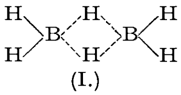
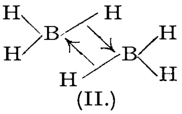
21. *Co-ordinate Links formed by Bonding Electrons: A Suggestion regarding the Structure of Diborane.*

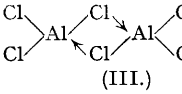
By A. D. Walsh.

It is pointed out that there is no reason to suppose that the formation of the "co-ordinate link" type of bond is confined to lone-pair electrons. Bonding electrons, under certain conditions, may also be donated to an acceptor atom. The conditions for this to happen are discussed and shown to be sufficiently stringent for the phenomenon to be rare. The possibility that the structure of diborane may be formulated in terms of donation of bonding electrons to vacant boron atomic orbitals is discussed in detail. The suggestion is made that rearrangements of certain hydrocarbon cations may also be understood in terms of co-ordinate links formed by bonding electrons.

The Structure of Diborane and the Boron Hydrides.—Several recent papers (Longuet-Higgins and Bell, *J.*, 1943, 250; Bell and Longuet-Higgins, *Proc. Roy. Soc.*, 1945, *A*, **183**, 357; Pitzer, *J. Amer. Chem. Soc.*, 1945, **67**, 1126) have made it reasonably certain that diborane, B_2H_6, has a structure not like that of ethane but rather of a bridge type similar to that found in the aluminium halides such as Al_2Cl_6. Two hydrogen atoms occupy special positions somewhat as in (I). The interpretation of this structure in terms of electronic theory is less clear. Longuet-Higgins and Bell (*loc. cit.*) attempted an interpretation in terms of resonance between structures containing only normal electron-pair bonds, but this was not completely satisfactory since it required additional postulates in order to explain why similar bridge structures were not found in certain other molecules. Burawoy (*Nature*, 1945, **155**, 328) supposed the central bonds to be similar to the "hydrogen bonds" found in, say, alcohols, but there are objections to this view, some of which have been expressed by Bell and Longuet-Higgins (*ibid.*, p. 328). There is little doubt that the structure is essentially dependent upon the existence of unfilled *L*-shell atomic orbitals of tervalent boron atoms. Pitzer (*loc. cit.*), realizing this, has described the bridge linkage as a "protonated double bond". A double bond is supposed to be formed from two BH_2^- units and in the anti-nodes of the second (π) bond two protons are embedded. The presence of the protons results in the B–B bond having a strength intermediate between those of double and single B–B bonds, though one would have thought that the magnitude of the B–B interaction found in the infra-red analysis (Bell and Longuet-Higgins, *loc. cit.*) was rather lower than this theory would indicate. Why protonated double bonds or their like are not more commonly found is not altogether clear.


(I.)


(II.)


(III.)

Although not necessarily disagreeing with much of the descriptions of the diborane molecule given by Longuet-Higgins and Bell and by Pitzer, the author thinks that another formulation is possible in language that is perhaps rather more familar and which may be helpful in explaining the rarity of occurrence of the bridge type of binding.

The idea of the "co-ordinate link" type of bond has long been familiar in valency theory.* If an atom, A, has an incomplete rare-gas structure and if another atom, B, has a lone pair of electrons, then B may "donate" its pair of electrons to form a bond between A and B. In terms of molecular orbitals, if B has a pair of electrons of wave function ψ_B and if A has an unfilled atomic orbital of wave function ψ_A, then on bringing A to B the initially ψ_B electrons of B will come to occupy a molecular orbital of form $a\psi_A + b\psi_B$; and if a and b are comparable in magnitude,† we say a co-ordinate link has been formed. It has always been assumed hitherto that the electrons "donated" to form a co-ordinate link must come initially from a lone pair. There is nothing in molecular orbital theory to indicate this, however. There is no sharp division between non-bonding and bonding filled orbitals : the paired electrons in each are qualitatively similar. The simple idea that we wish to suggest is the generalisation of the well-accepted concept of a co-ordinate link to include possible "donation" of bonding electrons as well as of lone-pair electrons.

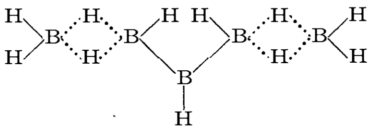
In general, donation of bonding electrons will not be very noticeable because they are too strongly bound. It is usually true that lone-pair electrons are much less strongly bound than bonding electrons. It is not therefore surprising that, hitherto, "co-ordinate links" have only been found when formed from lone pair electrons. The conditions for a co-ordinate link to be formed include (1) the existence of an incomplete rare-gas electron shell in the acceptor atom and (2) a low ionisation potential for the donating electrons. These mean that the formation of co-ordinate links from bonding electrons will be rare.

