THE STRUCTURES OF ELECTRON-DEFICIENT MOLECULES

By H. C. Longuet-Higgins, M.A., D.Phil.
(Department of Theoretical Chemistry, University of Cambridge)

The Structure of the Boron Hydrides.—In the last three decades or so a new branch of inorganic chemistry has come into being—the chemistry of electron-deficient compounds. This development is most clearly appreciated if one takes as a starting point Sidgwick's monumental book " The Electronic Theory of Valency ".[1] The concepts and generalisations put forward by Sidgwick in 1927 are still adequate for describing a large portion of structural chemistry, namely that of compounds in which every atom or ion has a completed valency shell of two, eight, or more electrons. Sidgwick's classification of chemical bonds into those which are essentially ionic and those which are essentially covalent, has been extended and deepened, of course, by the work of Pauling,[2] Mulliken,[3] and others, but the general validity of this classification has remained unchallenged, at least for the types of compound with which Sidgwick was mainly concerned. Nevertheless even in 1927 it was recognised that there were some relatively simple substances which defy classification within the Lewis–Langmuir–Sidgwick scheme ; one substance in particular was an outstanding anomaly, namely the simplest hydride of boron, diborane. The classical work of Alfred Stock [4] and his colleagues had established beyond doubt that this hydride has not, as might have been expected, the formula BH_3, but is dimeric, B_2H_6. In order to appreciate the structural problem raised by the existence of B_2H_6, it is necessary to consider the postulates on which classical valency theory was founded. It was implicitly assumed that any chemical bond, whether ionic, covalent, or intermediate, is a bond between two atoms only ; also, that if a molecule contains one or more essentially ionic bonds then the substance will be non-volatile, high-melting, and usually soluble in liquids of high dielectric constant. Diborane is a substance of high volatility resembling other non-metal hydrides such as ethane rather than ionic hydrides such as calcium hydride in its physical properties. On the basis of the above postulates the bonds in the molecule should be essentially covalent. This conclusion, however, leads to an immediate difficulty : a molecule composed of eight atoms requires at least seven " two-centre bonds " to hold it together ; seven covalent bonds demand fourteen valency electrons and in diborane the number of valency electrons is only twelve. In this sense, therefore, B_2H_6 is an " electron-deficient " molecule.

The early attempts to fit diborane into the classical scheme were, to

---

[1] Sidgwick, " The Electronic Theory of Valency ", Oxford Univ. Press, 1927.

[2] Pauling, " The Nature of the Chemical Bond ", Cornell Univ. Press, 2nd edn., 1940.

[3] Mulliken, *J. Chem. Phys.*, 1934, **2**, 782 ; *J. Chim. phys.*, 1949, **46**, 497.

[4] Stock, " The Hydrides of Boron and Silicon ", Cornell Univ. Press, 1933.

say the least, unsatisfactory. Pauling [2] suggested that diborane is a resonance hybrid between structures involving two-electron, one-electron, and no-electron bonds, and he supported this with the observation that such bonds would be most easily formed between two atoms of similar electronegativity, the electronegativities of boron and hydrogen being nearly equal. It was difficult to understand, however, why in these circumstances diborane should be diamagnetic, and also colourless, since a molecule with many resonance structures is usually coloured.

It soon became clear that the electronic structure of diborane would not be understood until definite evidence became available as to the geometrical disposition of the atoms in the molecule. (The situation might have been compared with that facing a theoretical chemist invited to account for the properties of a material whose empirical formula is compatible with several isomeric structural possibilities.) It had been assumed, on the basis of slender physical evidence, that diborane is geometrically similar to ethane; [5] early *X*-ray studies were consistent with this hypothesis [6] and electron diffraction appeared to favour it.[7] There were, however, indications that the ethane-like structure was not entirely satisfactory. Researches on the chemistry of the alkyl diboranes showed that it is possible to replace only four of the hydrogen atoms in B_2H_6 by methyl groups, and it was well known that BMe_3 was monomeric. The infrared [8] and the Raman [9] spectrum of diborane also presented acute difficulties of interpretation in terms of an ethane-like model; there were more strong absorption bands than could be accounted for without postulating low-lying electronic excited states, a hypothesis for which there was no independent evidence.

These unsatisfactory features of the ethane-like structure led to the re-examination of an alternative geometrical structure for B_2H_6 which had been suggested in the early days by Dilthey.[10] It was shown [11, 12, 13] that many of the above anomalies disappear if diborane is supposed to possess a bridged structure in which four of the hydrogen atoms are situated at the ends of the molecule, being attached to the two boron atoms by normal covalent bonds, the other two hydrogen atoms being situated in the middle of the molecule. This left open, of course, the question how the remaining four valency electrons could hold together the central bridge, but such a linkage could be conceived in terms of equivalent resonance structures, covalent [11] or ionic [12] or both.[13] It was, furthermore, possible to generalise this structural hypothesis to digallane and the volatile metal borohydrides, and the same hypothesis led to an explanation of the non-volatility of aluminium hydride and to the prediction [14] that beryllium should also form

[5] Schlesinger and Burg, *Chem. Rev.*, 1942, **31,** 1.

