THE STRUCTURE OF DIBORANE AND RELATED MOLECULES[1]

ROBERT S. MULLIKEN

Ryerson Physical Laboratory, The University of Chicago, Chicago, Illinois

Received July 10, 1947

The history of the two geometrical models hitherto proposed for diborane (ethane-like or D_3 model, and bridge model) is briefly reviewed. It is pointed out that once the geometrical model is known, the electronic structure follows from quantum mechanics. The writer's previous MO (molecular orbital) discussion of the electronic structure of diborane in its normal and lower excited electronic states for the D_3 model is reviewed, and a parallel discussion is now given for the bridge model. In contrast to the D_3 model, the bridge model gives diborane in its normal electronic state a very neat closed-shell electronic structure in terms of MO's. Such a closed-shell structure is much easier to correlate with the spectroscopic and other facts than the open-shell structure required by D_3. AO (atomic orbital) discussions of the electronic structure of diborane, though equally as valid as MO discussions, are more complicated because they require the use of several resonating valence-bond structures in proportions which it is difficult to estimate. This is true for both geometrical models.

[*Added in proof:* A computation of the overlap integral between two $2p\pi$ boron atom AO's shows that this is remarkably large, making it probable that boron can form strong double bonds even at single-bond distances. This gives added support to the bridge model for diborane and to Pitzer's proposed structures for the higher boron hydrides, and helps explain the stability of the boron trihalides and similar compounds.]

Methylated diboranes and other compounds related to diborane are discussed, and it is pointed out that all (including the aluminum halides, Al_2X_6) should be at least qualitatively similar to diborane in MO structure if the bridge geometrical structure is assumed. In terms of the LCAO MO approximation, it is clear that other atoms or radicals should in principle be capable of replacing the bridge hydrogens in diborane and related compounds. For example, a halogen atom $p\sigma$ orbital or a tetrahedral methyl group orbital should have qualitatively the same bridge-bonding capability as a 1*s* hydrogen orbital. The fact that $B(CH_3)_3$ is observed, and not $B_2(CH_3)_6$, does not disprove this, since it can be shown that boron trimethyl is strongly stabilized by trigonal hyperconjugation. A similar statement applies to the boron halides, where also the monomer, very strongly stabilized by trigonal conjugation, is observed. On the other hand, the observed existence of the dimeric forms in Al_2X_6, $Al_2(CH_3)_6$, and the like, may be attributed to lessened stability of the monomers in these cases, together with, in Al_2X_6, marked ionic stabilization of the bridge structure. Lower stability of the monomers is here expected because double-bond formation, hence all types of conjugation, are, as is well known, much weaker in other rows than in the first row of the periodic system. [*Added in proof:* An examination of band structures in new infrared spectrograms by W. C. Price in this Laboratory shows unambiguously that the bridge model of diborane is the correct one.]

[1] The material in this paper was mentioned in general terms in the abstract of the paper prepared for presentation at the Symposium on Color and the Electronic Structure of Complex Molecules, which was held under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society at Northwestern University, Evanston and Chicago, Illinois, December 30 and 31, 1946, but it was not discussed in the talk given at the Symposium.

I. GEOMETRICAL MODELS AND ELECTRONIC STRUCTURES

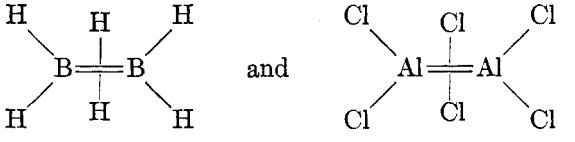
The boron hydrides, with their well-known electron deficiencies, furnish examples of the relative simplicity of MO as against AO descriptions when the AO method requires the use of resonating structures. Let us consider diborane as the simplest representative of these molecules.

There are two distinct questions: (*1*) What is the *geometrical structure?* (*2*) What is the *electronic structure?* In the literature, various answers have been given to both questions, but usually without making a clear distinction between them.

