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## Electronic Structures of Molecules

## XIII. Diborane and Related Molecules

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The electronic structure of diborane ( $B_2H_6$ ), which is known to have a nuclear arrangement similar to that of ethane but which has two less electrons, is determined. It is shown that there must be eleven low energy electron states (some singlet, some triplet), belonging to three electron configurations. To account for the colorless diamagnetic character of  $B_2H_6$ , it must be that all or most of these eleven states fall within an energy range of 1.5 volts or less, with the lowest state, somewhat accidentally, probably of  $^1A_1$  type. Derivatives of  $B_2H_6$  have similar structures. According to the present method there is nothing particularly anomalous about these structures. The structures here arrived at are in general agreement with the suggestions of Sidgwick and Pauling that the three H atoms in each  $BH_3$  in  $B_2H_6$  are held by two elec-

tron-pair bonds and one one-electron bond, although according to the present method one would say that the H atoms are held by two  $[s]$  and three  $[\pi]$  bonding electrons, a total of five, shared equally by the three H's. The present method shows clearly that in, e.g.,  $B_2H_2(CH_3)_4$ , there is no reason to suppose that the B-H bonds have fewer electrons per bond than the B-C bonds, the number being  $5/3$  in each case. Equal energy for  $B_2R_6$  and  $2 BR_3$  would mean equal effective strength of B-R and B-B bonds. It is noted that the B-B bond is a remarkably strong one. Reasons why  $BCl_3$  does not form  $B_2Cl_6$  are discussed. The desirability of magnetic susceptibility and perhaps molecular weight determinations, if possible at elevated temperatures, for some of the types  $BR_3$  and  $B_2R_6$  is pointed out.

## I. DIBORANE

THE electronic structure of the boron hydrides has long been a puzzling problem. It will be shown below, by fitting empirical data into the framework of the present theoretical method, that a completely satisfactory explanation can be obtained of the existence and main properties of such compounds, in particular  $B_2H_6$  (diborane).<sup>1, 2</sup>

X-ray crystal structure investigation of solid diborane<sup>3</sup> shows that the arrangement of the atoms must be similar to that in  $C_2H_6$ , but with a B-B distance of roughly 1.85Å, about 20 percent larger than the C-C distance in  $C_2H_6$ . This is just about what might be expected, because of the lower  $Z_{eff}$  and correspondingly larger size of

the B atom orbitals, if the B-B bond in  $B_2H_6$  is essentially a single bond of the same type as the C-C bond in  $C_2H_6$ .<sup>4</sup> The quantity  $\xi$  (cf. Table I of IX of this series<sup>4</sup>) comes out 1.14 for the B-B distance in  $B_2H_6$  as compared with 1.19 for the C-C distance in  $C_2H_6$ . Compared with  $C_2H_6$ ,  $B_2H_6$  has two less electrons; we can expect then to get at its electronic structure by considering the removal of two electrons from the normal  $C_2H_6$  structure (cf. (4) and (4a) of IX).

While considering the normal state of  $B_2H_6$ , it is necessary also to determine what excited states of low energy are expected. This will prove imperative because there are probably several states which are close competitors for the position of normal state, and because the structures assigned for the normal and excited states must be in agreement with the fact that  $B_2H_6$  (gaseous and solid) is colorless. The electron configurations must also be consistent with the fact that  $B_2H_6$  at room temperature is diamagnetic.<sup>5</sup>

<sup>1</sup> For a preliminary account of the subject of the present paper, cf. R. S. Mulliken, *Phys. Rev.* **43**, 765(L) (1933). Here it was predicted that  $B_2H_6$  should probably, but not certainly, be paramagnetic. This prediction fortunately stimulated research which has shown  $B_2H_6$  to be diamagnetic.<sup>5</sup> This result is of great value for the present paper in permitting more definite conclusions to be reached than would otherwise be possible.

<sup>2</sup> For earlier discussions of the nature of the binding in  $B_2H_6$  cf. among others A. Stock, *Ber. der deutschen Chem. Ges.* **A54**, 142 (1921); **A59**, 2226 (1926), etc.; N. V. Sidgwick, *Electronic Theory of Valency* (London, 1929), p. 103; M. Dunkel, *Zeits. f. physik. Chemie* **B7**, 81; **B10**, 434 (1930); G. Glockler, *Science* **68**, 305 (1928); G. Herzberg, *Leipziger Vorträge*, 1931, p. 167 (S. Hirzel, Leipzig); L. Pauling, *J. Am. Chem. Soc.* **53**, 3225 (1931); R. S. Mulliken, *Chem. Rev.* **9**, 347 (1931).

<sup>3</sup> H. Mark and E. Pohland, *Zeits. f. Kryst.* **62**, 103 (1925).

<sup>4</sup> R. S. Mulliken, *J. Chem. Phys.* **3**, 517 (1935): IX of this series.

<sup>5</sup> L. Farkas and H. Sachsse, *Trans. Faraday Soc.* **30**, 331 (1934) show by an indirect method that the normal state must be diamagnetic, and that any excited states of paramagnetic character must be at least 0.13 volt higher. Direct measurements in the Chemistry Department of this University also show diamagnetism at room temperature, but perhaps somewhat weaker than would be expected if there were no paramagnetic excited states.

For the normal and lowest excited states only the following possibilities need be considered (1s boron electrons are omitted):

$$[sa_1]^2[sa_1]^2[\sigma+\sigma, a_{1g}]^2[\pi e]^3[\pi e]^3, \\ {}^3A_{2g}, {}^1E_g, {}^1A_{1g}, {}^1A_{1u}, {}^3E_u, {}^3A_{2u}, \quad (1)$$

$$[sa_1]^2[sa_1]^2[\sigma+\sigma, a_{1g}][\pi e]^4[\pi e]^3, \\ {}^3E_g, {}^3E_u, {}^1E_g, {}^1E_u, \quad (2)$$

$$[sa_1]^2[sa_1]^2[\pi e]^4[\pi e]^4, {}^1A_{1g}. \quad (3)$$

The orbitals  $[sa_1]$  and  $[\pi e]$  are  $BH_3$  radical orbitals giving strong B–H bonding. Symmetry  $C_{3v}$  is assumed for each radical (cf. discussion of corresponding  $CH_3$  orbitals in  $C_2H_6$ ).<sup>4</sup> The orbital  $[\sigma+\sigma, a_{1g}]$  is primarily a B–B bonding orbital.

Symmetry  $D_{3d}$  (a center of symmetry) is assumed in (1)–(3) for  $B_2H_6$ . This keeps the H atoms, other things being equal, as far apart as possible, and presumably corresponds to the position of minimum energy, as in  $C_2H_6$ . For most purposes, however, it is probably more nearly correct to assume free rotation, the symmetry then being  $D_3$  except at special rotation angles which make it  $D_{3d}$  or  $D_{3h}$ . The formulations (1), (2), (3) are unchanged for symmetry  $D_3$  except that all subscripts  $g, u$  are dropped. Designations for symmetry  $D_{3h}$  are as follows, the symbols being given in the same order as the corresponding symbols in (1)–(3):  $a_1'$  instead of  $a_{1g}$ ; then  ${}^3A_2', {}^1E', {}^1A_1', {}^1A_1'', {}^3E'', {}^3A_2''$  in (1);  ${}^3E'', {}^3E', {}^1E'', {}^1E'$  in (2);  ${}^1A_1'$  in (3).

