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On the Bonding in Electron Deficient Compounds of Boron[1,2]

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The nature of the bonding in electron deficient compounds of boron is discussed with reference to their intermediate position as a class between ordinary covalent compounds and the metals. In particular, the bond lengths, which vary widely (*e.g.*, B–H = 1.15 to 1.40 Å., B–B = 1.66 to 1.93 Å.), are successfully correlated with Pauling's equation $r(n) = r(1) - 0.3 \log_{10} n$ with best $r(1)$ for boron about 0.80 Å. in a way which can also be used for molecules of unknown structure to obtain additional structural information from incomplete data.

The boron hydrides and their derivatives present very interesting problems in valence theory. Most of these compounds are essentially non-ionic and have the physical properties of ordinary covalent compounds; however, for lack of enough valence electrons they cannot be assigned classical covalent structures.

Progress toward an understanding of the nature of the bonding in these "electron deficient"[3] compounds has been slow, largely, perhaps, because knowledge even of their molecular configurations has been inadequate. For example, it was once widely supposed that in the boron hydrides boron had ligancy three or four and hydrogen ligancy one, and that although resonance among a number of one-electron bond and no-bond valence structures was involved, the molecules were configurationally similar to certain corresponding hydrocarbons.[4] In the cases now known, however, boron has ligancy five or six and hydrogen sometimes two (giving rise to orbital deficiency as well as electron deficiency[5]) and the over-all structures are novel. Indeed, they are not even very closely related to each other, and consequently Pitzer's attempt[6] to predict the configurations of the higher boron hydrides on the assumption of the generality of the "bridge bond" or "protonated double bond" unit that had become likely for diborane has been unsuccessful. It may be noted, however, that hydrogen bridge bonds do occur in all the boron hydrides and their derivatives so far investigated (diborane, B_2H_6,[7] stable pentaborane, B_5H_9,[8] decaborane, $B_{10}H_{14}$,[9] and the aminodiboranes, $H_2NB_2H_5$ and $(CH_8)_2NB_2H)_5$,[10] but, except for B_2H_6, they are all of the one-hydrogen rather than of the two-hydrogen type.

The structural information now available for B_2H_6, B_5H_9, $B_{10}H_{14}$ and $H_2NB_2H_5$ and $(CH_3)_2NB_2H_5$ and in particular the bond length values which are fairly numerous and widely various ($B\text{–}H_{\text{bond}}$ = 1.15[10] to 1.29 Å.,[9] $B\text{–}H_{\text{bridge}}$ = 1.33[7b] to 1.40 Å.,[9] B–B = 1.66[8b] to 1.93 Å.[10]), seems to provide a good basis for a fresh attack in the problems of electron deficient bonding. This paper is concerned primarily with the bond lengths in these compounds and in all the related boron compounds of reasonably well-known structure: an extension of Pauling's theory of the bonding in metals and intermetallic compounds[11] leads to a very satisfactory correlation of the observed distances and hence to the conclusion that typical electron deficient bonding, while of course not typically metallic, is surely rather closely related.

The Type of Bonding and Bond Distances.—In B_2H_6, B_5H_9, $B_{10}H_{14}$, and $(CH_3)_2NB_2H_5$ and $H_2NB_2H_5$ the boron atoms have five or six ligands, as in the metallic hexaborides,[12] boron carbide (B_4C),[13] and elementary boron.[14] Indeed, the boron skeleton of B_5H_9 has just the configuration of an octahedral B_6 group of the hexaborides from which one atom has been removed, and the skeleton of $B_{10}H_{14}$ has the configuration of an icosahedral B_{12} group of B_4C or elementary boron from which two adjacent atoms have been removed. In both B_5H_9 and $B_{10}H_{14}$ some of the hydrogen atoms are shared by adjacent boron atoms (as bridges); these bridges exist between boron atoms adjacent to those missing from the octahedral and icosahedral groups such that the high ligancy around boron is maintained or even increased. These similarities in configuration and boron ligancy suggest the existence of similarities in the bonding also.