[6] Mark and Pohland, *Z. Krist.*, 1925, **62,** 103.

[7] Bauer, *Chem. Rev.*, 1942, **31,** 43.

[8] Stitt, *J. Chem. Phys.*, 1941, **9,** 780.

[9] Anderson and Burg, *ibid.*, 1938, **6,** 586.

[10] Dilthey, *Z. angew. Chem.*, 1921, **34,** 596.

[11] Nekrassov, *J. Gen. Chem. Russia*, 1940, **10,** 1021, 1056.

[12] Syrkin and Dyatkina, *Acta Physicochim. U.R.S.S.*, 1941, **14,** 547.

[13] Longuet-Higgins and Bell, *J.*, 1943, 250.

[14] Longuet-Higgins, *J.*, 1946, 142.

a non-volatile hydride, a prediction which was subsequently verified.[15] A quantitative theoretical study of the vibrational spectrum of B_2H_6 lent very strong support to the bridged structure.[16]

Before we discuss the electronic nature of the bridge it will be well to refer to more recent evidence which confirms the bridged structure since upon it depends the validity of the current electronic theory. Price[17] examined the rotational lines in certain infrared absorption bands of B_2H_6 and found that they resembled very closely the corresponding bands in the spectrum of ethylene. In particular the rotational lines show a two-fold alternation of intensity which is immediately intelligible on the basis of a two-fold symmetry axis through the boron atoms, but would be unintelligible in terms of a three-fold axis, which would lead to an altered intensity in every third rotational line. Price's infrared work has been extended and confirmed by other workers.[18, 19, 20] The most recent and perhaps most conclusive evidence for the bridged structure comes, however, from a study of the nuclear magnetic resonance spectrum.[21] The isotopic species $^{11}B_2H_6$ shows three main regions of resonance absorption, due respectively to the ^{11}B atoms, the terminal hydrogen atoms, and the bridge hydrogen atoms (the last two regions of absorption are close together). The fine structure of these absorption bands is particularly interesting. The absorption due to the terminal protons is split into four equally spaced lines by the magnetic field of the neighbouring boron atom ; this is because the ^{11}B nucleus has a spin $\frac{3}{2}$ which can be oriented in four different directions $(\frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2})$ in the external magnetic field. The absorption due to the bridge protons is split into seven components by the pair of ^{11}B nuclei, whose joint spin is 3 and can be oriented in seven different ways (3, 2, 1, 0, −1, −2, −3). The absorption due to each ^{11}B nucleus is split into three main lines by the two terminal protons attached to it (the relevant component of their joint spin can be 1, 0, or −1) ; each of these main lines is further split into three closely spaced lines by the bridge protons, whose joint spin is also unity and can be oriented in three ways. The agreement between the observed and expected spectrum is perfect, and leaves no doubt whatever of the correctness of the bridged structure.

Having reviewed the evidence which led to the bridged structure for diborane we can now consider the electron distribution in this molecule. If we allow that the terminal hydrogen atoms are attached by ordinary two-electron covalent bonds the structural problem is reduced to explaining how the remaining four valency electrons can hold the bridge together (that the terminal bonds are " normal " is strongly suggested by their force constants, as calculated[16] by Bell and Longuet-Higgins). If one

---

[15] Finholt, Bond, and Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69,** 1199.

[16] Bell and Longuet-Higgins, *Proc. Roy. Soc.*, 1945, *A*, **183,** 357.

[17] Price, *J. Chem. Phys.*, 1947, **15,** 614 ; 1948, **16,** 894.

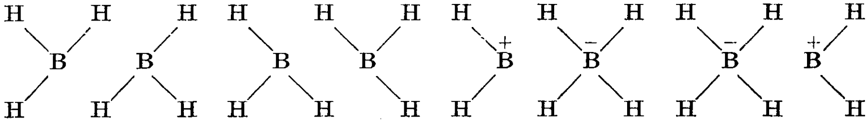
[18] Webb, Neu, and Pitzer, *ibid.*, 1949, **17,** 1007.

[19] Anderson and Barker, *ibid.*, 1950, **18,** 698.

[20] Lord and Nielsen, *ibid.*, 1951, **19,** 1.