For the geometrical structure, two main alternatives have been proposed. One is the ethane-like model, which seems to have been generally taken for granted until the 1920's. The other is the bridge model, apparently first proposed by Dilthey in 1921. This was but little regarded until it was recently advocated (1940–45) by investigators in Russia, Germany, and England, and by Pitzer (1945) in this country (4, 5, 9, 12, 15). For brevity, the ethane-like geometrical model will in the following be called the D_3 model, after the point-group symbol describing the symmetry. In ethane, the symmetry may be D_{3d} (staggered form) or perhaps D_{3h} (eclipsed form); for our purposes these two variants are not greatly different, and can both be covered by the designation "D_3 model." The bridge model has V_h symmetry, like ethylene (*cf.* figure 1).

With neither model is a simple AO description of the electronic structure possible. A variety of sets of resonating structures have been proposed by various investigators. It seems clear that an adequate description would require a considerable number of minor resonating structures in addition to two or three major ones. Of special interest is Wiberg's proposal (1928, 1936) of an ethylene-like electronic structure with two of the protons embedded therein; Wiberg was not specific about the geometrical model. Wiberg also proposed a butadiene-like structure for B_4H_{10}.

Eistert (7) explicitly combined the bridge model with Wiberg's embedded-proton electronic structure, and used a similar description for the aluminum halides Al_2X_6, where the V_h model has been accepted for some time. Eistert proposed symbols such as:



Pitzer likewise coupled the V_h bridge model with an ethylene-like electronic structure. He also extended the idea to various higher boron hydrides, by combining it with the additional idea that the ethylenic electronic structures conjugate with normal —B< structures. Pitzer in a later paper (13) rejected the ethylene-like electronic structure for $Al_2(CH_3)_6$ and related compounds.

II. MO METHOD FOR THE D_3 MODEL

In the MO method, once the *geometrical configuration* of a molecule is specified, a definite *electron configuration* can usually be written down at once on the basis of qualitative or semiquantitative considerations derived from existing general knowledge of molecular electronic structures. Let us examine these MO descriptions, first for the D_3 model, then for the V_h bridge model.

The present writer in 1932–35, assuming the correctness of the D_3 model which was then rather generally accepted, discussed the MO electron configuration of diborane and certain of its corollaries for the properties of the molecule (10). Since $B_2H_6^{--}$ is isoelectronic with ethane, the electron configuration for the D_3 model of diborane must be the same as that of ethane, minus two electrons. This approach leads unambiguously to the electron configuration[2]

$$1s)^2 1s)^2 \sigma_g)^2 \sigma_g)^2 \sigma_u)^2 \pi_u)^4 \pi_g)^2 \qquad (1)$$

with three states ${}^3A_{2g}$, ${}^1E_g$, ${}^1A_{1g}$, resulting from the half-filled π_g shell. On the other hand, in ethane the π_g shell is filled, giving a characteristically colorless, diamagnetic, saturated compound.

The predicted ${}^3A_{2g}$ normal state, which should make the substance paramagnetic, and the two low-lying excited singlet states, are closely analogous to the known normal and low excited states of oxygen, where also the last two electrons are in a half-filled π_g shell. However, π_g and π_u must be much closer together in energy in diborane than in oxygen, because in diborane the π orbitals are mainly B—H bonding.[2] As a result, the electron configurations $\ldots \pi_u)^3 \pi_g)^3$ and $\ldots \pi_u)^2 \pi_g)^4$ should give rise in diborane to a number of additional low-lying excited electronic states not found in oxygen.

Thus it is a definite and unescapable prediction that diborane, if the D_3 model is correct, must have a considerable number of singlet and triplet levels at low energies, i.e., between 0 and 2 or at most 4 or 5 ev., with the normal level probably a triplet and the substance therefore paramagnetic. Moreover, at least one strong and several weak electronic transitions among these levels, giving rise to electronic absorption bands in the infrared and/or visible or perhaps near ultraviolet, are predicted with certainty. By somewhat forced but not absurd assumptions (10), the normal state possibly could be diamagnetic.