The correctness of the electron states given above for the configurations in (1)–(3) will be justified at the end of this section. It will be advisable now to mention the relations of these configurations and states to those of two separated  $BH_3$  radicals. The free  $BH_3$  radical<sup>6</sup> is very probably of plane form (symmetry  $D_{3h}$ ), with a diamagnetic normal state

$$1s_B^2[sa_1']^2[\pi e']^4, {}^1A_1' \quad (4a)$$

and with lowest excited states

$$1s_B^2[sa_1']^2[\pi e']^3[\sigma a_2''], {}^1, {}^3E'' \quad (5a)$$

It appears likely (see below) that the  $BH_3$  radical becomes pyramidal when it enters into combination to form  $B_2H_6$ . For pyramidal  $BH_3$

(symmetry  $C_{3v}$ ), the symbolism (4a), (5a) needs to be somewhat altered, although there is of course no great change in the forms of the orbitals unless the pyramids become high. We then have

$$1s_B^2[sa_1]^2[\pi e]^4, {}^1A_1, \quad (4)$$

$$1s_B^2[sa_1]^2[\pi e]^3[\sigma a_1], {}^1, {}^3E. \quad (5)$$

Schemes (4a), (5a) may be considered as special cases of (4), (5).

If two pyramidal  $BH_3$  radicals are brought together with the pyramid-apices (B atoms) pointing toward each other and the pyramid axes coincident, it can be shown that two  ${}^1A_1$  radicals both in state (4) tend to give  $B_2H_6$  in state (3). [These and the results stated in the next paragraph will be justified at the end of this section.] According to Heitler-London theory, since  ${}^1A_1$  of  $BH_3$  is a closed-shell state, state (3) of  $B_2H_6$  should not be stable.

In a similar manner, if two  $BH_3$  are brought together head on, one in state (4), the other in state  ${}^3E$  of (5), they tend to give  $B_2H_6$  in one of the two states  ${}^3E_g$  or  ${}^3E_u$  of (2). If two  $BH_3$  each in  ${}^3E$  of (5) are brought together head on, the possibilities for the resulting state of  $B_2H_6$  which they tend to give include all the states of (1), together with some quintet states which will not interest us. Other possible combinations ( ${}^3E$  plus  ${}^1E$ ,  ${}^1E+{}^1E$ , etc.) will not be of interest here.

As noted above, Heitler-London theory indicates that (3) should be unstable. Examining (3), one sees that it contains no B–B bonding electrons, but only closed  $BH_3$  shells which should tend to produce a net repulsion. Configuration (2), however, contains one  $[\sigma+\sigma]$  electron, and configuration (1) two  $[\sigma+\sigma]$  electrons, of strongly B–B bonding character. Besides B–B bonding, each  $[\sigma+\sigma]$  should also give a little B–H bonding within each  $BH_3$  radical, at least if the latter is pyramidal. [Cf. the analogous  $[\sigma+\sigma]$  orbitals in  $C_2H_6$ .<sup>4</sup>]

The  $[\pi e]$  electrons in (1) and (2), in case those in the two  $BH_3$  groups should interact strongly, would offer a possibility of more or less additional B–B bonding, since the  $[\pi e]$  shells are not entirely closed. This effect should be stronger in (1) than in (2). If this  $[\pi]$  bonding should be strong (but see below), we would do well to replace the  $[\pi e]$  orbitals of the  $BH_3$  radicals by whole-molecule orbitals  $[\pi+\pi, e_u]$  and  $[\pi-\pi, e_g]$ . The former would be

<sup>6</sup> Cf. R. S. Mulliken, J. Chem. Phys. **1**, 492 (1933); V. Table I and pp. 500–503.

B—B bonding, the latter B—B antibonding, but both would also retain strong B—H bonding properties for H's at both ends of the molecule. Using  $[\pi \pm \pi]$ , (2) would break up into

$$\cdots [\pi + \pi, e_u]^4 [\pi - \pi, e_g]^3, {}^3, {}^1E_g \text{ and } \cdots [\pi + \pi, e_u]^2 [\pi - \pi, e_g]^4, {}^3, {}^1E_u. \quad (2a)$$

The derivation of this result can be seen from the discussion of a very similar case for  $C_2H_6$  (reference 4, page 521). In the  ${}^3, {}^1E_g$  there would be a net B—B bonding effect, in the  ${}^3, {}^1E_u$  a net B—B antibonding effect, from the  $[\pi \pm \pi]$  groups.

Similarly (1) would break up into

$$\cdots [\pi + \pi, e_u]^4 [\pi - \pi, e_g]^2, {}^3A_{2g}, {}^1E_g, {}^1A_{1g} \text{ and } \cdots [\pi - \pi, e_u]^2 [\pi - \pi, e_g]^3, {}^1A_{1u}, {}^3E_u, {}^3A_{2u}. \quad (1a)$$

[The configuration  $\cdots [\pi + \pi]^2 [\pi - \pi]^2$  would also give additional states  ${}^3A_{1u}, {}^1E_u, {}^1A_{1u}$ , but these do not correspond to any of the states of  $\cdots [\pi]^2 [\pi]^2$  in (1).] The formulation corresponding to (3) but using whole-molecule orbitals is

$$\cdots [\pi + \pi, e_u]^4 [\pi - \pi, e_g]^4, {}^1A_{1g}. \quad (3a)$$

If we reckon each net pair of B—B bonding electrons (B—B antibonding electrons being counted negatively) as one B—B bond, then the numbers of B—B bonds corresponding to (1), (1a), (2), (2a), (3), (3a) are, respectively, 1, 2,  $\frac{1}{2}$ , 1, 0, 0. In the case of (1a), this refers only to the  $g$  states; for the  $u$  states there is only 1 net bond.

At this point it may be noted that the states (1a) would be very closely related to low energy, mostly well-known, states of the  $O_2$  molecule, while (2a) and (3a) would be similarly related to high energy states of  $O_2$  which are not yet known experimentally. The lowest energy states of  $O_2$  are

$$2s^2 2s^2 (\sigma + \sigma, \sigma_g)^2 (\pi + \pi, \pi_u)^4 (\pi - \pi, \pi_g)^2, {}^3\Sigma^-_g, {}^1\Delta_g, {}^1\Sigma^+_g, \quad (6)$$

with  ${}^3\Sigma^-_g$  as the normal state. If we could split each O nucleus in  $O_2$  into nuclei of B+3H, then the respective states  ${}^3\Sigma^-_g, {}^1\Delta_g$ , and  ${}^1\Sigma^+_g$  of (6), it can be shown,<sup>7</sup> would go over continuously into  ${}^3A_{2g}, {}^1E_g$ , and  ${}^1A_{1g}$  of (1a) or (1). The probably next lowest group of states of  $O_2$ , of which the  ${}^3\Sigma^-_u$  and perhaps also the  ${}^3\Delta_u$  or  ${}^3\Sigma^+_u$  or both are known experimentally, are

$$2s^2 2s^2 (\sigma + \sigma, \sigma_g)^2 (\pi + \pi, \pi_u)^2 (\pi - \pi, \pi_g)^3, {}^1\Sigma^-_u, {}^3\Delta_u, {}^3\Sigma^+_u, {}^3\Sigma^-_u, {}^1\Delta_u, {}^1\Sigma^+_u. \quad (7)$$

These are related continuously to the respective states  ${}^1A_{1u}, {}^3E_u, {}^3A_{2u}$  given in (1a) or (1) and the additional states  ${}^3A_{1u}, {}^1E_u$ , and  ${}^1A_{2u}$  mentioned following (1a).

The most important difference between the orbitals  $(\pi \pm \pi)$  of (6) and (7) and the analogous orbitals  $[\pi \pm \pi]$  of  $B_2H_6$  in (1a) is that in the former only O—O bonding or antibonding is involved, while in the latter there is strong B—H bonding in addition to B—B bonding or antibonding. Because of this *competition* between B—H and B—B bonding, neither can be as strong as it would

otherwise be. In other words, any B—B bonding power which the  $[\pi + \pi]$  orbitals may have is partly at the expense of their B—H bonding power.