It seems reasonable to regard electron deficient compounds, and intermetallic compounds in which the ligancies of the atoms exceed the numbers of bonding orbitals by one or two, as forming a class somewhere between the metals, in which the orbital deficiency is much greater, and ordinary covalent compounds, where it is zero. Pauling's[11] concept of metallic bonding (covalent bonds are formed, the structure being stabilized by resonance

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[2] The substance of this paper was presented for the author by Prof. A. B. Burg at the Gordon Research Conference on Inorganic Chemistry, New Hampton, N. H., August, 1951.

[3] The term "electron deficient" is ultimately hard to define, but in practice no confusion seems to arise from its use. The metals and intermetallic compounds, it may be noted, are also electron deficient in the sense described.

[4] See S. H. Bauer, *Chem. Revs.*, **31**, 43 (1942).

[5] (a) V. Schomaker, *J. chim. phys.*, **46**, 262 (1949); (b) R. E. Rundle, THIS JOURNAL, **69**, 1327 (1947).

[6] K. S. Pitzer, *ibid.*, **67**, 1126 (1945).

[7] (a) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948); **15**, 614 (1947); (b) K. Hedberg and V. Schomaker, THIS JOURNAL, **73**, 1482 (1951).

[8] (a) K. Hedberg, M. Jones and V. Schomaker, *ibid.*, **73**, 3538 (1951); (b) W. J. Dulmage and W. N. Lipscomb, *ibid.*, **73**, 3539 (1951).

[9] J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

[10] K. Hedberg and A. J. Stosick, THIS JOURNAL, **74**, 954 (1952).

[11] (a) L. Pauling, *ibid.*, **69**, 542 (1947); (b) L. Pauling, *Phys. Rev.*, **54**, 899 (1938); (c) L. Pauling, *Proc. Roy. Soc.* (*London*), **A196**, 343 (1949).

[12] See the "Strukturbericht," **2**, 37 (1928–1932).

[13] G. S. Zbdanov and N. G. Sevast'yanov, *Compt. rend. acad. Sci., U.R.S.S.*, **32**, 432 (1941); H. K. Clark and J. L. Hoard, THIS JOURNAL, **65**, 2115 (1943).

[14] J. L. Hoard, S. Geller and R. E. Hugbes, *ibid.*, **73**, 1892 (1951).

TABLE I

Compound	Calcd. covalent boron radius, Å.	M	Calcd. atom charges, electrons[a] B	H_{bond}	H_{bridge}	Calcd. dipole moment, D	Ref.
B_2H_6	0.792		−0.22	+0.11	0		6b
B_5H_9	.795		− .44(B_1)	+ .22(H_1)	+0.06	1.1	7a
			− .24(B_2)	+ .23(H_2)			
	.779		− .46(B_1)	+ .22(H_1)	+ .10	0.4	7b
			− .24(B_2)	+ .20(H_2)			
$B_{10}H_{14}$	.810		− .29(B_1)	+ .28(H_1)	+ .05	1.4	8
			− .49(B_2)	+ .35(H_2)			
			− .32(B_3)	+ .25(H_3)			
			− .12(B_4)	+ .36(H_4)			
			− .41(B_5)	+ .33(H_5)			
			− .49(B'_5)	+ .33(H'_5)			
$H_2NH_2H_5$	.819	+0.08(N)	− .22	− .14	+ .12	7.3	9
		+ .40(H_N)					
$(CH_3)_2NH_2H_4$	.817	+ .36(N)	− .21	− .13	+ .12	6.9	9
		+ .23(C)					
BeB_2H_8	.804	− .04	− .56	+ .17	+ .12		18
AlB_3H_{12}	.818	+ .45	− .63	+ .08	+ .16		18
FeB	.809	+ .83	− .83				19
CoB	.786	+ .45	− .45				19
AlB_2	.768	− .26	+ .13				20
ZrB_2	.745	− .80	+ .40				21
C_3B_{12}	.798	+ .37(2c)	− .21(h_1)				13
		+ .82(1b)	− .05(h_2)				
CaB_6	.771	+2.64	− .44				22
ErB_6	.777	+1.98	− .33				23
UB_{12}	.814	+2.88	− .24				24
B	.797		− .16(2b)				14
			+ .28(8i)				
			+ .28(8i)				
			− .09(8i)				
			− .09(8i)				
			− .27(8i)				
			− .07(8i)				
Av.	.794						
Av. deviation	.016						