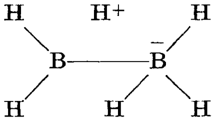
[21] Shoolery, *Discuss. Faraday Soc.*, 1955, **19,** 215.

accepts the existence of equivalent alternative resonance structures as a sufficient condition for stability, then one can invoke resonance between forms such as (I—VIII) to account for the diamagnetism and stability of

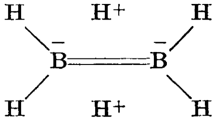


(I) (II) (III) (IV) (V) (VI) (VII) (VIII)

the system. However, the close proximity of the two boron atoms (1·78 Å) shows that there must be substantial overlap between the atomic orbitals of these atoms and that resonance forms such as (IX) and (X) should not



(IX)



(X)

be excluded from consideration. The resulting picture is unsatisfactorily complex and gives one little insight into the real nature of the bridge linkage. Recognising this, Pitzer [22] suggested a description of the bridge in which he compared it with the double bond in ethylene. In the ethylene molecule the bond between the carbon atoms involves four valency electrons, two of which move in a " molecular orbital " of type σ which is symmetrical about the C–C axis, and the other two of which move in a molecular orbital of type π formed by the sideways overlap of two $2p$ orbitals, one on each carbon atom. Pitzer proposed that one should regard the diborane bridge as a " protonated double bond ", in which the function of the four electrons is to bind the boron atoms together, the two hydrogen nuclei being situated at the points of greatest electron density in this bond. This description has an attractive simplicity, but suffers from the drawback of suggesting that the bridge protons should be acidic, whereas in their reactions diborane and similar molecules behave [15] as though they contained the hydride anion H^-.

The next step towards a description of the bridge was to consider explicitly the $1s$ atomic orbitals of the central hydrogen atoms.[23] A general principle of molecular-orbital theory [24] is that two orbitals or groups of orbitals of the same symmetry will interact to give two new orbitals which are respectively more and less strongly bonding than the original orbitals. This idea can be applied directly to the present situation.

To make this clear we will number the atoms of the bridge as shown in Fig. 1. Pitzer's σ orbital is then $(\sigma_1 + \sigma_2)/\sqrt{2}$ and his π orbital $(p_1 + p_2)/\sqrt{2}$ (the factor $1/\sqrt{2}$ is inserted for rough normalisation). The $1s$ orbitals of

---

[22] Pitzer, *J. Amer. Chem. Soc.*, 1945, **67**, 1126.

[23] Longuet-Higgins, *J. Chim. phys.*, 1949, **46**, 275.

[24] Coulson, *Quart. Rev.*, 1947, **1**, 144.

the bridge hydrogen atoms must be considered together ; the combination $(s' + s'')/\sqrt{2}$ has the same symmetry as the σ orbital, and the combination $(s' - s'')/\sqrt{2}$ has the antisymmetry characteristic of a π orbital. By combining these with the orbitals of the double bonds we obtain the new combinations *

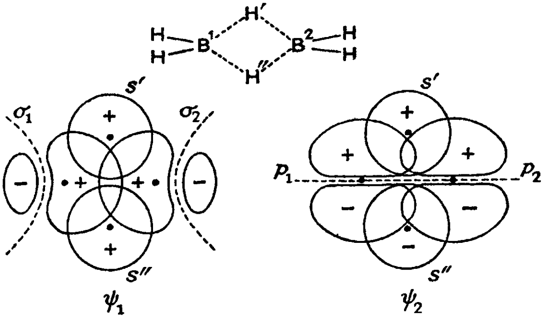


FIG. 1

$$\psi_1 = (\sigma_1 + \sigma_2 + s' + s'')/2, \quad \psi_2 = (p_1 + p_2 + s' - s'')/2$$
$$\psi_3 = (\sigma_1 + \sigma_2 - s' - s'')/2, \quad \psi_4 = (p_1 + p_2 - s' + s'')/2$$

the first two of which are illustrated diagrammatically in Fig. 1. Now there is another general principle of molecular-orbital theory, namely that if one assigns four electrons in pairs to each of two molecular orbitals ψ_1 and ψ_2 then a precisely equivalent description [25, 26] is to assign them instead to the orbital combinations $(\psi_1 + \psi_2)/\sqrt{2}$ and $(\psi_1 - \psi_2)/\sqrt{2}$.

Applying this principle to the orbitals depicted in Fig. 1 we obtain two new localised molecular orbitals of the form

$$\chi_1 = (\sigma_1 + p_1 + \sigma_2 + p_2 + 2s')/2\sqrt{2}, \quad \chi_2 = (\sigma_1 - p_1 + \sigma_2 - p_2 + 2s'')/2\sqrt{2}$$

These two orbitals are concentrated on either side of the central bridge, and by assigning an electron pair to each of them we obtain two " three-centre " bonds [23] each involving the two boron atoms and one of the hydrogen atoms.