Actually, diborane is diamagnetic, as was shown after the writer, assuming the D_3 model, had predicted it to be probably paramagnetic (10). Further, it

[2] The notation used here is that appropriate to a molecule with complete axial symmetry, like O_2 or CO_2. While this is not strictly accurate for C_2H_6 or B_2H_6, with its only threefold axial symmetry, it is essentially so for present purposes. The MO's are written in what the writer *now* believes to be substantially the correct order of diminishing ionization potential. The *main* bonding characteristics of the orbitals are: 1s, non-bonding K electrons of boron; first σ_g, B—B bonding; second σ_g, and σ_u, B—H bonding (distributed over all six B—H bonds); π_u and π_g electrons, B—H bonding (distributed over all six B—H bonds). It is also of importance here that π_u is slightly B—B bonding and π_g slightly B—B antibonding; this causes π_u to be somewhat more tightly bound than π_g. See reference 10 for further details.

has no electronic absorption between λ 12,000 and λ 2200, so that if the D_3 model is correct, the predicted low excited electronic levels must be very low indeed, and the corresponding electronic absorption must be in the infrared. Stitt's (14) investigation of the infrared spectrum indicated greater complexity than one would expect from the vibration spectrum alone for the D_3 model. The later work of Austrian and English investigators (4, 5, 9), however, shows fairly good agreement of the infrared and especially the Raman spectrum with what might be expected for the bridge model; nevertheless there are some discrepancies, including some unexplained infrared bands, though none of exceptional intensity.

Summarizing, it is seen that the MO method, using little more than qualitative reasoning, predicts with certainty the existence of a number of low elec-

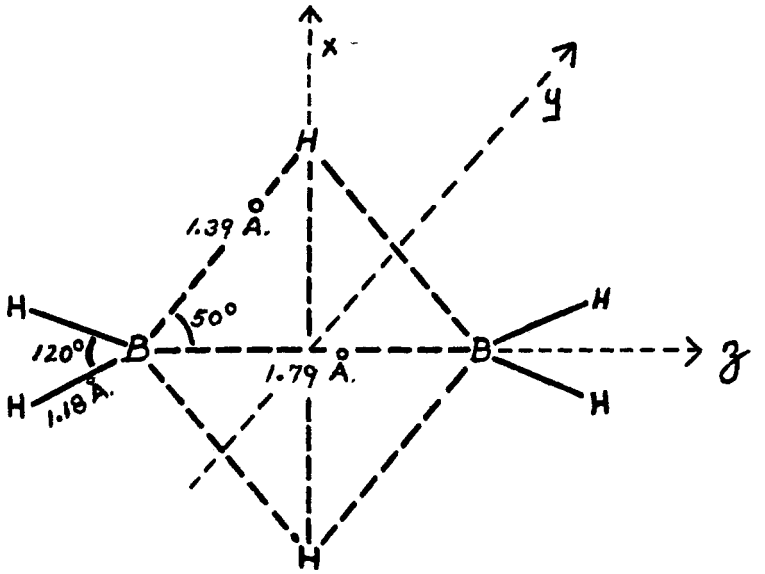


FIG. 1

tronic levels for diborane if the D_3 model is correct. The facts, however, lend no substantial support to these predictions and thus tend to controvert the D_3 model, although its disproof appears at present to be by no means conclusive.

III. MO METHOD FOR THE V_h BRIDGE MODEL

In view of the weight of evidence which seems to favor the bridge model (4, 5, 9, 12, 15), let us see what MO electron configuration this model requires. Although Pitzer has already indicated the general nature of the results, it appears worth while to go into more detail. (Pitzer says, "The molecular orbital picture of [the protonated double] bond is easily derived by breaking two protons off the carbon nuclei in ethylene and moving them to the indicated positions. It is readily seen that the same molecular orbitals are still appropriate,

though now concentrated more around the protons. The general properties of this structural unit are just those expected of a double bond with two protons imbedded in it.")

