETERS FOR THE ELECTRON DIFFRACTION PATTERN OF B_5H_9

Units: $s = 4\pi (\sin \theta/2)/\lambda$

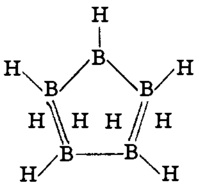
Obs. B. and P. Max.	Obs. B. and P. Min.	Calcd. B. and P.	Calcd. This research
3.36		4.18	3.1
5.34		5.59	5.4
	6.80	6.75	6.6
8.00		7.94	7.85
	9.67	9.40	9.5
11.49 (broad)		11.40	12.2[a]
15.61		15.54	15.2

This peak is very unsymmetrical; its center of gravity is near 11.5.

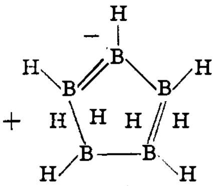
The calculated maxima and minima are based on the customary approximate equation, $I = \Sigma Z_i Z_j \sin sd_{ij}/sd_{ij}$ in which Z is the atomic number, d is the interatomic distance, and s, as defined in Table I, is a measure of the angle of scattering. The sum is taken over all pairs of atoms.

The fit of ring diameters is about as good as the Bauer and Pauling model. Comparison of intensities is equally indeterminate. The present model makes the peak near 5.4 stronger than that at 8, whereas the reverse is observed. On the other hand, the methyl cyclobutane model gives equal intensity to the peaks at 4 and 5.5, whereas the latter is observed as three times as strong. Otherwise, both models give satisfactory intensities. We conclude merely that either model is acceptable so far as electron diffraction is concerned.

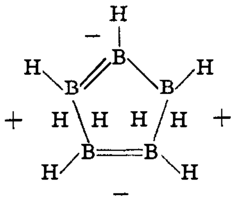
The details of the assumed model for B_5H_9 are based on the following electronic structures; the resonance within the protonated double bonds is not shown.



(A)



(B)



(C)

Here A is the normal form, B and its equivalent (left to right transposition) are large contributors, while C and its equivalent are minor contributors.

The assumed distances are B—B single bond (at bottom of diagrams) 1.7, conjugated single bond (at top of diagrams) 1.5, protonated double bond 1.75, B—H single bond 1.1, B—H in protonated double bond 1.25 Å. The protons in the double bond are displaced outward from the line between the boron atoms by 0.25 Å. and are 0.86 Å. above or below the plane of the other atoms. The ring angles are made as uniform as possible, the angle at the top as drawn being 113°.

These distances are reasonable in so far as present bond radii can be applied. Pauling[11] gives 1.76 Å. as the normal B—B single bond. Thus the single bond between the two double bonds, with its slight conjugation, should be about 1.7 Å. However, he finds a shortening of 0.09 Å. when only three orbitals are occupied. This, together with the very considerable double bond character, makes 1.5 Å. reasonable for the highly conjugated single bonds. We can only compare the 1.75 Å. for the protonated double bond with the value 1.8 Å. reported for the same bond in diborane.[1,4,5] The outward displacement of the double bond protons is due to electrical repulsion.

While all features are reasonably satisfactory, it remains for a thorough refitting of the electron diffraction data on all hydroborons to give us accurate interatomic distances.

X-Ray Diffraction.—The data of Mark and Pohland[16] on diborane give only the boron–boron distance and therefore allow either model. However, the work of Möller[17] on $B_{10}H_{14}$ would probably yield much information. Exploratory calculations by the writer indicate that the model with two five-membered rings joined by a protonated double bond (labelled A above) is acceptable whereas the naphthalene-like model is not.

Molecular Vibration Spectra.—Data are available only for diborane.[2,18] Briefly, neither the Raman spectrum[18] nor the infrared spectrum[2] of diborane bears any particular resemblance to that of ethane. Stitt[2] pointed out that these spectra for diborane could be interpreted on a bridge model without difficulty; however, he considered in detail only the ethane model and was forced to assume electronic transitions of low frequency. Longuet-Higgins and Bell[5] and Wagner[19] feel that the present model is far more consistent with the spectra than the ethane-like model. The former authors[5] have promised a complete analysis, hence only an indication of the possibilities is given here in Table II. Values for ethylene are given for comparison. This assignment accounts for all strong lines as fundamentals of reasonable frequency. However, it is not unique. The heat capacity, mentioned below, is consistent with reasonable values of the unobserved frequencies.

The symmetry classes are given conventional symbols, g meaning symmetric and u antisymmetric, with respect to the center of inversion. A_1 motions maintain all three two-fold rotation axes, B_1 maintains only the two-fold axis perpendicular to the plane of the borons and the

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(16) Mark and Pohland, *Z. Krist.*, **62**, 103 (1925).

(17) H. Möller, *ibid.*, **76**, 500 (1931).

(18) T. F. Anderson and A. B. Burg, *J. Chem. Phys.*, **6**, 586 (1938).