The idea of interpreting electron-deficient structures in terms of many-centre bonds has been taken up and extensively applied to all the known boron hydrides by Eberhardt, Crawford, and Lipscomb.[27] To Lipscomb and his colleagues is due the credit for having established firmly and in considerable detail the structures of the higher boron hydrides B_4H_{10},[28a] B_5H_9,[28b] and B_5H_{11} ; [28c] the structure of $B_{10}H_{14}$ was established crystallo-

---

[25] Lennard-Jones, *Proc. Roy. Soc.*, 1949, *A*, **198**, 14.

[26] Pople, *Quart. Rev.*, in press.

[27] Eberhardt, Crawford, and Lipscomb, *J. Chem. Phys.*, 1954, **22**, 989.

[28](*a*) Nordman and Lipscomb, *J. Amer. Chem. Soc.*, 1953, **75**, 4116 ; (*b*) Dulmage and Lipscomb, *ibid.*, 1951, **73**, 3539 ; (*c*) Lavine and Lipscomb, *J. Chem. Phys.*, 1954, **22**, 614.

* The qualitative justification for taking equal weights in these combinations is that the electronegativities of boron and hydrogen are close together.

graphically by Kasper, Lucht, and Harker.[29] The structures of these molecules are themselves interesting, but perhaps of even greater interest are the underlying structural principles. The logical foundation of Eberhardt, Crawford, and Lipscomb's theory is the description of diborane outlined in the last paragraph. The two localised molecular orbitals χ_1 and χ_2 can be regarded as formed from hybrid atomic orbitals, $(\sigma_1 \pm p_1)/\sqrt{2}$ and $(\sigma_2 \pm p_2)/\sqrt{2}$, on the two boron atoms and the $1s$ orbitals of the hydrogen atoms thus :

$$\chi_1 = \left\{\frac{\sigma_1 + p_1}{\sqrt{2}} + \frac{\sigma_2 + p_2}{\sqrt{2}} + \sqrt{2}.s'\right\}\Big/2$$

$$\chi_2 = \left\{\frac{\sigma_1 - p_1}{\sqrt{2}} + \frac{\sigma_2 - p_2}{\sqrt{2}} + \sqrt{2}.s''\right\}\Big/2 \quad \text{(see Fig. 2)}$$

One might, therefore, have taken as a starting point the four hybrid orbitals on the boron atoms and considered how they overlap with one another and with the two hydrogen orbitals. It is clear that these six atomic orbitals will overlap in two sets of three and that it would, therefore, be possible to consider each set of three mutually overlapping orbitals independently of the other set. Eberhardt, Crawford, and Lipscomb pointed out that when three atomic orbitals all overlap one obtains three molecular orbitals of which only one is strongly bonding ; this was the fundamental principle of their structural theory. In discussing a particular molecule one is at liberty to hybridise the atomic orbitals of a boron atom in any appropriate manner, provided that one subsequently takes into account the overlap of every hybrid with the orbitals of all neighbouring atoms. Let us then see how these ideas apply to the higher boron hydrides.

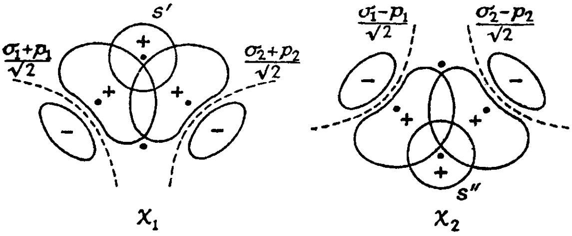


FIG. 2

Other Boron Compounds.—The next simplest hydride after B_2H_6 is tetraborane B_4H_{10}. The geometrical structure of this molecule, indicated in Fig. 3, is such that each boron atom is surrounded more or less tetrahedrally by the four atoms indicated. In setting up the molecular orbitals it is, therefore, appropriate to start with tetrahedral hybrids on the boron atoms and then to consider the mutual overlap between these and the $1s$ orbitals of the hydrogen atoms. The resulting situation is one in which every full line in the diagram represents a pair of mutually overlapping

---

[29] Kasper, Lucht, and Harker, *Acta Cryst.*, 1950, **3**, 436.

atomic orbitals ; these give rise to 7 two-centre bonds involving fourteen valency electrons. The remaining eight electrons can then be assigned to three-centre bonds of the same type as in diborane ; these bonds serve to bind together the atoms joined by broken lines. All the electrons being assigned to bonding orbitals, we obtain a closed-shell structure and the molecule is diamagnetic.