According to Bauer's reinterpretation (1), in terms of the bridge model, of his electron-diffraction data, the structure of diborane is about as shown in figure 1. The symmetry of this model (V_h, or D_{2h}) is the same as that for ethylene. (To obtain ethylene, remove the two bridge hydrogens, replace B by C, and tighten up all the bonds.)

The MO electron configuration and electronic state may be written in a manner formally identical with that for ethylene, as follows:

$1s)^2$	$1s)^2$	$a_g)^2$	$a_g)^2$	$b_{1u})^2$	$b_{2u})^2$	$b_{3g})^2$	$b_{3u})^2$,	^1A_g	
C	C	CC	H_2C,CH_2	H_2C,CH_2	H_2CCH_2	$H_2C\times CH_2$	CC,	(ethylene)	(2)
		H					H		
B	B	B B	H_2B,BH_2	H_2B,BH_2	H_2BBH_2	$H_2B\times BH_2$	B B,	(diborane)	
		H					H		

The symbols (except 1s for the two pairs of K electrons) are the usual MO symbols for symmetry V_h. Under each symbol is given a brief indication of the atoms which mainly are bonded by the MO in question. For ethylene, CC means mainly C—C bonding; H_2C,CH_2 means mainly C—H bonding, for all C—H bonds at once; H_2CCH_2 means H—C and C—C bonding in all bonds; $H_2C\times CH_2$ means C—C antibonding, but H—C bonding for all C—H bonds. For diborane everything is very similar, except that the two double-bond MO's a_g and b_{3u} now embrace the two bridge hydrogen atoms as well as the boron atoms.

In more detail, the forms of the MO's are qualitatively as follows. (Normalization factors are omitted, as are also certain coefficients which are not exactly equal; for example, $ss + \sigma_2$ means a linear combination, with more or less *unequal* coefficients, of the symmetry orbitals ss and σ_2.)

$$\begin{aligned}
\text{First } a_g &= \alpha(\sigma_1 + \sigma_1') + \beta(S'' + S''') \ * \\
\text{Second } a_g &= (ss + \sigma_2) + (\sigma_2 + ss)' \\
b_{1u} &= (ss + \sigma_2) - (\sigma_2 + ss)' \\
b_{2u} &= (s\bar{s} + \eta) + (\eta + s\bar{s})' \\
b_{3g} &= (s\bar{s} + \eta) - (\eta + s\bar{s})' \\
b_{3u} &= \gamma(\xi + \xi') + \delta(S'' - S''') \ *
\end{aligned} \tag{3}$$

In equations 3, the single-primed symbols refer to the atoms of the right hand BH_2 group in figure 1; the unprimed symbols to the left-hand BH_2 group. The symbol σ_1 refers to an inwardly directed digonal boron hybrid AO, i.e., $2^{-\frac{1}{2}}(2s + 2p_z)$. The symbol σ_2 refers to an outwardly directed digonal AO, i.e., $2^{-\frac{1}{2}}(2s - 2p_z)$; σ_2 strongly overlaps and so gives strong bonding with the composite hydrogen orbital ss, which is formed by adding 1s orbitals of the two hydrogen atoms of the BH_2 group (i.e., ss means $1s + 1s$, with equal coefficients for the two 1s AO's). The composite hydrogen orbital $s\bar{s}$ (abbreviation for a subtractive combination of 1s orbitals of the two hydrogen atoms of the BH_2

group) is of such a form as to give strong overlapping and bonding with the boron orbital η (abbreviation for $2p_y$; for the y-axis, see figure 1). Finally, ξ means $2p_x$, the characteristic unsaturation AO which forms the second bond of the double bond; for the x-axis, see figure 1. (The foregoing all applies also to ethylene, if one substitutes "carbon" for "boron".) In the orbitals marked *, the symbols S'' and S''' refer respectively to 1s orbitals of the bridge hydrogen atoms in diborane; these disappear (and α, γ become 1 in a_g and b_{3u}) for ethylene.