A similar competition does not exist or is unimportant in the case of the  $[\sigma + \sigma]$  orbitals in  $B_2H_6$ , since these have little if any B—H bonding power anyway. Nevertheless, any B—B bonding produced by an electron in a  $[\sigma + \sigma]$  orbital is ultimately at the expense of B—H bonding, since it can be secured only by first removing the electron from a B—H bonding  $[\pi]$  or  $[\pi \pm \pi]$  orbital in order to put it into  $[\sigma + \sigma]$ .

From the foregoing discussion it will be seen that in seeking to determine the nature of the normal and the low energy excited states of  $B_2H_6$ , we have inevitably to deal with a somewhat complicated system of possibilities. In order to clarify the situation, we may formulate three questions. (A). Is it a better approximation, for the molecular dimensions which exist in the actual normal state of  $B_2H_6$ , to use formulations (1), (2), (3) or to use (1a), (2a), (3a)? (B). If formulations (1), (2), (3) are better, which of these configurations gives the lowest mean energy, for the actual dimensions of the actual normal state? This is equivalent to asking whether  $[\sigma + \sigma]$  or  $[\pi]$  in (1)–(3) is the more firmly bound. If formulations (1a), (2a), (3a) are better, we ask an analogous question. (C). Having decided (B), what particular electron state of the lowest energy electron configuration is the normal state?

The answer to question (A) depends largely on the degree of overlapping of the  $[\pi]$  orbitals of the two  $BH_3$  radicals occurring in (1), (2), (3). If this is large, then there is strong interaction between them, and (1a), (2a), (3a) should be better; if small, (1), (2), (3) should be better. The decision depends on the effective  $\xi$  value for the  $[\pi]$  groups of the two  $BH_3$  (cf. discussion of  $\xi$  values for  $[\pi]$  groups of  $CH_3$  in  $C_2H_6$ , reference 4, p. 520). If the  $BH_3$  radicals are still plane in  $B_2H_6$ , the  $\xi$  is that given at the beginning of this paper, a value which (cf. Table I and discussion in reference 4) would mean considerable overlapping and interaction of the  $[\pi]$ 's, although less than if the  $[\pi]$ 's did not have strong B—H bonding power. More probably, however, the  $BH_3$  radicals are pyramidal for essentially the same reason that the  $CH_3$  radicals are pyramidal in  $C_2H_6$ . Each B atom would then be surrounded by four other atoms in approximately a tetra-

<sup>7</sup> R. S. Mulliken, Phys. Rev. **43**, 293–4 (1933): Tables III and IV.

hedral arrangement. In this case, the effective  $\xi$  would certainly be so large (cf. discussion of  $[\pi]$ 's of  $\text{CH}_3$  in reference 4) that there would be little overlapping and (1), (2), (3) would be preferable. Accepting the existence of this state of affairs tentatively (cf. justification near the end of this section), it will be noted that, among other things, the possibility of a really double-bonded  $\text{B}=\text{B}$  structure (1a) analogous to (6) of  $\text{O}_2$  is eliminated. Nevertheless there remains a more or less formal resemblance or at any rate a formal correlation of energy levels with those of  $\text{O}_2$ .

Next we have to decide between configurations (1), (2) and (3) for the lowest state of  $\text{B}_2\text{H}_6$ . As noted above, Heitler-London theory shows that (3) must be unstable. Hence, for the observed  $\text{B}-\text{B}$  distance  $r_e = 1.85\text{\AA}$  in  $\text{B}_2\text{H}_6$ , (3) must have a higher energy than  $2\text{BH}_3$ , although not necessarily much higher (perhaps 1 volt or less). The chemical existence of  $\text{B}_2\text{H}_6$ , however, shows that the normal state of the latter must have a lower energy than  $2\text{BH}_3$ , by perhaps 1 volt or at least 0.5 volt. Hence the normal state must apparently belong to configuration (1) or (2), more probably the former, since the mean energy of (2) should be intermediate between those of (1) and (3).

Thus it appears that the energy increases in the order (1), (2), (3), although overlapping of the groups of energy levels associated with the three configurations is possible. The energy differences between (1), (2), and (3) need not, in fact must not, be great, however; roughly, the energies of (1), (2), (3) may be about equal. [It is even not absolutely certain, in view of the existence of a "resonance" (see below) between (3) and the  $^1A_{1g}$  state of (1), that the order may not be (3), (2), (1); this could be possible if the resonance is very strong, but is not at all probable.]

The foregoing conclusions imply that  $[\sigma+\sigma]$  must be as firmly bound, or a little more firmly bound, than  $[\pi]$  in  $\text{B}_2\text{H}_6$ . It may be recalled that in the case of  $\text{C}_2\text{H}_6$  we concluded<sup>4</sup> that  $[\sigma+\sigma]$  is at least two volts less firmly bound than  $[\pi]$ . Can we account for such a difference between  $\text{C}_2\text{H}_6$  and  $\text{B}_2\text{H}_6$ ? One important factor tending in the right direction is the charge-transfer effect. The considerable negative charging of the C atoms in  $\text{C}_2\text{H}_6$  was estimated to decrease the

ionization potential  $I$  for  $[\sigma+\sigma]$  by 1 or 2 volts, while in  $\text{B}_2\text{H}_6$  the positive charging of the B atoms should tend in the opposite direction, since C is more but B less electronegative than H.

The  $I$ 's of  $[\sigma]$ ,  $[\pi]$ , and  $[\sigma+\sigma]$  in  $\text{B}_2\text{H}_6$  may be predicted by the methods of VIII of this series<sup>8</sup> (cf. the examples discussed in IX<sup>4</sup>). The results are:  $[\sigma]$ ,  $I > 14.45$  volts;  $[\sigma+\sigma]$ ,  $I > 8.63$  volts;  $[\pi]$ ,  $I > 11.08$  volts. No allowance for charge-transfer effects has been included. From these predictions, it would at first seem that  $[\pi]$  should be more firmly bound than  $[\sigma+\sigma]$ . If, however, the inequality sign represents a sufficiently larger value for  $[\sigma+\sigma]$  than for  $[\pi]$ , this need not be true. Although the necessary difference is surprisingly large, it must be accepted as empirically required by the observed stability of  $\text{B}_2\text{H}_6$ . It is also found that the necessary difference is not beyond credibility. For instance, the following set of  $I$ 's would be credible:  $[\sigma]$ ,  $I = 17$  volts;  $[\sigma+\sigma]$ , 13.0 volts;  $[\pi]$ , 12.6 volts. The inequality sign would then represent 4.4 volts for  $[\sigma+\sigma]$  and 1.5 volts for  $[\pi]$ . Of the 4.4 volts, perhaps 1.2 volts might be attributed to charge-transfer, leaving 3.2 volts as a measure of the strength of the bonding in  $[\sigma+\sigma]$ , as compared with 1.5 volts for  $[\pi]$ . While little significance should be attached to these precise figures, it is clear that the existence of  $\text{B}_2\text{H}_6$  must be in part a result of the possession of unusual strength by the  $\text{B}-\text{B}$  bond (cf. also section II below).

As we have seen, the energy must probably increase in the order (1), (2), (3). The spacings (2)-(1) and (3)-(2) are presumably about equal, using for the electron configurations (1) and (2) the centers of gravity of the two groups of electron levels associated with them. Another point of importance is this: since we have decided that the interaction is small between the two groups  $[\pi]^3$  in (1), the various energy levels of (1) should be close together in energy, very likely within a total range of half a volt or less. As for the order of the various levels within the group, a comparison of (1), or better (1a), with the analogous case of  $\text{O}_2$  in (6), (7) indicates that the order of increasing energy should be that given in (1), with  $^3A_2$  (analogous to  $^3\Sigma^-_g$  of  $\text{O}_2$ ) the lowest. This last cannot be correct, however,

<sup>8</sup> R. S. Mulliken, J. Chem. Phys. 3, 514 (1935); VIII.

since  $^3A_2$  would give paramagnetic properties,<sup>1</sup> contrary to the observed diamagnetism of  $B_2H_6$ . As will be seen below, there is a specific disturbing factor which can well account for this discrepancy. Besides, the comparison with  $O_2$  is not entirely conclusive as to the order of the levels of (1). Furthermore, since the levels should all be close together, the exact order is easily subject to disturbance by minor factors.

