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The Electronic Structures of Hydrides, Halides and Alkyl Compounds of Boron and Aluminum. II. Dimers

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The electronic structures of dimers containing boron and aluminum atoms, i. e., B_2H_6, $B_2H_2(CH_3)_4$, Al_2Cl_6, $Al_2Cl_2(CH_3)_4$ and $Al_2(CH_3)_6$, are investigated by an extended Hückel method. The calculations show that the central linkages are weak and that their bonding natures are very different from those of the bonds between the metals and terminal atoms. Judging from the orbital energies and populations, these dimers still hold a strong acidity, like that in the monomers, an acidity which depends mainly on the existence of the almost unfilled $p\pi$ orbitals of the metal atoms, where the electrons occupying the lower vacant orbitals in these dimers are almost localized. The results are compared with other calculations and experimental results. It is, further, shown by examining the electronic structures of two hypothetical compounds that these dimers can be easily formed by using the vacant valence orbitals of the metal atoms, and that the metal-metal bonds in some dimers are considerably strong.

The structures of dimers containing boron or aluminum atoms have attracted the interest of many researchers. The bridged model has been applied to the structures of these dimers, and several interpretations have been attempted.[1]

In the present paper, we will treat these dimers by the extended Hückel method proposed by Hoffmann.[2] In our previous paper, Part I,[3] the electronic structures of monomers and ions, including boron or aluminum atoms, were considered by the same method. These dimer compounds are the so-called "electron-deficient compounds," and the usual concept of the electron-pair bond fails as a basis for an interpretation of their electronic structures. Hoffmann's method represents the molecular orbitals (MO) in terms of the linear combinations of the atomic orbitals (AO) of all the valence electrons of the atoms in the compounds; therefore, it is not necessary to predetermine the hybridizations or the orientations of the base orbitals. For this reason, this approximate method is suitable for the treatment of those compounds which have unusual valencies or configurations.

The dimer compounds to be studied in the present paper are B_2H_6, $B_2H_2(CH_3)_4$, Al_2Cl_6, $Al_2(CH_3)_4Cl_2$, $Al_2(CH_3)_6$, and some related compounds. Their electronic structures will be calculated, and,

1) E. g., C. A. Coulson, "Valence," Oxford Univ. Press, Oxford (1952), 2nd edition (1961); H. Zeiss, ed., "Organometallic Chemistry," Reinhold Pub. Co., New York (1960).
2) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); ibid., **40**, 2474 (1964).
3) H. Kato, K. Yamaguchi, T. Yonezawa and K. Fukui, This Bulletin, **38**, 2144 (1965).

TABLE I. THE GEOMETRY OF DIMERS

Compound	Bond distance, Å			Bond angle, deg.	
	M–X	M–Y	M–M	∠XMX	∠YMY
B_2H_6	1.187	1.334	1.77	120	(83)*
$B_2H_2(CH_3)_4$	1.59	1.34	1.86	120	(83)*
Al_2Cl_6	2.06	2.21	3.410580	120	79
$Al_2Cl_2(CH_3)_4$	1.90	2.31	3.266834	120	90
$Al_2(CH_3)_6$	2.00	2.23	2.558150	120	110

* Approximate values calculated from bond distances.

TABLE II. THE M(A) and M(A–B) VALUES OF VARIOUS MONOMERS AND DIMERS

Compound	M(M)	M(X)	M(Y)	M(M–X)	M(M–Y)*
BH_3	2.562	1.146	—	0.852	—
B_2H_6	2.697	1.163	0.976	0.865	0.463
$BH(CH_3)_2$	2.143	4.726	1.238**	0.730	0.800**
$B_2H_2(CH_3)_4$	2.249	4.762	1.030	0.672	0.492
$AlCl_3$	1.029	7.657	—	0.488	—
Al_2Cl_6	1.084	7.681	7.553	0.472	0.328
$AlCl(CH_3)_2$	1.005	5.050	7.651**	0.384	0.496**
$Al_2Cl_2(CH_3)_4$	0.964	5.099	7.574	0.344	0.319
$Al(CH_3)_3$	0.985	5.049	—	0.382	—
$Al_2(CH_3)_6$	0.985	5.090	5.011	0.384	0.188

* The notations, M, X and Y refer to those given in Fig. 1.