The following two lowest *excited* MO's will also be useful (the second b_{3u} exists only in diborane, not in ethylene):

$$\begin{aligned} \text{Second } b_{3u} &= \delta(\xi + \xi') - \gamma(S'' - S''') * \\ b_{2g} &= \xi - \xi' \end{aligned} \tag{4}$$

It is notable that both these excited MO's should be fairly high in energy above the orbitals which are occupied in the normal state, *provided* the B—H binding

H

and the B═B binding in the B B bridge are both at least moderately strong.

H

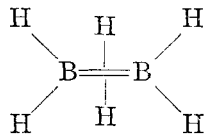
Under these circumstances, no infrared or visible electronic transitions would be expected. The second b_{3u} is B—B bonding but is antibonding with respect to the bridge hydrogens, while the b_{2g} is simply B—B antibonding.

Although there is a little uncertainty as to whether the MO's in the electron configuration given by expression 2 are all in exactly the correct energetic order, there is no question that this configuration, and its relation to that of ethylene, are correct if the V_h bridge model is correct. It is a very striking fact that the bridge model requires a diamagnetic, closed-shell electronic structure, with probably no low-lying excited levels and so no necessity of electronic absorption bands in the infrared or visible.

The electron configuration required by the bridge model provides eight electrons corresponding to the four normal B—H bonds. It also provides four electrons, in two orbitals, which do double duty in forming a B═B double bond and at the same time binding the two bridge hydrogens. From the forms of the two bridge MO's, it appears that the bridge hydrogens may be described as *bound to the double bond* rather than to the borons, though it would not be amiss to say that the two borons and the bridge hydrogens are all bonded together. The neatness of the arrangement is very striking if one sketches in to scale, on figure 1, the first a_g and the b_{3u} orbitals with forms as indicated by equations 3.

The foregoing results come out clearly and definitely using MO's, whereas in the AO method one must use a variety of resonating structures which give no very clear concept of the reasons why an unusual type of strong bond can be formed. The MO structure justifies to a considerable extent Pitzer's term "protonated double bond," but suggests that some such term as "four-atom bridge bond" would be preferable. This latter is especially true when one examines such geometrically similar bridged molecules as Al_2Cl_6 and probably $Al_2(CH_3)_6$ by the MO method. An appropriate symbol for the four-atom bridge bond would appear to be the following, similar to symbols used by Eis-

tert[3] in 1942 and by Wiberg in 1944, after he had accepted the bridge model: namely, $\doteqdot$, as for example in



(In this symbol it has of course to be understood that the plane of the normal B—H bonds should be perpendicular to the paper.)

IV. ULTRAVIOLET SPECTRUM OF DIBORANE

According to Blum and Herzberg (6), diborane gas shows weak continuous absorption beginning near λ 2200 and reaching a peak at about λ 1820. At the peak, if $I = I_0e^{-kcl}$, with c in mols per liter and l in centimeters, k is about 25. The absorption falls to a minimum at λ 1700 and then rises gradually to beyond λ 1550 ($k \geq 50$ at λ 1550). The absorption is accompanied by rapid photochemical changes.

The λ 1820 peak is so weak that it may reasonably be attributed to a forbidden electronic transition. If the bridge model is correct, the most plausible identification is with the transition of an electron from the normal bridge MO b_{3u} (*cf.* equations 2 and 3) to the second, bridge-antibonding b_{3u} (*cf.* equation 4). Another possibility is a transition from the b_{3g} to the second b_{3u} MO. Both are forbidden transitions. They have no analogues in the ethylene spectrum, in partial disagreement with Pitzer's statement (12, p. 27, item 6) that the electronic energy levels and spectra are very similar to those of ordinary double bonds.