Consideration of (2) from the same point of view indicates that the  $E_u - E_g$  intervals should be small, since they arise from the weak  $[\pi]$ ,  $[\pi]$  interactions. The intervals  ${}^1E_u - {}^3E_u$  and  ${}^1E_g - {}^3E_g$  should be larger (presumably as much as a volt, with the singlet levels higher), since they depend on interactions between  $[\pi]$  and  $[\sigma + \sigma]$ , which should be fairly strong.

As we have seen, the normal state of  $\text{B}_2\text{H}_6$  must apparently belong to configuration (1),—or possibly (2). Further, the diamagnetic character of this state immediately excludes all the triplet states of (1) and (2) as possibilities. Since the singlet states of (2) should lie above the triplet states, they are also excluded. This leaves only  ${}^1E_g$ ,  ${}^1A_{1g}$ ,  ${}^1A_{1u}$  of (1). We concluded above that these should lie close together, although  ${}^1A_{1u}$  should be somewhat above the others if the  $[\pi]-[\pi]$  interactions are at all appreciable. The  ${}^1E_g$  is also doubtful, since it is analogous to the paramagnetic  ${}^1\Delta_g$  of  $\text{O}_2$  and should probably be strongly paramagnetic, although this is uncertain without calculations. [It is a question of the extent to which the resultant angular momentum along the symmetry axis, present in  ${}^1\Delta_g$  of  $\text{O}_2$ , is preserved or has meaning in  ${}^1E_g$  of  $\text{B}_2\text{H}_6$ .]

It seems probable that the normal state is  ${}^1A_{1g}$  of (1), somewhat modified. Referring to (1), (2), (3), it will be noted that there are altogether two  ${}^1A_{1g}$  states, one from (1) and one from (3). Now, as we have seen earlier, the  ${}^1A_{1g}$  of (3) corresponds to a state where two unexcited  $BH_3$  radicals ( ${}^2A_1$  of (4)) are repelling each other. The  ${}^1A_{1g}$  of (1), on the other hand, corresponds to a state where two excited  $BH_3$  radicals ( ${}^2E$  of (5)) are attracting each other strongly. That is,  ${}^1A_{1g}$  of (3) should have a potential energy curve, for variation of the B—B distance  $r$ , which rises as  $r$  decreases, while  ${}^1A_{1g}$  of (1) should have a curve descending strongly as  $r$  decreases. According to

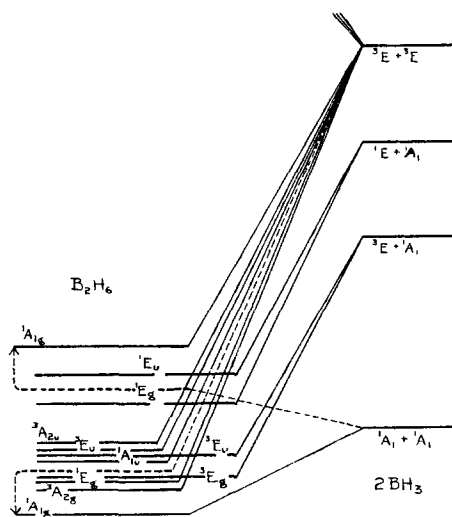


FIG. 1. Low energy electron levels of  $B_2H_6$  (approximate, estimated).  $B_2H_6$  levels (full horizontal lines at left) are all for a fixed nuclear configuration the same as that of the normal state. Longest horizontal lines are states of  $[\sigma + \sigma] \pi^2 [\pi]^2$ ,—cf. (2) of text. Remaining horizontal lines of  $B_2H_6$  are states of  $[\sigma + \sigma] \pi^2 [\pi]^2$  and of  $[\pi] \pi^2 [\pi]^2$ ,—cf. (1) and (3) of text. Dotted horizontal lines represent estimated positions of two  ${}^1A_{1g}$  states if they did not interact with each other; mutual perturbation pushes them apart, as indicated by arrows, to give normal state and probable highest state of group. Dissociation correlations are indicated by slanting lines, assuming symmetry  $D_{3d}$  preserved during dissociation, and assuming no predissociation nor breakdown in separability of electronic and vibrational wave functions. Dotted slanting lines show correlations for the two  ${}^1A_{1g}$  states if they did not interact with each other; actual interaction causes crossing of these correlation lines to be avoided, with upper  ${}^1A_{1g}$  now going to  ${}^3E + {}^3E$ , lower to  ${}^1A_1 + {}^1A_1$ . The scale may be judged by the following (very uncertain) estimates used in the figure:  ${}^3E - A_1 = 2.0$  volts for  $BH_3$ ; dissociation energy of lowest  $B_2H_6$  state = 0.9 volt.

this, the  ${}^1A_{1g}$  curves of (1) and (3) should most probably cross, or at least come close together.

Perturbation theory shows, however, that the wave functions of the two  ${}^1A_{1g}$  states should mix more or less, especially near the probably expected crossing point. If the mixing tendency is strong, as is perfectly reasonable (see below), two new curves should result, the lower one with a considerably lower energy minimum than the original curve of (1) but dissociating to two unexcited  $\text{BH}_3$  like the original curve of (3). This pushing down of the  ${}^1A_{1g}$  curve of (1) by admixture with (3),—or possibly *vice versa* if the two

original "unperturbed" curves do not cross,—serves to explain the at first rather unexpected fact that the paramagnetic  ${}^3A_{2g}$  state of (1) is not the normal state. The  ${}^3A_{2g}$  and other states of (1) and (2) must, however, be not far above the normal state (see below).

A plausible estimate of the positions of the "original" (unperturbed) and the final resulting curves is shown diagrammatically in Fig. 1, the former by dotted lines, the latter by full lines. A crossing of the unperturbed  ${}^1A_{1g}$  curves is shown, although the correctness of this is of course not absolutely certain. Curves corresponding to the remaining states of (1) and (2) are also shown diagrammatically in Fig. 1. The horizontal straight lines for  $B_2H_6$  show estimated positions of the various energy levels for vertical excitation from the  ${}^1A_{1g}$  normal state (*unchanged B—H and B—B distances*). The estimates are based on the considerations advanced previously as to positions of energy levels, and are merely illustrative so far as their detailed arrangement is concerned. Their dissociation-correlations should, however, be essentially correct, at least for dissociation processes in which the original symmetry is preserved throughout the dissociation, and neglecting possible predissociation short-cuts. If the figure were modified to show the minimum energy, in each case, instead of the vertical energy relative to the normal state nuclear configuration, all the excited levels would be lowered more or less, since adiabatic excitation processes would in each case surely involve more or less change in

the equilibrium B—B and B—H distances. For instance, the B—B equilibrium distance would surely be increased for the states of electron configuration (2).