** The values correspond to the hydrogen atom and the chlorine atom in $BH(CH_3)_2$ and in $AlCl(CH_3)_2$ respectively.

especially, the nature of the bonds and some physico-chemical properties will be discussed.

The values of the parameters used in this paper (the Coulomb and resonance integrals) were given in Part I of this series.[3] The coordinates of the above compounds are shown in Fig. 1, where the notation M denotes the boron or aluminum atom; Y, the bridge atom or group, and X, the terminal atom or group. The two M and four X atoms are on the XY plane, and the two Y atoms are on the Z-axis (one in the + region and the other in the − region). The px, py and pz orbitals of each atom have their positive parts in the X, Y and Z directions, respectively, of the coordinates in Fig. 1. The bond distances and bond angles are estimated with reference to the values given in Ref. 4. For the sake of simplicity in the calculation, however, the values listed in

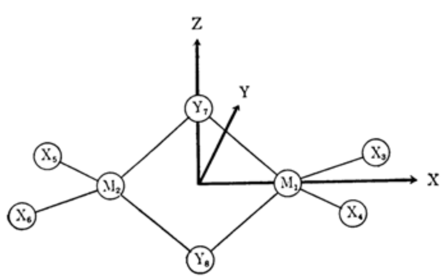

Fig. 1. The coordinates of dimers.

Ref. 4 have been modified slightly; for all the methyl groups, the valence angle is assumed to be tetrahedral, and the C–H bond distance is set equal to 1.09 Å throughout the calculations. The adopted values are summarized in Table I.

The Electronic Structures of the Dimers

Population Analysis. — The calculated values of the atomic populations of the atom A, M(A), and those of the atom bond populations between A and B atoms, M(A–B),[5] are listed in Fig. 2, where the M(A) values are represented by the numbers on the atom A, and the M(A–B) values, by those between the A–B bond (the values of the hydrogen atoms in the methyl groups are omitted for the sake of simplicity). The results given in Fig. 2 show that the M(A) and M(A–B) values in these dimers are similar to those in their monomers as given in Table II (the values of which are taken from our previous paper),[3] except for the quantities related to the bridge atoms or groups.

They also show that two types of bonds exist in these dimeric compounds; one is the M–X bond (corresponding to M and X in

4) A. D. Mitchell and L. C. Cross, eds., "Table of Interatomic Distances and Configurations in Molecules and Ions," The Chemical Society, London (1958).

5) K. Morokuma, H. Kato, T. Yonezawa and K. Fukui, This Bulletin, **38**, 1263 (1965).

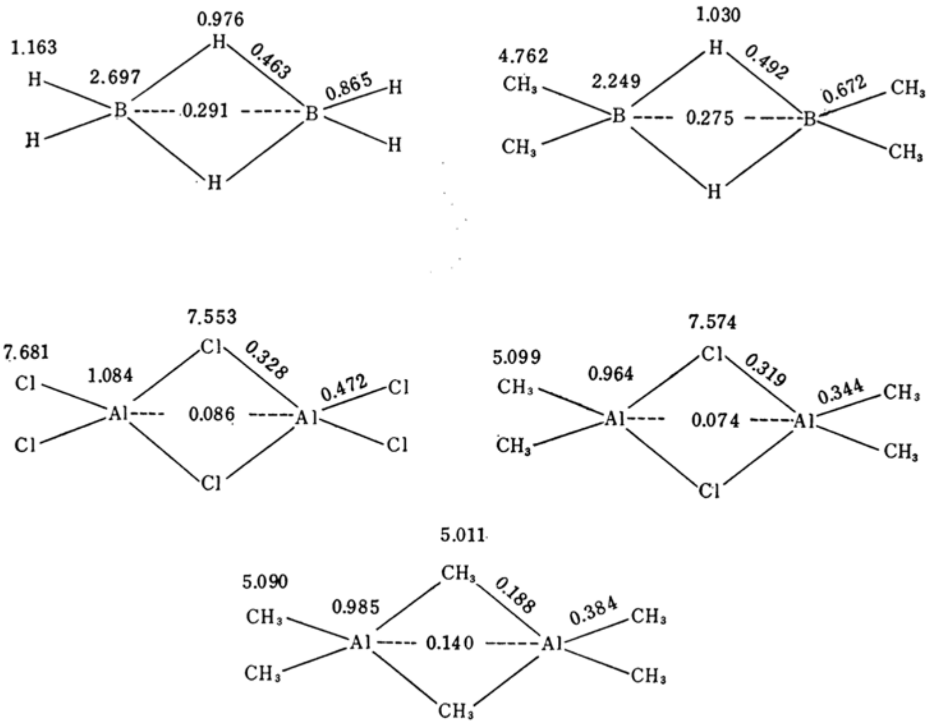

Fig. 2. The M(A) and M(A–B) values of dimers.