The transition from the first b_{3u} to the excited b_{2g} of equation 4 is one which definitely should be intense, being analogous to the very intense $N \rightarrow V$ ($b_{3u} \rightarrow b_{2g}$) transition in ethylene, with peak intensity at λ1630. Evidently the peak of this transition must lie below λ 1500.

If the bridge model is correct, the surprisingly large interval between the normal electronic level of diborane and the first observed singlet excited levels can only be explained if the two b_{3u} MO's—normal and excited—differ greatly in energy. (The peak at λ 1820 corresponds to 6.8 ev.) This requires that the first b_{3u} contribute very strongly to binding the bridge hydrogens.

V. WORK IN PROGRESS[4]

Work is in progress at this laboratory on the investigation of the infrared, ultraviolet, and vacuum-ultraviolet spectra of diborane. The infrared spectrum between 1 μ and 15 μ has been remapped by W. C. Price. This will permit a review of the conclusions which have been drawn from Stitt's infrared data.

[3] See references 5, 7, 9, and 15 for discussion and references. Pitzer and Gutowsky (13) disagree with the bridge structure for dialuminum hexamethyl. *Added in proof:* However, R. E. Rundle (J. Am. Chem. Soc. **69**, 1327 (1947)) gives strong arguments against the structures proposed in reference 13.

[4] As of June, 1947. This work is being assisted by Office of Naval Research Contract N6ori-20, T.O.IX.

Comparison with the spectra of isotopic diboranes, in particular B_2D_6, which is in course of preparation in Professor H. I. Schlesinger's laboratory, offers good prospects for a final decision between the D_3 and V_h models, or the possible arrival at some other model.[5]

VI. BOND DISTANCES

The electrons in the first b_{3u} MO correspond to the π bond of the B=B double bond as well as being bridge-hydrogen bonding. The first a_g MO, whose electrons correspond to the σ bond of the B=B double bond, is also presumably strongly bridge-hydrogen bonding as well as B—B bonding. It might, however, be questioned whether these conclusions are in harmony with the approximately 1.79 A. B—B distance (see figure 1). This distance is approximately equal to the B—B distance corresponding to Pauling's single-bond radius (0.88 A.) for the boron atom. Thus one might question whether the observed distance is small enough for an effective B=B double bond.

In possible answer, the following points appear relevant: (*1*) The electron-diffraction value for the B—B distance is not very accurately known. (*2*) The form of the bridge MO's is such that strong bridge bonding B—H—B may be present even if the B—B distance is somewhat large and the direct B—B bonding rather weak. (*3*) In boron and carbon, the effective mean nuclear charge of the field in which $2p$ electrons move should be somewhat smaller than that for $2s$ electrons. In boron, this difference should be more pronounced than for carbon. Hence, since the ξ AO's (*cf.* equations 3, 4) are pure $2p$ with no $2s$ admixture, and since the size of an AO is inversely proportional to the effective nuclear charge of the field in which the electron moves, the second bond of a double bond formed by a boron atom may become fairly strong at a surprisingly large distance.

[*Added in proof:* A subsequent calculation of the overlap integral S between two $2p\pi$ Slater AO's for nuclear charge $Z_{ef} = 2.6\ e$ (Slater's effective value for boron), on centers 1.79 A. apart, gives $S = 0.23$. Assuming B^- AO's, with $Z_{ef} = 2.25$ (a case which is of interest since the boron atoms in diborane certainly have some excess negative charge), the value $S = 0.36$ is obtained. Thus the value of S for the π-π bond in diborane is as large as in ethylene, where $S = 0.27$, using Slater AO's. Since degree of overlap of valence AO's is recognized to be closely correlated with bond strength, this result indicates that 1.79 A. is not too large for strong B=B bonding. It also suggests that at its normal double-bond distance, boron should form remarkably strong double bonds. Further, it gives strong support to Pitzer's proposed structures for the higher boron hydrides, since it indicates that these structures would be strongly stabilized by conjugation of $2p\pi$ AO's on the various boron atoms, occupied by borrowed electrons; without unusual strength of π-π bonds at single-bond distances, it would be difficult to understand how such conjugation could be

[5] *Added in proof:* Subsequent examination of the new infrared data has shown unambiguously that the bridge model is correct: see W. C. Price, Letter to the Editor, J. Chem. Phys., August, 1947.

effective. The stability of trigonal conjugation in the boron trihalides, boric acid, and other compounds is also made more understandable.]