[a] Structurally different atoms are identified as in the original articles.

of these bonds among the available positions) should accordingly be applicable to electron deficient compounds. The empirical equation[11]

$$D(1) - D(n) = 0.6 \log_{10} n$$

where n is the bond number and $D(1)$ and $D(n)$ are the lengths of a single bond and of the bond under consideration, might be expected to apply. Indeed, the equation might well meet with greater success here than for the metals, since the electron deficient compounds are more closely related to the covalent substances upon which its semi-theoretical derivation is based.

The values 0.88,[15] 0.85[16] and 0.80 Å.[11a] previously considered for the boron radius are inconsistent and it has therefore seemed advisable to calculate a value from each compound. The agreement would then be the index of success. Pauling's equation and the Schomaker–Stevenson rule[17] and radii for atoms other than boron were applied, together with the condition that the sum of the bond numbers of the bonds formed by an atom summed over all the atoms be equal to the numbers of bonding electrons, to all compounds of well-known structure where the ligancy of boron is four or greater. In B_5H_9, for example, the B–B distances are 1.696 and 1.800 Å. along the edge and base of the pyramid, respectively, and the B–H distances involving the ordinary and bridge hydrogen atoms are 1.226 (five) and 1.356 Å. (eight),[8a] respectively.

Solution of the equations

$$2r_B - 1.696 = 0.6 \log n(B\text{–}B_{edge})$$
$$2r_B - 1.800 = 0.6 \log n(B\text{–}B_{base})$$
$$r_B - 0.865 = 0.6 \log n(B\text{–}H_{bond})$$
$$r_B - 0.995 = 0.6 \log n(B\text{–}H_{bridge})$$

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(15) L. Pauling and M. L. Huggins, *Z. Krist.*, [A] **87**, 205 (1934).

(16) S. H. Bauer and J. Y. Beach, This Journal, **63**, 1394 (1941).

(17) V. Schomaker and D. P. Stevenson, *ibid.*, **63**, 37 (1941). This scheme in general is more successful in predictions and discussions of interatomic distances, at least for first row elements, than the Pauling–Huggins (ref. 15). Values of the boron radius have also been calculated using the Pauling–Huggins scheme, however, and average 0.808 Å. with an average deviation of 0.208 Å. and a range of deviations of 0.051 Å.

(18) S. H. Bauer, *ibid.*, **72**, 622 (1950).

(19) T. Bjurström, *Arkiv Kemi Mineral. Geol.*, **11A**, No. 5, 125 (1933).

(20) W. Hoffmann and W. Janicke, *Z. physik. Chem.*, **31B**, 214 (1934).

(21) P. M. McKenna, *Ind. Eng. Chem.*, **28**, 767 (1936).

(22) L. Pauling and S. Weinbaum, *Z. Krist.*, **87**, 181 (1934).

(23) M. Steckelberg and F. Neumann, *Z. physik. Chem.*, **B19**, 314 (1932). The boron parameters were assumed the same as was found in CaB_6, reference 22.

(24) F. Bertaut and P. Blum, *Compt. rend.*, **229**, 666 (1949).

$$4n(\mathrm{B{-}B_{edge}}) + 4n(\mathrm{B{-}B_{base}}) + 5n(\mathrm{B{-}H_{bond}}) + 8n(\mathrm{B{-}H_{bridge}}) = 12$$

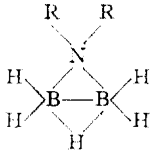
gives 0.795 Å. for the radius of boron.

The results (Table I) are encouragingly consistent, having an average deviation of only 0.016 Å. Since the average values for non-hydrogen and hydrogen containing compounds are 0.785 and 0.804 Å., respectively, slightly better consistency could be obtained by using a hydrogen radius somewhat greater than 0.37 Å.