Fig. 1), which is nearly the same as the normal electron-pair bond, and the other is the M–Y bond (Y in Fig. 1), which is weak and which may be called a "semi-bond." For example, the calculated values of M(B–H_T) (where H_T indicates the terminal hydrogen) are 0.852 in BH_3 and 0.865 in B_2H_6, while that of M(B–H_B) (H_B denotes the bridge hydrogen) is 0.463. For $Al(CH_3)_3$, the values of M(Al–C_T) are 0.382 in the monomer and 0.384 in the dimer, while the M(Al–C_B) value is 0.188.

As to the M(A) values in M_2A_6-type compounds, those of the atoms in the bridge are slightly smaller than those of the terminal atoms. However, this result is partly in conflict with other results, as is mentioned below. For B_2H_6, our result leads to the $M(H_T) > M(H_B)$ relation, whereas the results of an LCAO SCF calculation by Yamazaki indicate $M(H_T) < M(H_B)$;[6] Yamazaki's findings agree with the experimental findings. On the other hand, it was reported, for Al_2Br_6, on the basis of a PQR measurement,[7] that the charges in the bridge bromine atoms are smaller than those in the terminal atoms; in this case, accordingly, this tendency may agree with our finding for Al_2Cl_6.

Our M(A) and M(A–B) values and some orbital energies for B_2H_6 are listed in Table III, together with the results obtained by Yamazaki. Except for the $M(H_B)$ and some MO energy values, the agreement between them is satisfactory.

TABLE III. COMPARISON OF THE CALCULATED RESULTS FOR B_2H_6

		Present	Yazaki's SCF
M(A)	M(B)	2.697	2.78
	$M(H_T)$	1.163	0.99
	$M(H_B)$	0.976	1.24
M(A–B)	M(B–H_T)	0.865	0.85
	M(B–H_B)	0.463	0.39
	M(B–B)	0.291	0.34
Orbital energy, eV.		$-21.58(a_g)$	$-23.57(a_g)$
		$-18.00(b_{2u})$	$-19.27(b_{2u})$
		$-14.39(b_{3u})$	$-17.96(b_{1u})$
		$-14.20(b_{1u})$	$-16.58(b_{3u})$
		$-13.29(b_{1g})$	$-15.40(b_{1g})$
		$-13.20(a_g)$*	$-13.83(a_g)$*
		$-6.53(b_{3g})$**	$+2.62(b_{1u})$**

* The highest-occupied orbitals.
** The lowest-vacant orbitals.

Energy Levels.—The calculated energy values (in eV.) of the highest occupied (HO) orbitals and the lowest vacant (LV) orbitals of some monomers, dimers and ions are collected in Table IV (those of the monomers and ions were given in Part I). Through the monomers, dimers and ions, the energies of the HO orbital of these compounds do not change significantly, although the LV levels become higher, and those of the dimers lie close

6) M. Yamazaki, *J. Chem. Phys.*, **27**, 1401 (1957).
7) P. A. Casabella, P. J. Bray and R. G. Parnes, *J. Chem. Phys.*, **30**, 1393 (1959).

TABLE IV. THE HO AND LV ORBITAL ENERGIES OF SOME MONOMERS, DIMERS AND IONS

Compound	Orbital energy, eV. HO	LV
BH_3	−13.91	−8.53
B_2H_6	−13.20	−6.53
BH_4^-	−13.71	+10.02
$AlCl_3$	−14.94	−4.73
Al_2Cl_6	−13.86	+1.28
$AlCl_4^-$	−14.81	+13.21
$BH(CH_3)_2$*	−12.50	−6.97
$B_2H_2(CH_3)_4$	−12.28	−5.23
$AlCl(CH_3)_2$*	−12.12	−4.91
$Al_2Cl_2(CH_3)_4$	−12.00	+1.04
$Al(CH_3)_3$*	−12.14	−5.01
$Al_2(CH_3)_6$	−12.03	−0.78

* The MO energies of these ions have not been calculated.