It may possibly be that the stability of the normal state of  $B_2H_6$  is critically determined by the above-discussed "resonance" of the two  ${}^1A_{1g}$  states. At any rate, it is advisable to justify somewhat more fully the existence of the assumed rather strong resonance. Of the eleven states of configurations (1)–(3), for symmetry  $D_{3d}$ , there are six whose types ( ${}^1A_{1g}$ ,  ${}^1E_g$ ,  ${}^3E_u$ ) are alike in pairs (cf. (1), (2), (3)). For symmetry  $D_3$  there are more duplications of type, since the  $g, u$  distinctions are lost. For symmetry  $D_{3h}$  there are again three pairs of types  ${}^1A_1'$ ,  ${}^1E'$ ,  ${}^3E''$ . On examining the correlation of states between symmetries  $D_{3d}$  and  $D_{3h}$ , however (cf. paragraph following (3)), it is found that of the three pairs of states which agree in type for  $D_{3d}$ , only one pair still agrees for  $D_{3h}$ , and *vice versa*. This one pair comprises the  ${}^1A_{1g}$  states of (1) and (3), which both become  ${}^1A_1$  for  $D_3$  and  ${}^1A_1'$  for  $D_{3h}$ . Without such agreement in type for all angles of rotation, one could not expect a strong mutual perturbation; in view of the existence of such agreement in the case of the  ${}^1A_{1g}$  of (1) and (3), our assumption of rather strong resonance between these two states becomes tenable.

The nature of the normal state of  $B_2H_6$  being thus fairly accurately determined, it is of interest to consider the excited states shown by (1)–(3) and in Fig. 1. The positions of these, taken in connection with electronic selection rules, must be consistent with the colorlessness of  $B_2H_6$ . This lack of color shows that any absorption must be confined to the infrared and ultraviolet. From the  ${}^1A_1$  normal state, the electronic selection rules (cf. IV of this series,<sup>7</sup> p. 290) permit transitions to the following among the various states of (1)–(3).

$$\begin{array}{llll} \text{Sym. } D_{3d}: & \text{From } {}^1A_{1g} \text{ to} & {}^3E_u, {}^3A_{2u}, {}^3E_u, & {}^1E_u. \\ \text{" } D_3: & \text{" } {}^1A_1 \text{ " } {}^3A_2, & {}^1E, {}^3E, {}^3A_2, {}^3E, & {}^1E, {}^1E. \\ \text{" } D_{3h}: & \text{" } {}^1A_1' \text{ " } & {}^1E', & {}^3A_2'', {}^3E', {}^1E'. \end{array}$$

We may expect transitions which are not allowed for all angles of rotation (i.e., not for all the possible symmetries), as well as all transitions to triplet states, to be relatively very weak. This leaves only the transition to the  ${}^1E_u$  of (2) as a probably fairly intense one. The possibility that this lies in the ultraviolet can be immediately excluded, since that would require that configurations (1) and (2) should differ far too much in energy, while (3), higher in energy than (2), would correspond to far too strong a repulsion.

Hence the transition to  ${}^1E_u$  of (2) must lie in the infrared, i.e., at a wave-length not less than say about  $\lambda 8000$ , which corresponds to 1.55 volts. Since it is probable from the theory that  ${}^1E_u$  is the highest level of (2), and is higher than any level of (1), we conclude that all the levels of (1) and (2) are probably crowded into a space of not more than about 1.5 volts on the energy level diagram (for vertical excitation, but even less for adiabatic excitation). The level (3) can be higher; absorptive transitions to it are, however, rigor-

ously forbidden for all the possible symmetries. Fig. 1 has been constructed in accordance with the foregoing results and other considerations discussed earlier. It is of course only qualitative and diagrammatic.

It was tentatively assumed at one point in the foregoing discussion, and thenceforward, that the  $\text{BH}_3$  radicals in  $\text{B}_2\text{H}_6$  are of pyramidal form. If so,  $[\pi]$ ,  $[\pi]$  interactions are small. Conversely, the absence of visible absorption and the consequent limitations on Fig. 1 are found on examination to indicate that the  $[\pi]$ - $[\pi]$  interactions cannot in fact be very large; hence they constitute empirical evidence that the  $\text{BH}_3$  radicals really are pyramidal in  $\text{B}_2\text{H}_6$ . For if the  $[\pi]$ - $[\pi]$  interactions were large, the states of (1) and (2) would spread out, and probably the  ${}^3A_{2g}$  of (1) or perhaps the  ${}^3E_g$  of (2) would come very near or below the  ${}^1A_{1g}$  and make  $\text{B}_2\text{H}_6$  paramagnetic. Without calculations, the argument is not entirely conclusive, however. A further argument in favor of small  $[\pi]$ - $[\pi]$  interactions and pyramidal  $\text{BH}_3$  is that the observed B-B distance<sup>2</sup> in  $\text{B}_2\text{H}_6$  is about what would be expected for a single B-B bond. If there were a real double bond (strong  $[\pi]$ - $[\pi]$  interactions, and (1a) better than (1)), the B-B distance should be smaller. Nevertheless quite possibly the  $\text{BH}_3$  pyramids in  $\text{B}_2\text{H}_6$  are considerably flatter than for tetrahedral angles, with *some*  $[\pi]$ - $[\pi]$  bonding and *some* tendency toward (1a). On the whole, however, there appears to be little doubt that (1), (2), (3), modified by resonance between the  ${}^1A_{1g}$  of (1) and (3), and with more or less free rotation around the B-B bond, give a reasonably accurate description of the normal and low-energy excited states of  $\text{B}_2\text{H}_6$ .

It now remains to justify, as promised above, the nature of the electron states associated with electron-configurations (1)-(3), and their correlations with corresponding states for symmetry  $D_{3h}$ ; and also to justify certain correlations given above between states of  $\text{B}_2\text{H}_6$  and those of  $2\text{BH}_3$ . These problems are all, or can be reduced to, examples of a type of correlation problem similar to that solved by Wigner and Witmer for diatomic molecules.<sup>9</sup> It will be better to postpone a detailed discussion for a separate paper dealing generally with this subject, but something of the method will be outlined here.

Configurations and states (1), (2), (3) can be imagined

as obtained from certain corresponding states (8), (9), (10) of  $\text{O}_2$  by a continuous process in which each O nucleus is split into B+3H. Omitting  $2s^2 2s^2$  in each case, we have

$$(\sigma + \sigma, \sigma_g)^2 2p\pi^2 2p\pi^3, {}^3\Sigma_g^-, {}^1\Delta_g, {}^1\Sigma_g^+, {}^1\Sigma_g^-, {}^3\Delta_u, {}^3\Sigma_u^+, \quad (8)$$

$$(\sigma + \sigma, \sigma_g) 2p\pi^4 2p\pi^3, {}^3\Pi_g, {}^3\Pi_u, {}^1\Pi_g, {}^1\Pi_u, \quad (9)$$

$$2p\pi^4 2p\pi^4, {}^1\Sigma_g^+. \quad (10)$$

The symmetry here for  $\text{O}_2$  is  $D_{\infty d}$ . Depending on the arrangement of the resulting B and H nuclei, the symmetry may be reduced on splitting the O nuclei to  $D_{3d}$ ,  $D_3$ ,  $D_{3h}$ , or some other type. Definite rules<sup>7</sup> show how the states for symmetry  $D_{\infty d}$  must go into those of  $D_{3d}$  or  $D_{3h}$  (or of  $D_3$ , which may be obtained from either  $D_{3h}$  or  $D_{3d}$  by further reducing the symmetry).

By comparing the list of states for symmetry  $D_{\infty d}$  with those respectively obtained for  $D_{3h}$  and  $D_{3d}$ , it is possible to establish a set of correlations showing how the classification type of each actual electronic state varies during rotation as the symmetry goes successively through  $D_{3d}$ ,  $D_3$ , and  $D_{3h}$ . It must be noted, however, that this set of correlations is not a universal one, but is applicable in its details only to the particular electron configurations here considered. For instance, state  ${}^1E_g$  of (1) becomes a  ${}^1E$  for symmetry  $D_3$ , which becomes a  ${}^1E'$  for symmetry  $D_{3h}$ ; but  ${}^1E_g$  of (2), after becoming a  ${}^1E$  for  $D_3$ , then becomes a  ${}^1E''$  for  $D_{3h}$ . In general, a state  $X$  of symmetry  $D_3$  may be correlated with either an  $X_g$  or an  $X_u$  of  $D_{3d}$ , and with either an  $X'$  or an  $X''$  of  $D_{3h}$ . The actual correlations depend on the particular case.