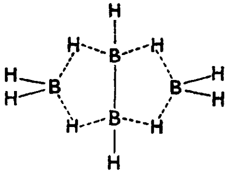


FIG. 3

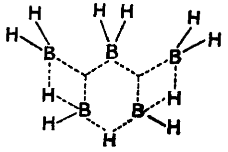


FIG. 4

B_5H_{11} presents a more complicated situation. In Fig. 4 the lines radiating from each atom make roughly tetrahedral angles with each other. The external B–H bonds use up sixteen electrons and ten are left to be assigned to the rest of the system. Of these, six are required to form three-centre bonds involving the bridge hydrogen atoms, leaving four to hold the boron framework together. This is achieved by the formation of two three-centre bonds of a different type, involving the mutual overlap of two groups of three tetrahedral hybrid boron orbitals. Again we obtain a closed shell.

The molecule B_5H_9 can be described [30] in similar terms. The geometry of this molecule is that of a square pyramid. The four neighbours of each basal boron atom are again disposed in a nearly regular tetrahedron. The external B–H bonds consume ten electrons and the B–H–B bridges between them another eight, leaving six to bind the apical boron atom to the base of the pyramid. To see how this is done it is simplest to consider separately the 2*s*, 2*px*, and 2*py* valency orbitals of the central boron atom, the 2*pz* orbital being already involved in a bond to a hydrogen atom. The 2*s*, 2*px*, and 2*py* orbitals have the same symmetries as the combinations (see Fig. 5)

$$(t_1 + t_2 + t_3 + t_4)/2 \quad (-t_1 + t_2 + t_3 - t_4)/2 \quad (t_1 + t_2 - t_3 - t_4)/2$$

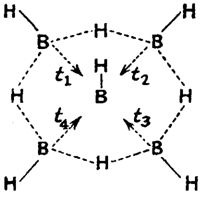


FIG. 5

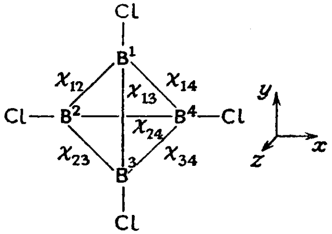


FIG. 6

respectively and will interact with these to give six molecular orbitals of

---

[30] Longuet-Higgins, *J. Roy. Inst. Chem.*, 1953, **77**, 179.

which three will be bonding and three antibonding [the seventh molecular orbital arising from the seven atomic orbitals $2s$, $2px$, $2py$, t_1, t_2, t_3, t_4, namely $(t_1 - t_2 + t_3 - t_4)/2$, does not involve the central boron atom and is in fact antibonding between the basal atoms]. There is, therefore, room for three pairs of bonding electrons and this is the number which remains after the attachment of the hydrogen atoms to the framework.

The structure of $B_{10}H_{14}$ has been interpreted in detail by Eberhardt, Crawford, and Lipscomb, but the underlying principles are the same and there is no need to describe this molecule in detail here. Lipscomb and his colleagues have also investigated a B_6 hydride [31] and a B_9 hydride [32] and have suggested structures for them.

It will be seen from these examples that the structural principles applying to the electron-deficient molecules are rather different from those appropriate to saturated molecules. The reason for this is essentially as follows. In saturated molecules composed of the atoms hydrogen, carbon, nitrogen, oxygen, and other atoms possessing at least half the number of electrons required for a stable valency shell, the valency shell of each atom can be completed by the formation of two-centre bonds alone. Further, if the total number of electrons in a molecule exceeds the total number of valency atomic orbitals, then there will be unshared pairs—for example in water there are six valency orbitals altogether and eight electrons so that we obtain 2 two-centre bonds and two unshared pairs. The filling of the valency shell of each atom then imposes geometrical restrictions on the disposition of its neighbours. These restrictions, arising essentially from Pauli's exclusion principle, require that different electron pairs shall avoid one another as far as possible. In a molecule such as diborane, however, the usual stereochemical restrictions become relaxed ; [33] each boron atom is in proximity to five other atoms although the four electron pairs contributing to its valency shell are, as already explained, disposed in what can be regarded as a tetrahedral manner.

An interesting molecule whose geometrical structure has been established by Atoji and Lipscomb,[34] but not hitherto accounted for, is boron monochloride B_4Cl_4. In this molecule the boron atoms are linked together in a regular tetrahedron and to each is attached an outlying chlorine atom. In this molecule there are clearly insufficient valency electrons to allow each full line in Fig. 5 to be interpreted as a two-centre electron-pair bond. The explanation of this structure is probably as follows. To start with, it is natural to regard each boron atom as forming a two-centre bond with the $3p\sigma$ orbital of the neighbouring chlorine atom. This uses up eight valency electrons. Disregarding for the moment the $3p\pi$ electrons of the chlorine atoms, we are then left with eight valency electrons to hold together the boron tetrahedron. These electrons can be assigned to molecular orbitals compounded from the six equivalent bonding orbitals χ_{ij} between the boron

---

[31] Eriks, Lipscomb, and Schaeffer, *J. Chem. Phys.*, 1954, **22**, 754.