Atom Charges and Dipole Moments.—By summing the bond numbers of the bonds formed by an atom its formal charge can be calculated; these formal charges may then be redistributed in accordance with the ionic character of the bonds[25] to obtain values for the actual charge. This was done by multiplying the ionic character of a given bond (as indicated by the electronegativities of the constituent atoms corrected for formal charge[26]) by the bond number, a procedure which it was felt would give a fair first approximation to the charge shift. The results are listed in Table I where column M relates to atoms other than boron or hydrogen. Except for positive values in AlB_2 and ZrB_2 (and, of course, in metallic boron itself) boron is found to have charges between about −0.12 and −0.8, which is not surprising since it has an extra orbital available for bonding and none of the other atoms in the compounds, with the exception of nitrogen in the aminodiboranes, is significantly more electronegative. The charge on hydrogen ranges from about 0 to +0.4 except for H_{bond} in the aminodiboranes; here the negative charges are derived from a B–H bond calculated to be shorter than a nominal single bond. The bond orders from which the formal charges were derived have the following ranges: B–B, 0.224[8] to 0.677[7b]; B–H_{bond}, 0.633[8] to 1.106[9]; B–H_{bridge}, 0.415[8] to 0.679[18]; M–B, 0.074[23] to 0.716[9]; and M–H_{bridge}, 0.196[18] to 0.128.[18]

It is of interest to consider the dipole moments which may be calculated for the non-centrosymmetric molecules from their charge distributions, since these dipole moments might be expected to provide an indication of the validity of the treatment. For B_5H_9 the calculated value 1.1 *D* is, considering the sensitive dependence of charge on distance, in agreement with the observed 2.13 *D*.[27] For $B_{10}H_{14}$ and the aminodiboranes no experimental values are available, but the calculated 1.6 *D* for the former is at least not unreasonable. For the aminodiboranes the values are certainly much too large, and from this and the anomalous shortness of the B–H_{bond} bonds (unless the dipole moment comparison is excessively sensitive) it appears that the simple straightforward calculation of the boron radius, although yielding values in fair agreement with the average from other compounds, is not valid.

These results for the aminodiboranes are not surprising in view of their unusual structures. The long B–N distances and the tetrahedral coördination of nitrogen imply in any event a dipole moment of about 5.5 *D*, and the small (76°) B–N–B angle, suggestive of strains, implies an unaccounted effect on the bond distances. An interpretation of the observed structures which leads to acceptable calculated dipole moments may be made in terms of two classes of resonance structures, one in which there are no unshared electron pairs (I) and one in which there is one unshared pair (II).



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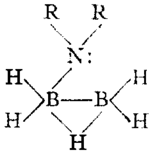

II

Making the arbitrary but reasonable assumptions that (a) the B–H_{bond} and N–R bonds are single bonds, (b) with no unshared pairs of electrons the boron radius would be 0.80 Å. with B–N compressed 0.04 Å. and B–B elongated 0.08 Å., (c) with an unshared pair of electrons the B–N and B–B single bonds would be 1.41 and 1.69 Å., respectively, and (d) B–H_{bridge} would be 1.40 Å. for both classes,[28] and then applying the criterion of bond number sum one obtains the following results: for the first class, B–N = 1.77 Å., B–B = 1.83 Å.; for the second B–N = 1.43 Å., B–B = 1.99 Å., which correspond to fractional contributions of 0.4 and 0.6, respectively, and lead therefore to a calculated dipole moment of 2.0 *D*.