VII. RELATED COMPOUNDS

As is well known, several partially methylated diboranes are known, but none with more methyl groups than $B_2H_2(CH_3)_4$. This suggests that hydrogen atoms, but not methyl groups, can take bridge positions. However, there may be another reason. As is well known, the halides BX_3 (X = F, Cl, Br, I) and similar compounds do not form dimers. Nevertheless, in the corresponding aluminum compounds, the dimers Al_2X_6, with bridge structure, are the stable forms. The bridge structure is also accepted for $Al_2X_2(CH_3)_4$, and is plausible too for the fairly well established molecule $Al_2(CH_3)_6$ (see footnote 3, p. 213).

Examination and visualization of the forms of the diborane a_g and b_{3u} bridge MO's of equations 3 reveal no good reason why a tetrahedral (sp^3 hybrid), or approximately tetrahedral, carbon AO of a methyl group could not take the place of a hydrogen 1s AO (S″ or S‴ of equations 3) in forming a bridge. It may be that the bridge bond so formed would be somewhat weaker (although even this does not appear obvious), but there appears to be nothing in the requirements of the bridge arrangement that would be detrimental to the strengths of the three C—H bonds of CH_3, while at the same time a tetrahedral or other σ-type carbon AO appears to be favorably shaped to show good bonding with the boron AO's in a_g and b_{3u} bridge MO's. A σ-type carbon AO apparently should be able also to act in a similar capacity in $Al_2(CH_3)_6$ with bridge structure.

Why, then, is $B(CH_3)_3$ found instead of $B_2(CH_3)_6$? As is well known, the boron halides, which are planar molecules, are strongly stabilized by a form of conjugation which may conveniently be called *trigonal conjugation*. The most striking empirical evidence of this, as Pauling pointed out, is to be found in the abnormally small B—X distances. The same phenomenon occurs in NO_3^-, CO_3^{--}, $B(OH)_3$, and similar entities. It results from the interaction of the excess π electrons of the outer atoms with the vacant π orbital on the central atom. The resulting stabilization is evidently so great that dimers B_2Cl_6 and so on are not formed, even though chlorine $p\sigma$ AO's should be capable of serving as bridge links (the argument is the same as that given above for σ AO's of methyl carbon atoms).

A consideration of the electronic structure of $B(CH_3)_3$ by MO methods shows that *trigonal hyperconjugation* should stabilize this molecule very considerably. A rough semiempirical MO computation, somewhat similar to that for the perpendicular form of ethylene, summarized in the following paper (11), indicates that this stabilization might amount to 1.5 or 2 ev. This conclusion appears to be in harmony with the B—C distance in $B(CH_3)_3$ and related compounds, as determined by electron diffraction.[6] Although Bauer (2, 3) concludes that the B—C distance in boron trimethyl (1.56 A.) is that corresponding to a normal

[6] See references 2, 3, and 8 for electron-diffraction studies of boron trimethyl and related molecules.

covalent single bond, it is 0.09 A. smaller than the sum of Pauling's covalent radii (0.88 + 0.77 A.); and, since there is some form of conjugation or strong hyperconjugation in most of the boron compounds whose interatomic distances have been accurately measured, there seems to be no sufficient reason to suppose that the normal single-bond covalent radius is much less than Pauling's estimated value. It seems likely, then, that the occurrence of exceptionally strong hyperconjugation in $B(CH_3)_3$, rather than any inherent unfitness of methyl to replace hydrogen in a bridge bond, is responsible for the non-existence of $B_2(CH_3)_6$.