[32] Dickerson, Wheatley, Howell, Lipscomb, and Schaeffer, *ibid.*, 1956, **25**, 606.

[33] Platt, *ibid.*, 1945, **22**, 1033.

[34] Atoji and Lipscomb, *ibid.*, 1953, **21**, 172.

atoms. Now the permissible combinations of these equivalent orbitals are fully determined by symmetry. They are, respectively,

$$A_1 \quad (\chi_{12} + \chi_{13} + \chi_{14} + \chi_{23} + \chi_{24} + \chi_{34})/\sqrt{6}$$

$$T_2 \begin{cases} (\chi_{12} + \chi_{34})/\sqrt{2} \\ (\chi_{13} - \chi_{24})/\sqrt{2} \\ (\chi_{14} - \chi_{23})/\sqrt{2} \end{cases}$$

$$E \begin{cases} (\chi_{12} - \chi_{23} + \chi_{34} - \chi_{41})/2 \\ (2\chi_{13} + 2\chi_{24} - \chi_{12} - \chi_{23} - \chi_{34} - \chi_{14})/\sqrt{12}. \end{cases}$$

The symbols A_1, E, and T_2 are those conventionally used to distinguish the different symmetry classes. The first molecular orbital, designated as A_1, is strongly bonding as it involves all the equivalent orbitals overlapping with the same sign. The next three orbitals, denoted as T_2, are also bonding ; for example $(\chi_{12} - \chi_{34})/\sqrt{2}$ binds atom 1 to atom 2, and atom 3 to atom 4. The next pair of orbitals, labelled E, presents an ambiguity. They have the same energy for reasons of symmetry, but if one expresses them in terms of the boron s and p orbitals one finds that, for example,

$$(\chi_{12} - \chi_{23} + \chi_{34} - \chi_{41})/2 = \{-(2px)_1 + (2py)_2 + (2px)_3 - (2py)_4\}/2$$

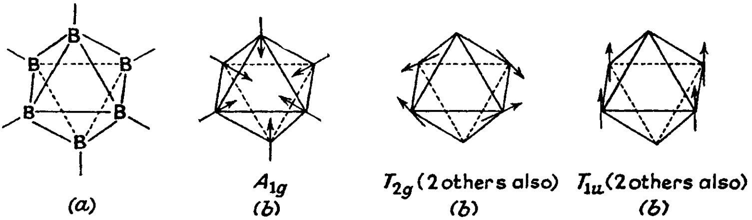
so that each of the E orbitals of the tetrahedron consists purely of $2p$ boron orbitals. Now it is not difficult to show that there are two combinations of the hitherto unconsidered $3p\pi$ orbitals of the chlorine atoms which also have the symmetry E. As a consequence there will be "back-co-ordination" from the chlorine atoms into the B_4 tetrahedron. This back-co-ordination will partly fill the E orbitals of the tetrahedron and render them no longer available for other electrons. We conclude that the eight electrons available for the boron tetrahedron will occupy the orbitals labelled A and T, but not those labelled E. In summary, the reason why only eight and not twelve valency electrons are used in B–B bonds is that two of the molecular orbitals which would otherwise be bonding within the tetrahedron are instead involved in accepting $3p\pi$ lone pairs from the chlorine atoms.

The Solid Borides.—An equally interesting problem, this time in solid structure, is presented by the hexaborides, of which a typical member is CaB_6. Crystallographic studies by Pauling and Weinbaum[35] established that the structure of the crystal is analogous to that of sodium chloride, the sodium ions being replaced by calcium atoms and the chloride ions by regular octahedra of boron atoms, each octahedron being linked to six neighbouring octahedra at a distance of 1·72 Å, which is also the interatomic distance within each octahedron. Longuet-Higgins and Roberts[36] interpreted this structure as follows. One may hybridise each boron atom in a digonal manner to give two hybrids, one pointing into the octahedron and the other outwards, leaving two $2p$ orbitals with axes perpendicular to the axes of the hybrids. The outward-pointing hybrids of neighbouring octahedra are then regarded as giving rise to two-centre electron-pair bonds between the octahedra, and this leaves fourteen valency electrons per

[35] Pauling and Weinbaum, *Z. Krist.*, 1924, **87**, 181.