(19) J. Wagner, *Z. physik. Chem.*, **B53**, 85 (1943).

TABLE II

POSSIBLE VIBRATIONAL ASSIGNMENT FOR B_2H_6

	B_2H_6				C_2H_4		
	BH Stretching		BH Bending				
Symmetry class	End H	Double bond H	End H	Double bond H	C–H Stretching	C–H Bending	C=C Stretching
A_{1g}	2523	2101	1180	792[a]	3019	1342	1623
A_{1u}			*ca.* 700 not obs.			825	
B_{1g}		2005	1008			950	
B_{1u}	2625		(1287	412)	3106	995	
B_{2g}	2488		*ca.* 1000 not obs.		3069	1055	
B_{2u}		1863	981			949	
B_{3g}			821				
B_{3u}	2558	1608	1178		2990	1440	

[a] This line at 792 has a satellite at 806 due to the lighter isotope of boron. It can also be described as the stretching mode of the protonated double bond.

double bond hydrogens, B_2 maintains the axis through the double bond hydrogens, while B_3 maintains the two-fold axis through the boron atoms. The parentheses about 1287, 412 indicates that these vibrations do not correspond clearly to end or double bond hydrogen motions, but are a mixture of both.

Probably the most striking feature is the very high absorption intensity of the infrared bands corresponding to vibration of the double bond protons. This is in accord with their polar nature as manifested in ammonia reactions,[8,12] etc. It is also in beautiful qualitative agreement with the high atomic polarization of diborane reported by Ramaswamy.[20] He finds a value of 1.55 cc. for diborane, in marked contrast to 0.0 for ethane, but similar to values[21] such as 1.2 for HCl, 1.9 for C_2H_2, 3.0 for CCl_4, and 5.3 for H_2O. Unfortunately, attempts to quantitatively correlate absorption coefficients with atomic polarizations have not been too successful.

Specific Heat.—Here again we have data only on diborane.[2] Until a complete vibration frequency assignment is available, all that can be said is that the observed specific heat is entirely consistent with the present model, which has no internal rotation. On the ethane-like model it was necessary to assign an unexpectedly high potential barrier to internal rotation in order to fit the data.

Optical Spectra, Diamagnetism.—As has been pointed out by others[8,12] the spectrum of diborane is similar to ethylene. This would be expected on the present model since the electronic structures are equivalent. Diborane is transparent in the near infrared,[22] visible,[22] and out to about 2200 Å. in the ultraviolet.[23] Tetraborane, B_4H_{10}, absorbs at somewhat longer wave lengths[24] as would be expected by analogy to the electronically equivalent 1,3-butadiene.

It may be mentioned that the much smaller diamagnetic susceptibility of diborane[25] (-17×10^{-6} per mole) as compared to ethane (-30×10^{-6}) supports the present structure with its similarity to ethylene (-15×10^{-6}).

The discussion by Longuet-Higgins and Bell[5] includes certain other properties and is usually appropriate to the present picture.

Conclusions.—1. The theory as presented above is consistent with quantum mechanical principles of electronic structure.

2. It gives stable structures to all observed hydroborons and accounts perfectly for the absence of others in the range experimentally studied.

3. The observed physical properties of these hydroborons are consistent with those expected from this theory. In view of the relative lack of successful correlation of other borane theories with all these facts, it seems most likely that the present theory is substantially correct.

The writer hopes soon to continue with a consideration of the various chemical reactions of hydroborons, which will contribute additional evidence. The structures of similarly electron deficient molecules are also to be considered.

Summary

A theory is proposed which assigns reasonable structures to all definitely identified hydroboranes and which predicts no others in the adequately studied range (molecules of six or fewer boron atoms). In addition, all physical properties of these molecules agree very satisfactorily with expectations based on the theory.

Specifically, it is proposed that a new type of bond exists in these molecules. This bond may be derived from an ethylenic double bond by breaking a proton off of each carbon nucleus and placing the protons symmetrically between the atoms (now boron) but one above and one below the plane of the rest of the molecule. In this position they are still well within the electron cloud of the double bond. An alternate formulation in terms of resonance forms is given for this bond which is named a *protonated double bond.*

Various properties to be expected of such a bond are listed. The most important is its ability to conjugate with the otherwise vacant orbital of an adjacent boron atom. If such a nominally vacant boron orbital is conjugated with two protonated double bonds it may be regarded as saturated. These principles, together with the expected one that rings of fewer than five boron atoms are unstable, comprise the essentials of the theory.

The physical properties considered include X-ray and electron diffraction patterns, Raman, infrared, and ultraviolet spectra, and specific

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[20] K. L. Ramaswamy, *Proc. Indian Acad. Sci.*, **2A**, 364, 630 (1935).

[21] C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., New York, N. Y., 1931, p. 164.

[22] H. J. Plumley (reported by Mulliken), *J. Phys. Chem.*, **41**, 305 (1937).

[23] E. Blum and G. Herzberg, *ibid.*, **41**, 91 (1937).