TABLE V. THE LV ORBITALS IN SOME DIMERS*

B_2H_6: $0.810(Z_{B1}-Z_{B2})$

$B_2H_2(CH_3)_4$**: $0.826(Z_{B1}-Z_{B2})-0.095(Z_{C3}+Z_{C4}-Z_{C5}-Z_{C6})$

Al_2Cl_6: $0.879(Z_{A11}-Z_{A12})-0.193(Z_{C13}+Z_{C14}-Z_{C15}-Z_{C16})-0.483(X_{C17}-XC_{18})$

$Al_2Cl_2(CH_3)_4$**: $0.900(Z_{A11}-Z_{A12})-0.153(Z_{C3}+Z_{C4}-Z_{C5}-Z_{C6})-0.459(X_{C17}-X_{C18})$

* The numbers in the suffices are given in Fig. 1 and the notations Z_{B1} and Z_{B2} denote the pz orbitals of the boron 1 and 2 atoms respectively, and so on.

** For the sake of simplicity, the values of the hydrogen atoms in the methyl groups and the smaller ones ($<10^{-2}$) are neglected.

to the monomers. This rising trend of the LV levels indicates that the dimeric compounds have an appreciable nucleophilic character, like that in the monomers pointed out in Part I.[3] Furthermore, the nucleophilic character of these dimers depends mainly on the existence of the almost unfilled $p\pi$ orbital of the metal atom, as may be seen in Table V, in which the values of the AO coefficients of the LV orbitals in some dimers are presented. It is there shown that the electrons in these orbitals are largely localized on the $p\pi$ orbitals of the metal atom, and that the anti-bonding character is strongest in the metal-metal bonds. Accordingly, the nucleophilic reagents or electron donors may coordinate with the metal atoms in the dimers, and the transfered electrons may primarily cause the metal-metal bonds to weaken or break. This result agrees with experience.[1]

Some Physico-chemical Properties. — The force constants of various Al-dimers have been evaluated;[8] the magnitudes have been shown to be parallel with those of the bond populations.[9]

TABLE VI. THE M(A–B) VALUES AND THE FORCE CONSTANTS OF Al-DIMERS

(a) Al–Al Bond

	M*	K**
Al_2Cl_6	−0.086	0
$Al_2Cl_2(CH_3)_4$	−0.074	0
$Al_2(CH_3)_6$	0.140	0.50

(b) Al–Cl Bond

	Terminal M	Terminal K	Bridge M	Bridge K
Al_2Cl_6	0.472	2.35	0.328	1.05
$Al_2Cl_2(CH_3)_4$	—	—	0.319	1.05

(c) Al–C Bond

	Terminal M	Terminal K	Bridge M	Bridge K
$Al_2Cl_2(CH_3)_4$	0.344	2.05	—	—
$Al_2(CH_3)_6$	0.384	2.05	0.188	0.83

* The atom bond population, M(A–B).

** The force constant (in the units of md./Å) taken from Ref. 8.

Those values are summarized in Table VI. It has been pointed out recently that the observed ^{13}C–H spin-spin coupling constants are proportional to the values of the square of the bond order, p, between the ls AO of the hydrogen and the 2s AO of the carbon atom.[10] For B_2H_6, the ^{11}B–H_T and ^{11}B–H_B coupling constants have been measured as 137 c.p.s. and 48 c.p.s. respectively.[11] The calculated p^2 values, 0.149 and 0.029 respectively, are in accordance with the above experimental values. For $Al_2(CH_3)_6$, the NMR signals of the bridge methyl protons are observed in the lower field, and those of the terminal methyl protons in the higher field, at a low temperature.[12] The values for the charges of the bridge and the terminal hydrogens are similar to each other. Thus, the experimental results can not be explained by our calculated charges of hydrogens.*

The Nature of the Bonds in Dimers

The above discussions point out that the M(A–B) values of the metal-terminal atom bond are very different from those of the metal-bridge atom bonds.

8) T. Onishi and T. Shimanouchi, *Spectro. chim. Acta*, **20**, 325 (1964).
9) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.*, **A193**, 456 (1948).
10) T. Yonezawa, I. Morishima, M. Fujii and K. Fukui, This Bulletin, **38**, 1224 (1965).
11) W. D. Phillips, H. C. Miller and E. L. Muetterlies, *J. Am. Chem. Soc.*, **81**, 4496 (1959).
12) N. Muller and D. E. Pritchard, ibid., **82**, 248 (1960).