[36] Longue -Higgins and Roberts, *Proc. Roy. Soc.*, 1954, *A*, **224**, 336.

CaB_6 unit. Now we consider the molecular orbitals available for binding together the atoms of an octahedron. Here again symmetry plays a simplifying rôle, and one finds that from the remaining three orbitals on each atom of the octahedron there arise eighteen molecular orbitals, of which seven are bonding and the remainder antibonding. The forms of these orbitals are roughly as shown in Fig. 7, where each arrow represents a directed atomic orbital, and they suffice to accommodate fourteen valency electrons. The final picture, therefore, is one in which all the valency electrons of the crystal are associated with the giant lattice of B_6 octahedra, the calcium atoms being required to contribute their valency electrons to this system. We thus obtain a closed-shell structure for the boron lattice, with calcium ions located in its interstices. It is interesting to note that the corresponding borides of lanthanum and cerium, which have three and four ionisable electrons respectively, are not insulators like CaB_6 but conduct electricity.[37]



(a) A_{1g} (b) T_{2g} (2 others also) (b) T_{1u} (2 others also) (b)

FIG. 7

(a) *A boron octahedron in* CaB_6.
(b) *The seven bonding molecular orbitals.*

An interesting corollary to these results is that the hypothetical hydride B_6H_6, whose existence has been discussed, would in all likelihood not have a closed-shell structure ; two more electrons would be required to fill the bonding orbitals.[25, 36]

Another interesting electron-deficient system which has been discussed in terms of the molecular-orbital theory is the icosahedron of boron atoms, in which every boron atom is linked to five other atoms within the icosahedron and to one atom outside. This structure occurs in boron carbide, B_4C,[38] and also probably in elementary boron.[39] Longuet-Higgins and Roberts [40] investigated these structures and were led to the conclusion, anticipated by Eberhardt, Crawford, and Lipscomb,[27] that an icosahedral hydride $B_{12}H_{12}$ would require two extra electrons to complete a closed shell. The reader is referred for details to their original paper.

Electron-deficient Carbon Compounds.—Electron deficiency is not confined to boron compounds. It occurs whenever the number of valency electrons in a molecule is less than $2(n - 1)$ where n is the number of atoms

---

[37] van Stackelberg and Neumann, *Z. phys. Chem.*, 1932, **19,** *B*, 314.

[38] Zhdanov and Sevastyanov, *Doklady Akad. Nauk, S.S.S.R.*, 1941, **32,** 432.

[39] Hoard, Geller, and Hughes, *J. Amer. Chem. Soc.*, 1951, **73,** 1892.

[40] Longuet-Higgins and Roberts, *Proc. Roy. Soc.*, 1955, *A*, **230,** 110.

in the molecule. Examples of electron-deficient substances not containing boron are the polymerised alkyls of metals of Groups I, II, and III ; for example Al_2Me_6 is electron-deficient,[41] and so is the polymeric $BeMe_2$. In these substances physical studies have established that pairs of neighbouring metal atoms are linked through bridges involving the methyl group.[42] It is not yet known whether the three-centre bonds which occur in these substances involve the fourth orbital of the methyl group or one or more of its hydrogen atoms ; [14] the former possibility seems more likely but experimental work is needed to settle the question. For example, a study of dimeric trimethylaluminium by nuclear magnetic resonance would be of great interest. If the central bridge involves hydrogen atoms in three-centre bonds one would expect three regions of proton resonance absorption, one due to the terminal methyl groups, one to the bridge hydrogen atoms, and one due to the remaining protons of the bridged methyl groups. The absence of three regions of absorption would indicate either that the bridge does not involve hydrogen atoms or that bridged and unbridged protons are too rapidly exchanged to give separate signals in the spectrum. Tetrameric tetramethylplatinum presents a similar problem, which has been only partially resolved by *X*-ray analysis.[43]

It is also possible to regard as electron-deficient certain unstable carbonium ions, some of which are intermediates in chemical reactions [44] and others of which have been identified in the mass spectrograph. Of the latter an intriguing example [45] is the species CH_5^+, which contains six atoms and only eight valency electrons. It is possible, of course, to represent this molecule as a resonance hybrid of five structures each containing an unbound proton, or to formulate it in terms of molecular-orbital theory, by assuming for example a bipyramidal configuration. At present, however, it is not possible to be sure of the molecular configuration, which in any case is probably very easily deformed ; hence the most satisfactory point of view is to regard the electrons as constituting a neon-like closed shell in which the five protons take up a configuration of minimum potential energy, presumably distorting the electron cloud to some extent.