B–H Bonds are known to be weak. For example, their stretching force constant in triborine triammine is only $3{\cdot}4 \times 10^5$ dynes/cm. as compared with $5{\cdot}0 \times 10^5$ dynes/cm. for the C–H bonds of methane and $6{\cdot}4 \times 10^5$ dynes/cm. for the N–H bonds of ammonia. Broadly speaking, there is a connection between force-constant values, bond strengths, and the ionisation potentials of bonding orbitals (Walsh, in course of publication). We think it safe to predict that the normal B–H bonding electrons have ionisation potentials at least as low as 10—12 v., *i.e.*, well within the range found for the ionisation energies of lone-pair electrons (cf. 10·8 v. for the lone-pair electrons of ammonia).

It is therefore possible to suppose that each B---H---B bond in the structure (I) consists of a filled molecular orbital of type $a\psi(\mathrm{BH}) + b\psi(\mathrm{B} : 2p_z)$ binding the three nuclei B, B, and H (cf. the way in which π electrons in conjugated structures bind several nuclei) ; and that (I) may be rewritten as (II), where the arrows denote co-ordinate links from the B–H *bonds* to the adjacent B atoms. This structure closely resembles that usually written for $\mathrm{Al_2Cl_6}$ (III). It has considerable resemblance to that proposed by Pitzer (*loc. cit.*), except in three respects. (1) Whereas he postulates the presence of filled σ and π orbitals between the boron atoms, somewhat as in (IV), the present suggestion is that two orbitals are occupied giving an electron-cloud picture somewhat as (V). (2) Pitzer's model predicts a "trigonal" arrangement of boron bonds as in ethylene, *i.e.*, it supposes outer HBH angles close to 120°. According to the present description, the disposition of the bonds is essentially tetrahedral and the outer HBH angles should be close to 109°. The angle in the bridge structure for $\mathrm{Al_2Me_6}$, as determined by electron

(IV.)

(V.)



(VI.)

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* It should be remembered, however, that, in certain cases, bonds previously represented by co-ordinate links are now known to be better represented by double bonds [*e.g.*, the higher oxides of elements in Groups V, VI, and VII (Phillips, Hunter, and Sutton, *J.* **1945**, 146) and certain metallic carbonyls (Long and Walsh, *Trans. Faraday Soc.*, in the press)].

† An example where a and b are not equal in magnitude occurs in carbon monoxide (Long and Walsh, *loc. cit.*). In this case the bonding power of the occupied orbital that has in the past been described as a co-ordinate link is very small, so that the formula C=O is a better approximation than $\overset{-}{\mathrm{C}}\equiv\overset{+}{\mathrm{O}}$, and the third occupied orbital in the bond might be better described as an "incipient co-ordinate link".

diffraction, is 110°. Pitzer's model implies a planar arrangement of all the nuclei except the two protons. A model according to the present suggestion shows that the planes of the two $\mathrm{BH_2}$ units would be nearly but probably not quite identical. A slight lack of coplanarity of the two $\mathrm{BH_2}$ units might possibly account for the imperfect fit of Pitzer's bridge model with the electron-diffraction data. Since in the wave function $a\psi(\mathrm{BH}) + b\psi(\mathrm{B} : 2p_z)$, the first term can itself be split into $c\psi(\mathrm{H}) + b\psi(\mathrm{B} : 2p_z)$, the two hydrogen atoms in the present (as in Pitzer's) model will be symmetrically placed with respect to the boron nuclei—as demanded by the infra-red spectrum. (3) The present model requires a close approach of the boron atoms without there being a strong boron–boron bond : of the two models, Pitzer's would seem to imply the stronger boron–boron bond.

It is probable that the polarity of the B–H bonds ($\mathrm{B^+H^-}$) would assist the formation of structure (II), since (*a*) the partial positive charge on the boron atoms will enhance their acceptor properties, and (*b*) the polarity will mean that the point of maximum electronic density will lie well away from the boron atom initially concerned and so all the nearer to the other boron atom. The existence of such a third condition for a structure of type (II) to be stable would further explain the rarity of its occurrence. Trimethylborine may have insufficient $\mathrm{B^+C^-}$ polarity in its B–C bonds to form a stable dimer. Trimethylaluminium should have polarity in its Al–C bonds much as in the BH bonds of borine and it is not surprising that it may dimerise like borine. Boron trifluoride probably has too high an ionisation potential for its bonding electrons to form a type (II) structure. The explanation of why (VI) does not use the central B–H bond to form a further linkage may lie in the lack of sufficient positive charge on that boron atom.