The configurations (8), (9), (10) for  $\text{O}_2$  respectively correspond, as is easily seen, to (1), (2), (3) of  $\text{B}_2\text{H}_6$ . Really, the use of  $2p\pi$  O atomic orbitals as in (8)-(10) does not represent a good approximation for the actual  $\text{O}_2$  molecule; instead molecular orbitals ( $\pi \pm \pi$ ) would be better (cf. the three states of (6) and the first three states of (7), which together correspond to the six states of (8)). This does not matter, however, since our argument depends (within limits) only on formal correlations. The use of (8)-(10) is equivalent to using the Heitler-London-Pauling-Slater mode of description for the  $\pi$  electrons of  $\text{O}_2$ , although still retaining one molecular orbital ( $\sigma + \sigma$ ).

Our  $\text{B}_2\text{H}_6$  problem is thus reduced to the problem of proving the correctness of the electron states given for the somewhat artificial  $\text{O}_2$  electron configurations in (8)-(10). This can be done by a consideration of the wave functions, best systematically after the manner of Wigner and Witmer. Electrons in closed shells can be disregarded. For the remaining electrons, only the resultant state or states of groups of equivalent electrons are important. In (8)-(10) only the two groups of  $\pi$  electrons, one on each atom, matter. The group  $\pi^4$  would give a  ${}^1\Sigma^+$  resultant state,  $\pi^3$  a  ${}^2\Pi$  state. Hence the determination of the resultant states of (8), (9), (10), is equivalent to finding those of the state-pairs  ${}^2\Pi + {}^2\Pi$ ,  ${}^2\Pi + {}^1\Sigma^+$ ,  ${}^1\Sigma^+ + {}^1\Sigma^+$ , respectively, for the case of two systems with identical nuclear force-fields (here those of atoms, but the results would apply equally to any pair of like radicals each of symmetry  $C_{\infty v}$  or  $D_{\infty d}$ ). Once the problem is stated in this form, there is no difficulty in solving it along the lines of

<sup>9</sup> E. Wigner and E. E. Witmer, Zeits. f. Physik **51**, 859 (1928).



the Wigner-Witmer method,<sup>9</sup> the results being those given in (8)-(10).

The problem of finding the states of  $B_2H_6$  obtained by bringing together two  $BH_3$  radicals in specified electronic states can be solved in a similar way. One considers the system  $O+O$  with  $O$  atoms in specified states, and notes the resulting  $O_2$  states. Then one imagines each  $O$  split into a  $BH_3$  and its states changed into  $BH_3$  states, and simultaneously one imagines  $O_2$  split into  $B_2H_6$  and its states changed into those of the latter. By comparison, the desired correlations between  $BH_3$  states and  $B_2H_6$  states are obtained, the results being those given (in part) above. These results are strictly applicable only insofar as predissociation short-cuts resulting from electronic-vibrational interactions do not occur.

## II. VALENCE IN DIBORANE AND RELATED MOLECULES

Diborane and related molecules and derivatives will now be discussed from the standpoint of valence theory. We shall also consider why some molecules  $B_2R_6$  are stable while others do not occur but are represented by  $2BR_3$ . Here  $R$  is supposed to represent any monovalent atom or radical, and formulas  $BR_3$  and  $B_2R_6$  are supposed to stand also for cases where not all the  $R$ 's are alike.

Empirically,  $B_2R_6$  molecules such as the following are known:  $B_2H_6$ ,  $B_2H_5Cl$ ,  $B_2H_5CH_3$ ,  $(H_3C)_2BH \cdot BH_3$ ,  $(H_3C)_2BH \cdot BH_2CH_3$ ,  $(H_3C)_2BH \cdot BH(CH_3)_2$ .<sup>10</sup> On the other hand, we have  $BCl_3$ ,  $B(CH_3)_3$ ,  $C_6H_5BH_2$ ,  $(CH_3O)_2BH$ .<sup>10</sup> From an inspection of this list it is obvious that there must often be a close competition between  $B_2R_6$  and  $2BR_3$  as to which is the more stable; also that the probability of  $B_2R_6$  is increased if some of the  $R$ 's are  $H$  atoms. The occurrence of various more complex boron hydrides, e.g.,  $B_4H_{10}$ ,  $B_5H_{11}$ ,  $B_{10}H_{14}$ , may also be noted.<sup>10</sup>

The analysis in Part I shows that by the present method, which is not fettered by the requirements of ordinary valence theory, it has been possible to arrive at a perfectly natural, unmysterious, and definite explanation of the electronic structure of  $B_2H_6$ . The results may be described essentially as follows. Suppose we start from  $2BH_3$ , where for each  $BH_3$  there are six  $B-H$  bonding electrons, i.e., one pair of electrons per

ordinary  $B-H$  chemical bond (cf. (4a)). The structure of  $BH_3$  in this, its normal, state is certainly of a saturated, closed-shell, diamagnetic type. There exists, however, the possibility of withdrawing one electron from  $B-H$  bonding and putting it into a state where it is capable of forming a new bond. The molecule  $BH_3$  is then in a low energy excited state (cf. 5a) with only five  $B-H$  bonding electrons and one free valence electron. If one requires to know how many  $B-H$  bonds there then are, one may reply that there are  $2\frac{1}{2}$ , distributed, however, equally among all the three  $H$  atoms. More accurately, one might say that there are one  $[\sigma]$  bond and  $1\frac{1}{2}$   $[\pi]$  bonds, the former type, incidentally, being less polar than the latter.

Two of the excited  $BH_3$  can now come together, each with its free valence electron, to form between them a strong  $B-B$  bond of the electron-pair type. The total number of bonds in the resulting  $B_2H_6$  is then  $2\frac{1}{2} + 1 + 2\frac{1}{2} = 6$ , just the same number as for two free  $BH_3$  each in its normal state. Hence the question of whether  $B_2H_6$  is more stable than  $2BH_3$  is essentially one of the relative stability of  $B-B$  and  $B-H$  bonds. The existence of  $B_2H_6$  indicates empirically that the  $B-B$  bond is slightly the more stable.

We may next ask why  $B_2H_6$ , with only five instead of the normal six electrons to hold the three  $H$  atoms to each  $B$ , is not unstable with respect to  $B_2H_4 + H_2$ .  $B_2H_4$  is not known experimentally; if it were, it would have one  $B-B$  bond and four  $B-H$  bonds, each bond with the normal quota of two electrons. It is to be noted that the total number of bonding electrons (twelve) is the same in  $B_2H_4 + H_2$ ,  $B_2H_6$  and  $2BH_3$ . The observed greater stability of  $B_2H_6$  as compared with  $2BH_3$  and  $B_2H_4 + H_2$  then merely indicates that the effective strengths of bonds are in the order  $B-B > B-H > H-H$ , which is not incredible, although the great strength thus indicated for the  $B-B$  bond (greatest of all known homopolar bond strengths) is remarkable. The doubtless comparatively small margin of stability of  $B_2H_6$  over  $2BH_3$  indicates that the inequalities just stated are small, hence subject to upset under the impact of comparatively minor factors. This delicate balance suffices in a qualitative way to make understandable the existence of the various hydrides

<sup>10</sup> Cf. A. Stock, *Hydrides of Boron and Silicon* (Cornell University Press, Ithaca, N. Y., 1933); H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.* **53**, 4321 (1931); **55**, 4020, 4025 (1933); **56**, 499 (1934); **57**, 621 (1935).