It is perhaps significant that the greatest deviations in the boron radii (Table I) occur for AlB_2, ZrB_2, CaB_6 and ErB_6. The relatively poorer results for these substances may be understood by noting that their crystal structures admit the possibility of strains and hence of compression and elongation of the bond distances. In AlB_2 and ZrB_2 sheets of boron atoms are held together by the metal atoms so that the metal–metal bonds may be compressed and the B–B bonds elongated. Similarly, in CaB_6 and ErB_6 the continuous network of boron octahedra may compress the metal–metal and metal–boron bonds and expand the B–B bonds. It is difficult to estimate the magnitude of these effects, but if in AlB_2 and ZrB_2 the metal–metal distances are ignored (corresponding to bond number zero), and if in CaB_6 and ZrB_6 the structures are assumed to be $M^{++}B_6^{=}$, the following maximum values are obtained for the boron radii: AlB_2, 0.791 Å.; ZrB_2, 0.806 Å.; CaB_6, 0.805 Å.; ErB_6, 0.803 Å. If the effect of strain on the B–B distances is taken into account, smaller values will be obtained.

An Application.—For molecules of known structure the boron radius may, of course, be used with other radii and the observed bond distances to calculate bond numbers, whose sum may then be compared with the sum expected. But, what is perhaps more interesting, these radii may be applied to molecules of unknown structure, for which some data on interatomic distances are available,[29] to give information about the configuration. For example, B_6H_9 has average B–H and B–B distances of 1.29 Å. and 1.75 Å.,[8a] respectively, giving n(B–H_{av}) = 0.598 and n(B–B_{av}) = 0.541 when the boron radius is taken as 0.795 Å. If it is assumed that there are 5 B–H_{bond} bonds (in hydrogen-containing electron deficient boron compounds

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(25) L. Pauling, *J. Chem. Soc.*, 1461 (1948).

(26) L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., Chapt. III, 1940.

(27) H. J. Hrostowski, R. J. Myers and G. C. Pimentel, *J. Chem. Phys.*, **20**, 518 (1952).

(28) The following points may be noted in justification of the assumptions. The observed B–H_{bond} length (1.15 Å.) and C–N bond length (1.48 Å.) compare well with the values 1.16 Å. (obtained using r_B = 0.80 Å.) and 1.47 Å., respectively. With no unshared pairs of electrons the expected distortion of the bonds is that calculated from assumed force constants in consideration of B–N–B angle strains (ref. 10). In structures having an unshared electron pair the assumed distances are those obtained from r_B = 0.83 Å., a value chosen as a compromise between the 0.80 and 0.85 Å. values displayed in compounds having for boron five- or six- and fourfold coördination, respectively.

(29) Such information might be obtained from electron diffraction studies; additional information, such as the relative numbers of the distances, may also be available.

there appears to be always at least one B–H_{bond} bond from each boron atom, *i.e.*, there are 4 H atoms in bridges and therefore 8B–H_{bridge} bonds), then the equation

$$0.598(5 + 8) + 0.541(\text{no. B–B bonds}) = 12.00$$

which expresses equality between the sum of the bond numbers in the molecule and the sum of the bonding electrons, leads to 7.8 as the number of B–B bonds, a value which is certainly satisfactorily close to the actual value of eight. The accuracy of a result derived by a calculation of this sort depends principally upon the correctness of the assumed number of B–H bonds and upon the closeness of the assumed values of r_B to the best value for the compound; it depends to a lesser extent upon the use of average values for what may actually be a distribution of distances. To illustrate using the B_5H_9 example, for the case 7 B–H_{bond}, 4 B–H_{bridge}, r_B = 0.795 Å.; 5 B–H_{bond}, 8 B–H_{bridge}, r_B = 0.800 Å.; and 5 B–H_{bond}; 8 B–H_{bridge}, r_B = 0.795 Å., but with the B–H bonds split 0.13 Å.; one calculates 10.0, 7.2 and 8.2 B–B bonds, respectively.

It is to be noted that consistent values for the boron radius may be obtained only from compounds in which boron has high ligancy, 5 or 6; compounds of lower boron ligancy give values over the wide range 0.896 to 0.751 Å.[30] At present little can be said about the reasons for this lack of consistency, but certainly a wider range of calculated boron radii are to be expected for compounds of low ligancy, where in bonding the use of both three and four boron orbitals are encountered, than for compounds of high ligancy when usually only three are used.

