The Electronic Structure of Some Hydrides, Halides and Alkyl Compounds of Boron and Aluminum. I. Monomers and Ions

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Boron and aluminum atoms are known as typical group III elements of the periodic table which are very electro-positive and which are strong electron acceptors. Many experimental studies have been performed on compounds containing these two elements,(1) and theoretical investigations have been performed, especially on the basis of the valency theory.(2)

In the present paper, some boron and aluminum compounds, i.e., hydrides, halides, alkyl compounds, and their related ions will be treated by

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1) "Organometallic Chemistry," Ed. by H. Zeiss, Reinhold Pub., New York (1960).

2) E. g., C. A. Coulson, "Valence," Oxford (1952), II (1961).

TABLE I. THE VALUES OF THE COULOMB INTEGRALS (eV.) AND THE EFFECTIVE NUCLEAR CHARGES (Z^*)

		H	B	C	F	Al	Cl
	Z^*	1.00	2.60	3.25	5.20	3.50	6.10
H_{ii}[a]	s	−13.60	−15.15	−21.43	−40.16	−12.74	−25.26[b]
	p	—	− 8.53	−11.42	−20.98	− 6.67	−15.09

a) H. A. Skinner and H. O. Pritchard, *Chem. Revs.*, **53**, 745 (1955).

b) Estimated value by the observed atomic spectra (C. E. Moore, "Atomic Energy Levels").

the extended Hückel method proposed by Hoffmann.[3] The electronic structures and some physico-chemical properties of these compounds, such as their electron-accepting characters, and the stabilities of these monomers will be investigated. In addition, a problem of stereochemical interest—the two configurations of the B_2Cl_4 molecule—will be briefly discussed.

The electronic structure of the dimers will be treated in Part II, while the aspects of the chemical behavior which are important in the synthetic process will be discussed in Part III.

The Parameters Used

In the present method, the values of the Coulomb integral, H_{ii} are given by changing the sign of the valence-state ionization potentials of valence electrons, and the values of the resonance integral, H_{ij}, are evaluated by the following equation:[3]

$$H_{ij}=0.875(H_{ii}+H_{jj})S_{ij}$$

where S_{ij} is the overlap integral between the ith and the jth atomic orbitals (AO). The adopted values of the Coulomb integrals and the effective nuclear charges of various AO's are collected in Table I, where the notations s and p denote the values of H_{ii} of the 2s and 2p orbitals for the second row elements and of the 3s and 3p orbitals for the third row elements of the periodic table respectively.

The bond distances and the bond angles are determined with reference to those cited in Ref. 4. Those values which have not yet been measured are estimated on an assumption that, for example, the B–H bond distance in the monomeric BH_3 is equal to the terminal B-H distance in the dimer. These values are cited in Table II, together with their symmetry groups.

TABLE II. THE ADOPTED VALUES OF THE BOND DISTANCES, BOND ANGLES AND SYMMETRIES OF VARIOUS COMPOUNDS

Compounds	Sym.	Bond distance (Å) and bond angle (deg.)*
BH_3	C_{3v}	B-H=1.187
BH_4^-	T_d	B-H=1.25
BCl_3	D_{3h}	B-Cl=1.75
BF_3	D_{3h}	B-F=1.30
BF_4^-	T_d	B-F=1.40
B_2Cl_4	D_{2d}, D_{2h}	B-B=1.77, B-Cl=1.73, ∠ClBCl=120
$BH(CH_3)_2$	C_{2v}	B-H=1.20, B-C=1.56, ∠HBC=120
$B(CH_3)_3$	C_{3v}	B-C=1.56
$BC_2H_3(CH_3)_2$ $B(C_2H_3)_2CH_3$	C_{2v}	B-C=1.56, ∠CBC=120
$B(C_2H_3)_3$	C_{3v}	B-C=1.56, ∠CBC=120
AlH_3	C_{3v}	Al-H=1.65
AlH_4^-	T_d	Al-H=1.70
$AlCl_3$	D_{3h}	Al-Cl=2.10
$AlCl_4^-$	T_d	Al-Cl=2.13
$Al(CH_3)_2Cl$	C_{2v}	Al-Cl=2.1, Al-C=2.0, ∠ClAlC=∠CAlC=120
$Al(CH_3)_3$	C_{3v}	Al-C=2.0
$Al(C_2H_5)_3$	C_{3v}	Al-C=2.0

* As to the methyl, ethyl and vinyl groups, the used values are as same as ones in these parent molecules.