* The proton chemical shift is influenced by other factors, such as the magnetic anisotropy of the adjacent carbon atom. Hence, it is impossible at the present stage to determine whether or not our result is valid.

The difference between these bonds will be examined further in this section by means of the values of the AO bond population, N(r–s). For instance, the N(s–s)/M(A–B) ratio, where N(s–s) denotes the AO bond population between the valence s AO's belonging to the A and B atoms, may be used as a measure of this difference. In other words, these values represent the s-nature of the bond X–Y. For B_2H_6, the values obtained are 0.27 for the B–H_B bond and 0.37 for the B–H_T bond. For Al_2Cl_6, the values are 0.20 for the Al–Cl_B bond and 0.29 for the Al–Cl_T bond. For $Al_2(CH_3)_6$, the values are 0.14 for the Al–C_B bond and 0.20 for the Al–C_T bond. Thus, the s-natures of these two bonds in the dimers are clearly different from each other; therefore, if one wants to use the hybrids of the metal atoms to explain the electronic structures of these dimers, at least two kinds of hybrids should be used. A similar point has already been made in Ref. 6.

For a further discussion of these points, two hypothetical compounds are considered. One is the compound which is produced by the symmetrical cleavage of the dimer without changing other conditions; it is named the "deformed monomer." The other is the compound which is produced by omitting the two bridge atoms or groups from the dimers; it is named the "omitted dimer." The shapes of these two compounds and the calculated M(A) and M(A–B) values are given in Fig. 3, in which the deformed monomer is indicated by MX_2Y, and the omitted dimer, by M_2X_4 (the notations M, X and Y are given in Fig. 1).

Some information can be drawn from the results in Fig. 3. For the deformed monomers, the M(M–Y) values (where Y is situated at the same position as the bridge atom in the dimer) are not appreciably different from the M(M–X) values (where X is the terminal atom in the dimer);

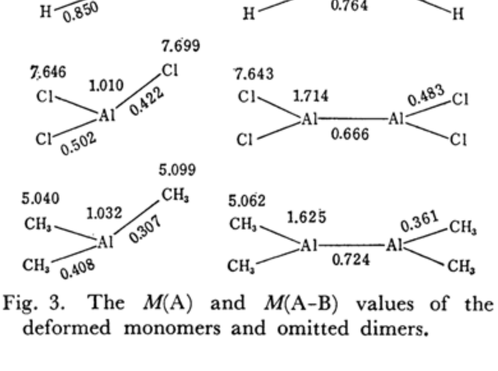

Fig. 3. The M(A) and M(A-B) values of the deformed monomers and omitted dimers.

upon dimerization, though, the M(M–Y) values decrease largely, while the M(M–X) values remain almost constant. For instance, the M(M–Y) values are 0.772 in the deformed BH_3 monomer and 0.463 in the dimer, while the M(M–X) values are 0.850 in the deformed monomer and 0.865 in the dimer. In the deformed monomers, the M(Y) values are slightly larger than the M(X) values; this tendency is reversed in the dimers, as has already been shown. Thus, as a result of the dimer formation the metal-bridge atom bonds become very weak, and a small amount of charge transfer may occur from the "bridge" atom to the other deformed monomer. As to the result for the omitted dimers, the M(M–M) values are quite large, showing that the metal-metal bonds are normal covalent bonds, such as those in B_2Cl_4.[3] The M(A) and M(A–B) values of the other parts are mostly comparable to the corresponding values in the normal dimers. For B_2H_4, the M(B–B) value is 0.764; this value decreases to 0.291 in B_2H_6. For Al_2Cl_4, the M(Al–Al) value is 0.666, and for Al_2Cl_6, –0.086, showing that the Al–Al bond becomes anti-bonding. Thus, as a result of the addition of the two bridge atoms to the omitted dimers, the metal-metal bonds become very weak.