NOTE ADDED IN PROOF.—The dipole moment of $B_{10}H_{14}$ has recently been reported [A. W. Laubengayer and R. Bottei, THIS JOURNAL, **74**, 1618 (1952)] as 3.52 *D*. Although this value and the value for B_5H_9 (mentioned above) are considerably greater than the calculated values, they cannot be regarded as invalidating the treatment. The sizes of these two molecules and the nature of the calculated charge distributions are such as to require shifting only relatively small amounts of charge to bring about complete agreement. Indeed, considering the sensitive dependence of atom charge on bond distance the observed and calculated values are satisfactorily close.

Acknowledgment.—I wish to thank Professor Verner Schomaker for his continuing interest throughout the course of this work and for many helpful suggestions concerning the interpretations of the results.

[30] These values are derived from borazole, $B_3N_3H_6$ (S. H. Bauer, THIS JOURNAL, **60**, 524 (1938)) and BF_3 (D. M. Gage and E. F. Barker, *J. Chem. Phys.*, **7**, 455 (1939)), respectively.

PASADENA, CALIFORNIA

[A CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF WISCONSIN]

Addition Compounds of Zirconium and Hafnium Tetrachlorides with Phosphorus Oxyhalogen Compounds[1]

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Zirconium and hafnium tetrachlorides react with $POCl_3$ and $POFCl_2$ to give addition products of the composition 2 POX_3·MCl_4 which decompose under reduced pressure at 50 to 60° to give POX_3·MCl_4. With POF_2Cl and POF_3, the metal tetrahalides give only POX_3·MCl_4 at room temperature. All the 1:1 products when heated decompose with the evolution of the phosphorus oxyhalide, with the temperature at which the decomposition is first observed decreasing with increasing fluorine content of the POX_3. No significant difference is observed in the behavior of the zirconium and hafnium compounds. If the contact time of the MCl_4 with excess $POFCl_2$ or POF_2Cl is long enough, complete halogen exchange within the phosphoryl molecule occurred and $2POCl_3$·MCl_4 was crystallized from solution.

Addition compounds of zirconium (hafnium) tetrachloride with phosphorus pentachloride and phosphorus oxychloride[3] can be distilled and consequently are of interest since they can be employed[3,4] to separate zirconium from hafnium by a fractional distillation process. It was therefore thought desirable to make a study, wider in scope, of the reactions of zirconium and hafnium tetrachlorides with phosphorus oxyfluorides and oxychlorides to determine whether there were other distillable compounds formed.

All of the substances concerned in this work reacted readily with moisture, so operations involving transfer of solid materials were performed in a "dry-box," while all transfers of the volatile reactants were made in a vacuum system. The physical properties of the reactants are: $POCl_3$, m.p. 1.25°, b.p. 105.1°; $POFCl_2$, m.p. −80.1°, b.p. 52.9°; POF_2Cl, m.p. −96.4°, b.p. 3.1°; POF_3, m.p. −39.4°, b.p. −39.8°.

Experimental Procedure

Materials Used.—The zirconium and hafnium tetrachlorides were prepared by the action of gaseous chlorine on a sugar charcoal–metal oxide mixture, in a manner similar to that for the preparation of zirconium tetrabromide by Young.[5] The crude tetrachloride was heated in hydrogen at 450° and then sublimed under reduced pressure at 350°. Analysis of the purified product gave a Cl/Zr atomic ratio of 3.98. The zirconium oxide contained only 0.04% hafnium, and the hafnium oxide 0.75% zirconium according to spectrographic analyses.[6]

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[2] W.A.R.F. research assistant, 1947–1949. Recipient of du Pont grant-in-aid, Summer, 1949.

[3] A. E. Van Arkel and J. H. de Boer, *Z. anorg. Chem.*, **141**, 289 (1924).

[4] D. M. Gruen and J. J. Katz, THIS JOURNAL, **71**, 3843 (1949).

[5] R. C. Young and H. G. Fletcher, *Inorganic Syntheses*, **1**, 49 (1939).

[6] C. Feldman, Oak Ridge National Laboratory.