Results and Discussion

The calculated values of the atomic population of an atom X, M(X), and the atom bond populations between X atoms and Y atoms, M(X–Y), for various monomers and ions are summarized in Fig. 1.

The Charge Distribution in Monomers.—By referring to the values of M(X) in Fig. 1, it may be seen that boron atoms have positive charges and that aluminum atoms are more positive in these monomers. That is to say, even in the BH_3 and AlH_3 molecules, each hydrogen atom bears more than one unit charge, and, in their alkyl compounds, the boron-carbon and aluminum-carbon bond are polarized in such a way as $B^{+\delta}$-$C^{-\delta}$ and $Al^{+\delta}$–$C^{-\delta}$. The atomic population of the methylene carbon atom in triethyl aluminum, 4.897, is larger than that of the methyl carbon atom, 4.386. This finding agrees with that of the NMR study described in Ref. 1. In the halides of boron and aluminum, the polarization of M–X bonds (M=boron or aluminum and X=halogens) is more remarkable than in alkyl compounds. An example is presented by the aluminum trichloride monomer, in which the value of M(Al) is calculated to be 1.029 and that of M(Cl) as 7.657. In this connection the result of Casabella et al. is worth our attention. They estimated, by the PQR

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[3] R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963); ibid., **40**, 2474 (1964).

[4] A. D. Mitchell, L. C. Cross L. E. Sutton and D. G. Jenkin, "Table of Interatomic Distances and Configuration in Molecules and Ions," The Chemical Society, London (1958).

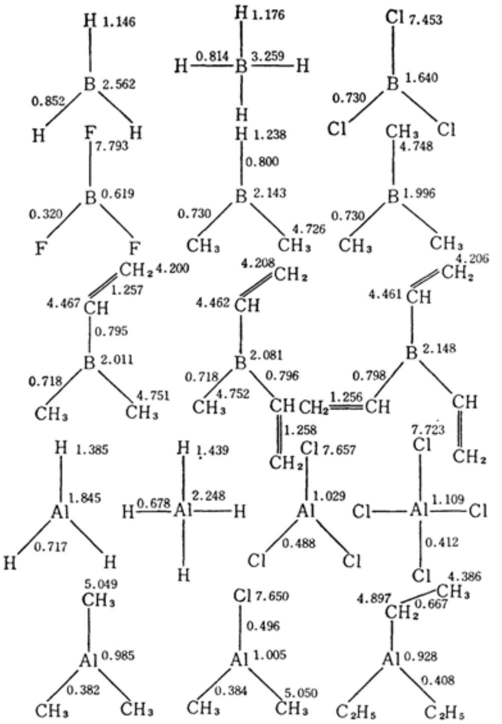

Fig. 1. The M(X) and M(X-Y) values of various compounds.

measurement, that the total electronic densities of various atoms in the aluminum tribromide dimer are 1.26 on the aluminum atom, 7.65 on the terminal bromine atom, and 7.44 on the bridged bromine atom.[5] With these values in mind, our results are not very extreme.

TABLE III. THE $N(r)$ VALUES ON THE BORON AND ALUMINUM ATOMS IN VARIOUS MONOMERS

	N(s)	N(x)	N(y)	N(z)
(a) B-Compounds				
BH_3	0.912	0.825	0.825	0.0
BF_3	0.295	0.122	0.122	0.082
$BH(CH_3)_2$	0.861	0.546	0.624	0.113
$B(CH_3)_3$	0.812	0.522	0.522	0.140
$BC_2H_3(CH_3)_2$	0.818	0.509	0.534	0.150
$B(C_2H_3)_2CH_3$	0.823	0.553	0.526	0.175
$B(C_2H_3)_3$	0.833	0.556	0.553	0.207
BCl_3	0.646	0.387	0.387	0.220
(b) Al-Compounds				
AlH_3	0.850	0.497	0.497	0.0
$Al(CH_3)_3$	0.603	0.165	0.165	0.052
$Al(CH_3)_2Cl$	0.569	0.176	0.187	0.073
$AlCl_3$	0.505	0.206	0.206	0.111
$Al(C_2H_5)_3$	0.594	0.142	0.142	0.042

(s: 2s or 3s AO; x, y, z: 2px or 3px, 2py or 3py, 2pz or 3pz AO's)

The atomic orbital populations of the rth AO, $N(r)$, are collected in Table III(a) for the boron atoms and in Table III(b) for the aluminum atoms in various monomers, where the pz orbitals of these atoms consist of the pπ orbitals of these monomers. In BH_3 and AlH_3 molecules, the values of N(s) (the s denotes the 2s orbital on boron or the 3s orbital on aluminum) are almost comparable to those of N(x) and N(y), and N(z) is zero at both atoms (x, y, and z denote 2px, 2py, and 2pz AO's on boron or 3px, 3py, and 3pz AO's on aluminum). This result may be interpreted as meaning that in these atoms the promotion of the valence eletrons occurs from the s^2p ground state to the sp^2 valence state. The strong electron-accepting ability of these compounds may also partly be attributed to the existence of pure, or almost-unfilled π orbitals on the metal atom.