As far as can be seen, the explanations possible on Pitzer's theory (Pitzer, *loc. cit.*; Longuet-Higgins, *J.*, **1946**, 139) would also be possible on the present theory. Though a definite decision between the two theories must await further experimental evidence, we think the underlying idea of the present communication—that bonding electrons under certain conditions may form co-ordinate links—should be kept in mind. In particular, we think that the idea may prove helpful in understanding the electronic mechanism of certain molecular rearrangements of hydrocarbon cations and radicals.

The Mechanism of Certain Molecular Rearrangements.—We have in mind, particularly, those rearrangements, such as that of Wagner–Meerwein, which occur in cations of the type $\mathrm{CH_3{\cdot}\overset{+}{C}H_2}$ (*i.e.*, containing an atom of even stronger acceptor properties than the boron atom of a $\mathrm{BH_3}$ group). We have to suppose that sufficient deviation from the tetrahedral bond angles occurs for the electrons in the weakest bond on the saturated carbon atom (since these will be the least strongly bound bonding electrons) to become partly donated to the other carbon atom. Rearrangement in the *radical*, as well as in the ion (Dostrovsky, Hughes, and Ingold, *J.*, **1946**, 192—193), is not surprising because in both cases we should expect the actual electronic system (when a particular nuclear configuration is attained) to be described by a wave function of form $a\psi_A + b\psi_B$: with the radical this would be interpreted as a three-electron bond, with the ion as a co-ordinate link. The ratio $a : b$ will be determined by the bond energies in the initial and final states respectively of the rearrangement : if b is greater than a then, on approach of an appropriate anion, the full rearrangement will be likely to occur. In the change $\mathrm{CMe_3{\cdot}\overset{+}{C}H_2 \longrightarrow \overset{+}{C}Me_2{\cdot}CH_2Me}$, since a secondary C–C bond is stronger than a tertiary, b will be greater than a and the rearrangement will occur. The change $\mathrm{CMe_3{\cdot}\overset{+}{C}HPh \longrightarrow \overset{+}{C}Me_2{\cdot}CHPhMe}$, however, will not occur since a bond next but one to a phenyl group is weaker than usual (Walsh, *Trans. Faraday Soc.*, in the press) and a will be greater than b.

Though the language differs, this account includes much the same thought content as that in terms of " mesomerism " (see Watson, " Modern Theories of Organic Chemistry ", Oxford, 1941, p. 208). However, there are one or two advantages of the present formulation : (1) It shows that the bond on C_α which donates electrons to C_β (*i.e.*, the bond which may break on C_α and reform on C_β) will be, for example, a C–C rather than a C–H bond—since C–C bonds have ionisation energies less than 12 v., whereas C–H bonds have ionisation energies $\sim$ 2 v. greater. In other words, a methyl group may migrate, but not a hydrogen atom. (2) It indicates a possible connection between a detail of the Wagner rearrangement and the structure of the boron hydrides.

I am indebted to J. N. Agar for stimulating discussion and to C. A. Coulson, R. P. Bell, and H. C. Longuet-Higgins for kindly criticism.

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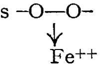
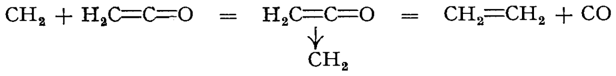
Note, added July 15*th*, 1946.—Since this paper was submitted for publication, Dewar (*J.*, 1946, 406) has published an account of benzidine-type rearrangements based on the idea that π electrons may be capable of forming dative bonds. However, there seems no reason to limit the idea to π electrons: it is not the symmetry properties of the orbital that determine the power of donation so much as its spatial spread, and this is determined primarily by the ionisation potential. Where a σ orbital has an ionisation potential less that that of a π orbital, it may act as a donor. We have discussed above the importance to the understanding of the structures of the boron hydrides of the expectation that B–H bonding electrons have a large spatial spread. The peroxide bond is also weak and its σ bonding orbital is therefore expected to have an extensive spatial distribution. This expectation is likely to prove of importance in the understanding of peroxide chemistry. For example, the well-known fact that ferrous ions can cause a splitting of the O–O bond may be due to the formation of an intermediate peroxide–ferrous ion complex, which can plausibly be formulated as



$$-\underset{\substack{\downarrow\\ Fe^{++}}}{O}-O-$$

Other examples of the utility of the idea of co-ordinate links from bonding electrons may be selected as follows.