This conclusion is in harmony with the existence of $Al_2(CH_3)_6$, and the likelihood of a bridge structure for this compound.[3] In the case of the halides, the fact that Al_2X_6 bridge molecules are formed rather than AlX_3 may of course, be explained largely on electrostatic grounds; the bridge form could be understood as a purely electrostatic equilibrium structure built of Al^{+3} and X^- ions. An additional factor favoring the dimeric forms may, however, be the familiar fact that only the first-row elements form strong double bonds; hence all types of conjugation should be weakened in the aluminum compounds and, in particular, trigonal conjugation stabilizing the monomeric molecules AlX_3 should be much weaker than for BX_3. It also follows, of course, that Al=Al double bonding should contribute very little to the stability of Al_2X_6 or $Al_2(CH_3)_6$. Nevertheless, a set of MO's qualitatively describable by equations 3, even though strongly polar, may well be present in Al_2X_6 and especially $Al_2(CH_3)_6$; an analogue of the suggestion on π bonds in Section VI is here pertinent. It seems possible that in the halides the bridge structure is primarily ionic but is nevertheless appreciably reinforced by covalent bridge bonding similar to that in diborane. In addition, the π electrons of the halogen atoms should make at least a small contribution in stabilizing these structures.

Other molecules which may be similar in structure to B_2H_6 are known, for example, Ga_2H_6 (5, 9).

VIII. SUMMARY

The respective MO electron configurations required by the ethane-like and the bridge geometrical models of diborane are discussed, and their predicted consequences for the properties of diborane, including its electronic spectra, are stated and compared with available evidence. The evidence favors the bridge model, but is not conclusive.[5] The electronic structures of related compounds, including Al_2X_6, are briefly discussed. It is pointed out that methyl groups should be able to assume bridge positions in derivatives of diborane and similar compounds. It is pointed out that boron trimethyl must be stabilized by trigonal hyperconjugation, and this is used to explain the fact that it does not dimerize.

REFERENCES

(1) BAUER, S. H.: Chem. Rev. **31**, 43 (1942). Bauer did not advocate the bridge model but, because it had been so much discussed, he included in his review a reinterpretation of the electron-diffraction data showing how these might be interpreted in terms of the bridge model.

(2) BAUER, S. H., AND BEACH, J. Y.: J. Am. Chem. Soc. **63,** 1394 (1941).
(3) BAUER, S. H., AND HASTINGS, J. M.: J. Am. Chem. Soc. **64,** 2686 (1942).
(4) BELL, R. P.: Proc. Roy. Soc. (London) **A183,** 328 (1945) and references there given.
(5) BELL, R. P., AND LONGUET-HIGGINS, H. C.: Proc. Roy. Soc. (London) **A183,** 357 (1945).
(6) BLUM, E., AND HERZBERG, G.: J. Phys. Chem. **41,** 305 (1937).
(7) EISTERT, B.: Z. physik. Chem. **B52,** 202 (1942).
(8) LÉVY, H. A., AND BROCKWAY, L. O.: J. Am. Chem. Soc. **59,** 2085 (1937).
(9) LONGUET-HIGGINS, H. C.: J. Chem. Soc. **1946,** 139–43.
(10) MULLIKEN, R. S.: Phys. Rev. **41,** 756 (1932); **43,** 765L (1933); and especially J. Chem. Phys. **3,** 635 (1935).
(11) MULLIKEN, R. S., AND ROOTHAAN, C. C. J.: Chem. Rev. **41,** 219 (1947).
(12) PITZER, K. S.: J. Am. Chem. Soc. **67,** 1126 (1945); references to the work of other investigators are given here.
(13) PITZER, K. S., AND GUTOWSKY, H. S.: J. Am. Chem. Soc. **68,** 2204 (1946).
(14) STITT, F.: J. Chem. Phys. **8,** 981 (1940); **9,** 780 (1941).
(15) WIBERG, E.: Ber. **A77** (1944) (seen in proof through the kindness of Professor H. I. Schlesinger).