[24] Hausser, reported by Stock (ref. 9), p. 153.

[25] S. Freed and H. G. Thode, reported by S. H. Bauer (ref. 1).

heat. The electron diffraction pattern of B_5H_9 was calculated for the present model, and a possible vibrational assignment offered for B_2H_6.

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[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,[1] PHILADELPHIA, PENNSYLVANIA]

Catalytic Air Oxidation of Methyl Oleate and Characterization of the Polymers Formed[2]

BY DANIEL SWERN, H. B. KNIGHT, JOHN T. SCANLAN AND WALDO C. AULT

Reaction of oxygen with unsaturated fatty materials is a complex phenomenon and, although much has been published on this subject, the mechanisms involved are not understood. The natural triglycerides, on which much of the work has been done, are complex mixtures. This, together with the fact that some investigators[3] have based their conclusions upon analytical data obtained on unfractionated oxidation mixtures, has made it difficult to determine the real nature of the reactions. It is true that within the last fifteen years some workers in this field[4,5,6,7] have directed their investigations to relatively simple materials of known structure and, in general, of high purity, but even with such materials the occurrence of many simultaneous reactions was observed. In some of these cases, the simple monomeric oxidation products were isolated and identified, but in every instance a large proportion of high-boiling material remained uncharacterized.

The purpose of the present investigation was to determine the effect of catalytic air oxidation upon pure methyl oleate, with particular emphasis on the characterization of the high-boiling substances produced. Methyl oleate, with cobalt oleate as catalyst, was oxidized at 65° with air until the iodine number became substantially constant. The product, an orange-red oil, was saponified with aqueous sodium hydroxide. When the resulting product was acidified, a mixture of an ether-insoluble, white solid and an ether-soluble oil was precipitated. The white solid was the high melting 9,10-dihydroxystearic acid. The ether-soluble material was converted to methyl esters and steam distilled under reduced pressure from a Claisen flask. The volatile material was fractionally distilled (Table I). Pelargonic, azelaic, and both the low and high melting 9,10-dihydroxystearic acids were identified in the distillate. This corroborated substantially the findings of Skellon[4] and Ellis,[5] who also identified these substances in addition to numerous others, such as octanoic and suberic acids. These workers did not, however, fractionate and characterize the material corresponding either to fraction 4, Table I, or to our original distillation residue. The latter was a dark, reddish-brown, viscous oil and constituted about 30 to 40% of the total oxidation products. By molecular distillation, this residue was separated into fractions of increasing molecular weight, ranging in color from light yellow to dark brown (Table II).

Fraction 4, Table I, was converted to free acids, and by fractional crystallization both 9,10-dihydroxystearic acids were isolated and identified. The oil obtained from the crystallization filtrate (usually at least 80% by weight of fraction 4) was reconverted to methyl esters. On the basis of the analytical characteristics alone, it might be concluded that this material consists of 35% unreacted methyl oleate, 25% methyl 9,10-dihydroxystearate (or 60% methyl 8- and 11-monohydroxyoleate[7a]) and 40% methyl esters of polymeric acids, probably dimers. This hypothesis is untenable, since oxidative splitting of this material with potassium permanganate in acetone solution yielded only minor quantities of pelargonic and azelaic acids. If fraction 4 consisted mainly of methyl oleate and methyl 9,10-dihydroxystearate, or methyl 8- and 11-hydroxyoleate, considerable quantities of pelargonic and azelaic acids would have been obtained. The major scission products consisted of heptanoic, pimelic, suberic and sebacic acids, as well as a mixture of short-chain scission products with a much lower boiling point than that of heptanoic acid. We believe that the isolation of such a variety of split products, considered in conjunction with the analytical characteristics of fraction 4, is reasonably satisfactory evidence for the presence in this fraction of methyl esters of several isomeric monohydroxy derivatives of one or more mono-unsaturated acids in which the double bond has been shifted from the 9,10-position. No previous evidence of a double-bond shift during oxidation of methyl oleate has come to our attention, although previous investigators have demonstrated that the double bonds of poly-unsaturated compounds are shifted during oxidation and have suggested that such shifts might also occur in mono-olefinic substances.[8] The residue remaining after distillation of the products of the permangate oxidation of

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

[2] Original manuscript received August 31, 1944.

[3] Overholt and Elm, *Ind. Eng. Chem.*, **32**, 378, 1348 (1940); **33**, 658 (1941); Powers, Overholt and Elm, *ibid.*, **33**, 1257 (1941).

[4] Skellon, *J. Soc. Chem. Ind.*, **50**, 382 (1931).

[5] Ellis, *Biochem. J.*, **26**, 791 (1932); *ibid.*, **30**, 753 (1936).

[6] Henderson and Young, *J. Phys. Chem.*, **46**, 670 (1942).

[7] (a) Farmer and Sutton, *J. Chem. Soc.*, 119 (1943); (b) Sutton, *ibid.*, 242 (1944).

[8] Farmer, Koch and Sutton, *ibid.*, 541 (1943).