(1) The methylene molecule has proved unexpectedly difficult to observe. This may be explained as due to the facts that (*a*) its carbon atom has strong acceptor properties, and (*b*) it is usually produced in the presence of molecules such as keten or diazomethane containing bonds involving orbitals expected to have low ionisation potentials. The C=C bond of keten is known to be weaker, and therefore probably has a lower first ionisation potential, than that of ethylene (Walsh, in the press): it also has a lower ionisation potential than the C=O group and we expect the reaction

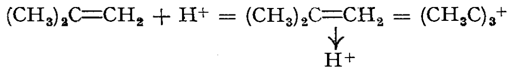


$$CH_2 + H_2C{=}C{=}O \;=\; H_2\underset{\substack{\downarrow\\ CH_2}}{C}{=}C{=}O \;=\; CH_2{=}CH_2 + CO$$

the second stage occurring because it reduces the energy of the system. Norrish, Crone, and Saltmarsh (*J.*, **1933**, 1533) have indeed found this overall reaction to occur. In the complex, two electrons are binding three nuclei: these electrons occupy an orbital of form $a\psi_A + b\psi_B$, where ψ_A represents the π C–C orbital of keten and ψ_B the *L*-shell carbon atomic orbital that is vacant in the methylene molecule.

(2) Many reactions involving carbonium or hydrogen ions are likely to be capable of formulation in terms of these co-ordinate links, because of the strong acceptor properties of these ions. Good examples are to be found in Whitmore's scheme for the hydrogen ion-catalysed polymerisation of olefins (*Ind. Eng. Chem.*, 1934, **26**, 94):

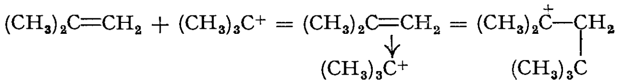
Initiation.—We expect a reaction between, say, *iso*butylene and a proton as follows:



$$(CH_3)_2C{=}CH_2 + H^+ = (CH_3)_2\underset{\substack{\downarrow\\ H^+}}{C{=}}CH_2 = (CH_3C)_3{}^+ \quad . \; . \; . \; . \; . \; . \quad (1)$$

The overall reaction is that postulated by Whitmore. Minimisation of the energy of the systems results in the second step, $(CH_3)_3C^+$ and not $(CH_3)_2CH{\cdot}\overset{+}{C}H_2$ being formed because (*a*) the C=C polarity is such that the intermediate complex is already well towards $(CH_3)_3C^+$, and (*b*) a primary C–H bond is stronger than a secondary.

Propagation.—We expect reaction between *iso*butylene and the ion $(CH_3)_3C^+$ as follows:

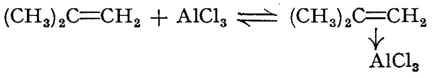


$$(CH_3)_2C{=}CH_2 + (CH_3)_3C^+ = (CH_3)_2\underset{\substack{\downarrow\\ (CH_3)_3C^+}}{C{=}}CH_2 = (CH_3)_2\overset{+}{C}-\underset{\substack{|\\ (CH_3)_3C}}{C}H_2$$

the second step occurring for similar reasons to those given for (1), and the overall reaction being that postulated by Whitmore.

One sees the importance for ease of these reactions of a low ionisation potential for the olefin employed: *iso*butylene has a markedly lower π^{-1} ionisation potential (8·9 v.) than has ethylene itself (10·45 v.).

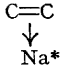
When Friedel–Crafts catalysts are employed in polymerisation or alkylation, the propagation step may be similar, but complications may occur of the form



$$(CH_3)_2C{=}CH_2 + AlCl_3 \rightleftharpoons (CH_3)_2\underset{\substack{\downarrow\\ AlCl_3}}{C{=}}CH_2$$

(I am grateful to Mr. K. E. Russell for discussion on these polymerisation reactions.)

(3) Norrish and Smith (*Proc. Roy. Soc.*, 1940, *A*, **176**, 295) found unsaturated hydrocarbons to be very much more powerful quenchers than paraffins of the resonance radiation of sodium. They note that unsaturated molecules possess "large external fields" relative to the paraffins, and we may add to this that their results indicate that the effective quenching cross-section increases with decreasing π^{-1} ionisation potential for a series of olefins. The quenching action may therefore be conveniently described as due to the formation of a complex which may be formulated as



$$\underset{\substack{\downarrow\\ Na^*}}{C{=}C}$$

where the excited sodium atom is held by two electrons occupying an orbital $a\psi_A + b\psi_B$, where ψ_A is the original π orbital of the olefin and ψ_B is the original 3*s* orbital of the sodium atom. This complex only exists while the outer sodium electron is excited to leave vacant the 3*s* atomic orbital. As soon as it reverts to the ground state (*i.e.*, energy transfer occurs), dissociation of the complex must occur.