$B_2H_6$ ,  $B_4H_{10}$ ,  $B_6H_{12}$ ,  $B_{10}H_{14}$  etc. No attempt will be made here, however, to explore in detail the electronic structures of these.—In connection with the above reference to the unknown  $B_2H_4$ , the fact that  $B_2Cl_4$  is experimentally well established<sup>10</sup> should be mentioned.

The foregoing discussion of the relative strengths of B—B and B—H bonds needs minor qualification, or explanation, in some respects. For one thing, the stability of the normal state of  $B_2H_6$ , as we have seen in Part I, is greater than it would otherwise be because of an interaction between the  $^1A_{1g}$  states of electron configurations (1) and (3). The resulting extra stability increases the effective strength of the B—B bond in  $B_2H_6$ , and probably in its derivatives, although really the extra strength does not inherently belong to this bond. It may even be that this resonance effect is a decisive factor in making these compounds more stable than  $2BR_3$ .

Another point is that the B—B bond in  $B_2H_6$  must have some tendency, although probably small (see Part I) to be a double bond. This no doubt increases the effective strength of the bond at least a little.

Still a further qualification in our discussion arises from the fact that the B—H bonding electrons in  $B_2H_6$  and  $BH_3$  are of two types,  $[\sigma\sigma]$  and  $[\pi\pi]$ . The B—H bond strength defined in the ordinary chemical manner really corresponds to a weighted average of strengths due to  $[\sigma]$  and  $[\pi]$ . Our statement that the bond strengths are in the order  $B-B > B-H > H-H$  should then really be modified to say that the effective B—B bond strength (cf. two preceding paragraphs) exceeds the effective strength of the  $[\pi]$  type of B—H bonds, while this in turn exceeds the H—H bond strength. For it is just the  $[\pi]$  type of B—H bonding electrons which are sacrificed if  $B_2H_6$  or  $B_2H_4 + H_2$  is formed from  $2BH_3$ . The relation  $B-B > B-H > H-H$  might possibly not be true if the bond strengths were measured according to ordinary chemical definitions; it is, however, doubtful whether data are available for testing this point.

In seeking further to understand the stability of molecules of the type  $B_2R_6$ , a comparison with the case of  $NR_3$  may be instructive. Here there is no tendency to form  $N_2R_6$ . This is intimately connected with the fact that the outer shell of the N atom is full with  $[\sigma]^2[\pi]^4[\sigma]^2$  in  $NR_3$ , while the two  $[\sigma]$  places are vacant in  $BR_3$ , or at least in  $BH_3$ . In the case of  $BH_3$ , one  $[\pi]$  electron can be withdrawn from the B—H bonding and put into the vacant low energy  $[\sigma]$  state (cf. 5a). Then it is capable of forming a strong  $[\sigma+\sigma]$  B—B bond with another  $BH_3$  in the same condition, so that there is no net change in number of bonds in going from  $2BH_3$  to  $B_2H_6$ . With  $NH_3$ ,

however, there is no excited state of as low energy as the  $^3E$  of (5a) for  $BH_3$ . The lowest excited state is probably  $[\sigma]^{-1}3s$ ,  $^3A_1$  (cf. VII of this series). Here, to be sure, there is a certain advantage over the  $BH_3$  case in that the  $[\sigma]$  electron excited is of little value for the N—H bonding, but this is balanced by the fact that the  $(3s+3s)$  N—N bond, which the excited  $3s$  electrons of two  $[\sigma]^{-1}3s$  molecules of  $NH_3$  could form, would be very weak.

The present method is in general agreement with the conclusion of Sidgwick<sup>2</sup> that in  $B_2R_6$ , one R on each B is held by a one-electron bond, the others by ordinary electron-pair bonds. Nevertheless the description in terms of one-electron bonds tends to be rather misleading (cf. Pauling<sup>2</sup>) unless one thinks of each such bond as circulating exceedingly rapidly among the three R's, so that no one of them is disfavored. The present method, by describing the situation in a way which does not require the localization of bonding electrons between particular atom-pairs, makes this point clear at once. Thus it shows that in each  $BR_3$  in  $B_2R_6$  there are five B—R bonding electrons shared equally by three R's if the latter are alike, or nearly equally if they are not too unlike.

The present method shows that it is not correct, even in a molecule such as  $(CH_3)_2BH \cdot BH(CH_3)_2$ , to suppose that, e.g., the  $CH_3$  radicals are held by electron-pair bonds and the H atoms by one-electron bonds. On the contrary, it shows that the five bonding electrons within each group  $(CH_3)_2BH$  must be distributed fairly equally in the service of the B—H and the two B—C bonds, i.e., one may speak of a 5/3-electron bond to each C and to the H. This does not of course imply that the *strength* of the B—H bond is precisely the same as that of the two B—C bonds, but only that the distribution of bonding electricity is fairly symmetrical with respect to these three bonds.

To make the matter clearer, it may be advisable to give the electronic structure of  $B_2H_2 \cdot (CH_3)_4$ . Assuming the substance to be diamagnetic, the normal state should be closely analogous to  $B_2H_6$ , which is given essentially by  $^1A_{1g}$  of (1). The structure may be written approximately, omitting  $1s$  electrons, as

$$\begin{array}{ccccccc} [sa_1]^{2 \times 4} [s]^2 & [s]^2 & [\pi e]^{4 \times 4} [\sigma + \sigma]^2 & [\pi]^3 & [\pi]^3 & & {}^1A. \\ \text{CH}_3 & \text{BHC}_2 & \text{BHC}_2 & \text{CH}_3 & \text{B}-\text{B} & \text{BHC}_2 & \text{BHC}_2 \end{array} \quad (11)$$

Since the molecule as a whole, as well as the  $(\text{CH}_3)_2\text{BH}$  groups within it, are probably without symmetry, the usual representation symbols have been omitted, except those for the orbitals  $[sa_1]$  and  $[\pi e]$  of the four  $\text{CH}_3$  radicals. In (11), the orbital  $[s]$  within each  $\text{BH}(\text{CH}_3)_2$  connects the B with the H and the two C's, just as in  $\text{B}_2\text{H}_6$  the  $[sa_1]$  of each  $\text{BH}_3$  connects the B with the three H's. Similarly, the  $[\pi]$ 's of the  $\text{BH}(\text{CH}_3)_2$  also connect the B with the H and two C's. Thus the substitution of the four  $\text{CH}_3$ 's for H's does not essentially alter the bonding action of the B atom. (Cf. discussion in VII and others of this series in regard to minor complications caused by substitutions.)

If we consider the series  $\text{B}_2\text{H}_6, \dots, \text{B}_2\text{H}_2(\text{CH}_3)_4, \text{B}_2(\text{CH}_3)_6$ , we have evidently an increasing tendency to split at the B—B bond, a tendency which is actually realized in the last compound. This can be understood if the effective strength of the B—C  $[\pi]$  bonds in  $\text{B}_2(\text{CH}_3)_6$  is slightly greater than that of the B—B bond, so that the molecule splits, but that in  $\text{B}_2\text{H}_6$  the effective strength is appreciably weaker for the  $[\pi]$  bonds than for the B—B bond. Similarly the nonoccurrence of  $\text{B}_2\text{Cl}_6$  suggests greater effective strength for B—Cl bonds of  $[\pi]$  type than for B—B bonds. Can these variations be understood?

In the first place, we recall (see above), that the *effective* strengths of bonds are often affected by more or less accidental minor factors which may turn the scales one way or the other. It would hardly be possible without detailed analysis and computation to estimate the net effect of all such minor factors. We may nevertheless ask if there are any obvious new factors which enter when  $\text{CH}_3$  or Cl is substituted for H, and which would tend to produce a relative decrease in the effective strength of the B—B bond. Of course for one thing, the B—C and B—Cl  $[\pi]$  bonds might directly be stronger than the B—H  $[\pi]$  bond, but this is not easily proved or disproved theoretically.