Examples of electron-deficient intermediates are becoming more common. There is evidence [46] that the propyl cation is not a three-carbon chain, but a *cyclo*propane molecule with an additional proton attached to the ring. One manner in which such a system could be formed is illustrated in Fig. 8 ; if a mechanism of this sort is realised it provides a ready explanation for the great ease with which the hydrogen and carbon atoms in such carbonium ions are " shuffled "—an effect which has been known for many years. Another such system is the carbonium ion shown by Roberts, Mazur, and Chambers to be an intermediate in the solvolysis of *cyclo*butyl

[41] Pitzer and Gutowsky, *J. Amer. Chem. Soc.*, 1946, **68,** 2204.

[42] Snow and Rundle, *Acta Cryst.*, 1951, **4,** 348.

[43] Rundle and Sturdivant, *J. Amer. Chem. Soc.*, 1947, **69,** 1561.

[44] Dewar, *Bull. Soc. chim. France*, 1951, **18,** *C*, 79.

[45] Hamill, personal communication.

[46] Rylander and Meyerson, *J. Amer. Chem. Soc.*, 1956, **78,** 5799.

chloride or *cyclo*propylmethyl chloride[47, 48] (see Fig. 9). Winstein and his collaborators[49, 50] have postulated the occurrence of analogous intermediates in the reactions of certain norbornyl derivatives.

It is also usual to regard as electron-deficient certain inorganic complexes containing a metal atom linked to an unsaturated hydrocarbon radical or molecule. Of these, well-known examples are the ethylene complexes of bivalent platinum[44, 51] and the transition-metal *cyclo*pentadienyls, of which ferrocene was the first to be discovered.[52] In these compounds, however, the bonding is rather different in type from that occurring in diborane. For example, the linkage of an ethylene molecule to a platinous ion involves the *p* orbitals of both partners and the *d* orbitals of the metal.[44] The π electrons of the olefin form a dative bond to the metal which in turn donates a pair of *d* electrons into the antibonding π orbital of the carbon–carbon double bond. The resulting situation is alternatively described by saying that each carbon atom forms a covalent bond to the platinum atom, and if this point of view is adopted, the electron deficiency is formally removed.

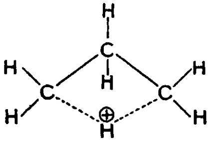


FIG. 8

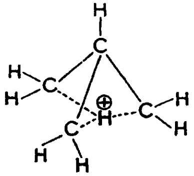


FIG. 9

The structure of ferrocene is also describable in terms of *d–p* bonding between the metal and the two hydrocarbon rings ; the details of this structure have been fully discussed in the literature ;[53, 54] again it is a matter of preference whether one classifies such molecules as electron-deficient or not.

Summary.—We can set down the following generalisations about the structures of electron-deficient molecules :

(1) The most restrictive and perhaps the most clear-cut definition of electron deficiency is that the number of valency electrons is less than $2(n - 1)$, where n is the number of atoms in the molecule. This definition covers the boron hydrides, the volatile metallic borohydrides, the non-ionic metal hydrides, the polymerised metal alkyls and certain unstable carbonium ions.

(2) In such molecules the idea of an electron-pair bond can be retained if we allow that some bonds may involve atomic orbitals from more than

---

[47] Roberts and Mazur, *J. Amer. Chem. Soc.*, 1951, **73,** 2509, 3542.

[48] Roberts and Chambers, *ibid.*, p. 5034.

[49] Winstein and Trifan, *ibid.*, 1949, **71,** 2953.

[50] Winstein, Walborsky, and Schreiber, *ibid.*, 1950, **72,** 5795.

[51] Chatt and Duncanson, *J.*, 1953, 2939.

[52] Kealy and Pauson, *Nature*, 1951, **168,** 1039.

[53] Moffitt, *J. Amer. Chem. Soc.*, 1954, **76,** 3386.

[54] Dunitz and Orgel, *J. Chem. Phys.*, 1955, **23,** 954.

two atoms in the molecule. Thus in diborane the central bridge comprises two three-centre bonds each of which involves both the boron atoms and one of the bridge hydrogen atoms.

(3) Although the polymerised alkyls presumably contain many-centre bonds it is not well established whether the bridged alkyl groups are bound by carbon orbitals or hydrogen orbitals, though the former hypothesis seems more likely on theoretical grounds.

(4) Certain complexes formed by metals with unsaturated hydrocarbons are superficially electron-deficient, but in many cases it is possible to assign to them conventional covalent-bond structures, it being understood that in such cases the bonding involves the *d* orbitals of the metal and the *p* orbitals of both partners.

(5) As regards their chemical properties electron-deficient molecules normally behave as Lewis acids—all of them react with water and other Lewis bases. This is because 2 two-centre electron-pair bonds represent a more stable situation than one unshared electron pair and one three-centre electron-pair bond.