Table VII presents the calculated values of the AO population, N(r). Those of the AO bond population, N(r–s), are given in Table VIII for various compounds including the boron atoms. The results in these tables indicate that the py orbital of the boron atom takes part in the boron-terminal hydrogen bonding, and that the pz and px orbitals take part in the boron-bridge hydrogen and the boron-boron bondings respectively.* In addition, the N(r) values of the px and pz orbitals of the boron atoms vary considerably, while the M(B) values do not change significantly, with the change in the structure from monomer to dimer. The changes in the configuration seem to take place easily by means of the rearrangement of valence electrons in an atom, since the valence orbital (in

TABLE VII. THE N(r) VALUES OF THE BORON ATOMS IN VARIOUS COMPOUNDS

	$N(S_B)$	$N(X_B)$	$N(Y_B)$	$N(Z_B)$	M(B)*
B_2H_4	0.979	0.893	0.811	0	2.683
B_2H_6	0.833	0.588	0.811	0.464	2.696
deformed BH_3	0.911	0.554	0.825	0.242	2.532
BH_3	0.912	0.825	0.825	0	2.562

* The notations $N(S_B)$ and $N(X_B)$ denote the atomic orbital populations of the 2s AO and the 2px AO of the boron atom respectively, and so on.

* From the results in Table VIII, it may be seen that the B–B bond in B_2H_6 has some π character; the same tendency is observed for the other M–M bonds in dimeric forms.

TABLE VIII. THE N(r–s) VALUES OF VARIOUS B-COMPOUNDS

a) B_2H_6

s \ r	S_{B1}	X_{B1}	Y_{B1}	Z_{B1}*
S_{B2}	−0.012	0.034	—	—
X_{B2}	0.034	0.166	—	—
Y_{B2}	—	—	−0.028	—
Z_{B2}	—	—	—	0.096
h_T	0.320	0.128	0.416	
h_B	0.126	0.124	—	0.228

b) B_2H_4

s \ r	S_{B1}	X_{B1}	Y_{B1}	Z_{B1}
S_{B2}	0.094	0.176	—	—
X_{B2}	0.176	0.346	—	—
Y_{B2}	—	—	−0.028	—
Z_{B2}	—	—	—	—
h_T	0.332	0.120	0.416	—

c) Deformed BH_3

s \ r	S_{B1}	X_{B1}	Y_{B1}	Z_{B1}
h_T	0.332	0.108	0.410	—
h_B	0.334	0.310	0	0.228

* The notations, S_{B1}, $X_{B1}\cdots Z_{B1}$ denote the 2s, 2px⋯2pz orbitals of the boron atom 1, and h_T and h_B are the 1s orbital of the terminal and bridge hydrogen atoms respectively.

this case, the pz orbital of the boron atom)** remains unoccupied.

Figure 4 lists the correlations between the orbitals in the omitted and normal BH_3 dimers. In B_2H_4, the HO orbital is mainly the σ-type bonding orbital between the boron atoms, while the LV orbital is the π-type bonding orbital between the boron atoms. When hydrogens are added to the bridge, these HO and LV orbitals are stabilized remarkably,

* For the compounds with boron and hydrogen atoms, these results appear more clearly, since the electronegativities of the B and H atoms are almost equal to each other, and the effect of the migration of the electron between the atoms is negligible.

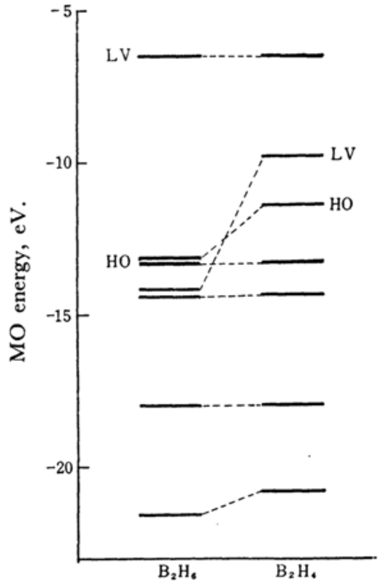

Fig. 4. The MO energies of B_2H_6 and B_2H_4.

and the LV orbital turns out to be the occupied orbital of the BH_3 dimer. These results agree with the tendency of the N(r) values; further, this change in the LV orbital may indicate that the bridge hydrogens are caught by the vacant pπ orbitals of the boron atoms.

Accordingly, our results may be summarized as follows:

1) In a dimer such as the M_2X_6 type, at least two kinds of M–X bonds exist.

2) The metal-terminal atom bonds are almost unchanged upon changes in the structure.

3) The metal-bridge atom bonds become quite weaker.

4) The metal-metal bonds are strong in some dimers.

5) The unfilled p orbitals of the metal atoms play an improtant role in the structural changes.

The calculations were carried out on the IBM 7090 computer of the Japan IBM Co., by the permission of the UNICON Committee, whose kindness we acknowledge.