Another possibility is a sort of "steric hindrance,"—not to be interpreted too literally, however. In  $(\text{CH}_3)_3\text{B}$ , each  $\text{CH}_3$  radical contains a set of closed shells  $1s^2[s]^2[\pi]^4$ ,—cf. (11). If the

closed shells, particularly the  $[\pi]$  shells, of the  $\text{CH}_3$  groups attached to one B atom came too close to those attached to a second B atom in a molecule  $(\text{CH}_3)_3\text{BB}(\text{CH}_3)_3$ , a considerable repulsion would result which has no counterpart in  $\text{B}_2\text{H}_6$ . This might be a sufficient factor, especially if, for the strongest B—B bonding, the  $\text{BH}_3$  or  $\text{BC}_3$  pyramids in  $\text{B}_2\text{H}_6$  or  $\text{B}_2(\text{CH}_3)_6$  are relatively flat, to throw the balance of stability in favor of 2  $\text{B}(\text{CH}_3)_3$ .

When Cl is substituted for  $\text{CH}_3$ , there is a set of closed shells,  $\dots s^2p\pi^4$  for each Cl atom, analogous to  $\dots [s]^2[\pi]^4$  of the  $\text{CH}_3$  radicals. Since it has been possible to carry Cl substitution in  $\text{B}_2\text{H}_6$  probably only as far as  $\text{B}_2\text{H}_5\text{Cl}$ , while  $\text{CH}_3$  substitution has been carried as far as  $\text{B}_2\text{H}_2(\text{CH}_3)_4$ , it would appear that the Cl atom closed shell repulsions are even more potent than those of  $\text{CH}_3$  radicals.<sup>11</sup> However, there are also other possibilities. In fact there is one very definite factor tending to stabilize molecules like  $\text{BCl}_3$ , which can hardly be so effective for  $\text{B}(\text{CH}_3)_3$ . This factor is a bonding action which should exist between the B atom and the three  $(p\pi)^4$  shells of the Cl atoms. Such action is completely analogous to a similar action in the molecules  $\text{BO}_3^-$ ,  $\text{CO}_3^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_3$ , etc., and which may be considered as a determining factor for the stability of the latter. This action, which may be called "cap-bonding," has been mentioned briefly in the end of I and in II (p. 56) of this series, and will be discussed more fully in a later paper.

Whatever may be the detailed explanations, it can be predicted that energy level diagrams similar to Fig. 1 are applicable to all molecules  $\text{BR}_3$  and  $\text{B}_2\text{R}_6$ , with changes only in the relative positions and spacings of the energy levels. Strong cap-bonding would raise very considerably, relative to the normal level of  $\text{BR}_3$ , the energies of the  $\text{B}_2\text{R}_6$  and the excited  $\text{BR}_3$  levels which correspond to levels in Fig. 1. If the form  $\text{B}_2\text{R}_6$  is the stable form, that means that the lowest energy on the diagram is that of some  $\text{B}_2\text{R}_6$  level,

<sup>11</sup> In conversation, Dr. A. B. Burg has informed the writer of unpublished evidence tending to indicate the existence of higher chlorine derivatives, presumably including  $\text{B}_2\text{H}_4\text{Cl}_2$  at least.

probably a  ${}^1A_{1g}$  as in Fig. 1 in most if not all cases. A study of magnetic properties of various  $B_2R_6$  at various temperatures would help to decide this.

If  $2BR_3$  is more stable than  $B_2R_6$ , this means that the lowest  $B_2R_6$  energy is close to or higher than the energy of  $2BR_3$ . In case the difference is not large, as is probably often true, then, if it is feasible to heat the substance sufficiently, a fraction of the molecules should go over into (one or more of the states of)  $B_2R_6$ . Similarly on heating a substance of the type  $B_2R_6$ , a fraction of the molecules should of course go over into  $BR_3$ . Other fractions should also go into some of the low excited states of  $B_2R_6$  appearing in Fig. 1. Since some of these are paramagnetic, the substance should begin to show paramagnetism if

the temperature can be raised sufficiently without decomposition.

Measurements of magnetic susceptibilities of substances of the  $B_2R_6$  and even perhaps some of those of the  $BR_3$  type (e.g.,  $B(CH_3)_3$ ) should give interesting results, especially if temperatures can be raised. Studies leading to determinations of the splitting energies of  $B_2R_6$  into  $2BR_3$  would naturally also be of interest. An investigation of the photographic infrared absorption spectrum of  $B_2H_6$ , in order to look for the probably expected  ${}^1A_{1g} \rightarrow {}^1E_u$  bands, is being undertaken at this University.

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## The Structure of Potassium Hexachlorothallate Dihydrate

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Potassium hexachlorothallate dihydrate is shown from x-ray data to possess a body centered tetragonal unit of structure with  $a_0 = 15.841 \pm 0.020\text{\AA}$ ,  $c_0 = 18.005 \pm 0.020\text{\AA}$  containing  $14 K_3TiCl_6 \cdot 2H_2O$ . A structure with nineteen determinable parameters is developed from  $D_{4h}^{17} - I 4/mmm$ , and accounts satisfactorily for observed intensity data.  $TiCl_6^{3-}$  ions occur as well-defined groups. 24 of the  $42 K^+$  ions are closely surrounded by 8  $Cl^-$ , 16  $K^+$  by 7  $Cl^-$  and 2  $H_2O$ , and the remaining 2  $K^+$  by 6  $H_2O$ ; these  $K(H_2O)_6^+$  groups are situated in regions of definitely negative potential. The structure is very compact, but has

quite satisfactory interatomic distances throughout. The evidence from this and from a previous structural determination of  $Cs_3Ti_2Cl_9$  shows that thallic thallium tends to form six stable covalent bonds with chlorine with a  $Tl-Cl$  separation of about  $2.55\text{\AA}$ , in agreement with the covalent radii of Pauling and Huggins. It is shown also that a compound of empirical formula  $Rb_3TiBr_6 \cdot (8/7)H_2O$  probably possesses essentially the same type of structure as  $K_3TiCl_6 \cdot 2H_2O$ ; dimensional relations in the bromothallate permit the alkali ions of  $2(b)$  to coordinate eight rather than six molecules of water.

### INTRODUCTION

THE coordination and bonding properties of such heavy metal forming elements as thallium and lead, lying in the B subgroups of the periodic system, have as yet been comparatively little studied. With a view toward elucidating the characteristic structural properties of trivalent thallium, we have undertaken x-ray studies of a number of its complex salts. The results of one such investigation, dealing with cesium enneachlorodithallate,  $Cs_3Ti_2Cl_9$ , have already been reported;<sup>1</sup> we describe in the present paper the structure of potassium hexachlorothallate dihydrate,  $K_3TiCl_6 \cdot 2H_2O$ , and summarize briefly

our present knowledge of the structural properties of thallic thallium.

Good crystals of  $K_3TiCl_6 \cdot 2H_2O$ , from one to two mm on an edge, were prepared without difficulty according to the directions of Meyer.<sup>2</sup> In habit and in general appearance the crystals seemed to agree closely with the description of Groth,<sup>3</sup> who lists them as tetragonal bipyramidal,  $c/a = 0.7913$ . Laue and oscillation photographs were used as a source of x-ray data.

### DETERMINATION OF THE STRUCTURE

The smallest tetragonal unit of structure is one with  $a_0 = 15.841 \pm 0.020\text{\AA}$ ,  $c_0 = 18.005$

<sup>2</sup> Meyer, *Zeits. f. anorg. allgem. Chemie* **24**, 321 (1900).

<sup>3</sup> Groth, *Chemische Kristallographie*, Engelmann, Leipzig, **1**, 424 (1908).

<sup>1</sup> Hoard and Goldstein, *J. Chem. Phys.* **3**, 199 (1935).