The Energy Levels of Monomers.—The calculated energy values of the highest-occupied orbitals (HO) and the lowest-vacant orbitals (LV) are presented in Table IV(a) for the boron compounds and in Table IV(b) for the aluminum compounds. The LV energies fall in a definite range, i. e., -9—-6 eV. for the boron compounds and -7—-5 eV. for the aluminum compounds; these values are considerably lower than those of the carbon atoms of saturated bonds. (The LV energies calculated by Hoffmann[3] are $+3.13$ eV. for the ethane and -8.23 eV. for the ethylene molecule.) Thus, these compounds might easily accept the electrons of donors and are very liable to the attack of nucleophilic reagents. Furthermore, these LV orbitals are pπ type orbitals, and the electron in them is almost localized on the pπ orbital of the boron or aluminum atom. For example, the atomic orbital population in the LV orbital is calculated to be 1.00 on the boron or aluminum atom in the hydrides (a pure pπ orbital), 0.97 on the aluminum atom in trimethylaluminum, and 0.94 on the aluminum atom in the aluminum trichloride monomer.

TABLE IV. THE HO AND LV ORBITAL ENERGY (eV.) OF VARIOUS MONOMERS

	HO	LV
(a) B-Compounds		
BH_3	-13.91	-8.53
BF_3	-20.71	-6.25
$BH(CH_3)_2$	-12.50	-6.97
$B(CH_3)_3$	-12.36	-6.23
$BC_2H_3(CH_3)_2$	-12.08	-8.91
BCl_3	-14.58	-5.91
(b) Al-Compounds		
AlH_3	-13.86	-6.67
$Al(CH_3)_3$	-12.14	-5.01
$Al(C_2H_5)_3$	-11.54	-5.08
$Al(CH_3)_2Cl$	-12.12	-4.91
$AlCl_3$	-14.94	-4.73

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[5] P. A. Casabella, P. J. Bray and R. G. Barnes, *J. Chem. Phys.*, **30**, 1393 (1959).

With regard to the value of the HO energy, unfortunately, there seem to be no experimental results available to compare it with.

π-Conjugation in Monomers.—The magnitude of the π-conjugation has been supposed to be a measure of the stability of these monomer molecules. For instance, Mulliken described how the existence of trimethyl and trihalogenated boron monomers depends on the extent of stabilization due to π-conjugation in these monomers (hyperconjugation in the trimethylborane monomer).[6] Similarly, Ritter and his co-workers discussed the relation between the π-conjugation energy and the acid strength or the rate of disproportionation in vinyl boron derivatives.[7]

According to Table III, the orders of the magnitude of the $N(z)$ of boron atoms in various monomers are $BCl_3 > B(C_2H_3)_3 > B(C_2H_3)_2(CH_3) > BC_2H_3(CH_3)_2 > B(CH_3)_3 > BH(CH_3)_2 > BF_3 > BH_3$. Except for BF_3,* this order is reasonable, since it is known that BH_3 and $BH(CH_3)_2$ exist as in the dimeric form, and trimethyl boron and trihalogenated boron, as in the monomeric form.[6] The magnitude of $N(z)$ in aluminum compounds is smaller than that of the respective boron compounds, and the $N(z)$ of aluminum in the $AlCl_3$ monomer, which is the largest of the aluminum compound monomers presented here, is comparable to the $N(z)$ of boron in the $BH(CH_3)_2$ monomer; in fact, these two compounds are known to form dimers at room temperature.

Good and Ritter[7] treated the π systems of vinyl boron compounds by a simple LCAO method. The calculated total π electron densities for the $C_1{=}C_2{-}B$ system (dimethylvinylborane) are 0.84 on atom C_1, 1.05 on C_2, and 0.11 on the boron atom, whereas the $N(r)$ values of these π orbitals in the present treatment are 0.941, 1.003, and 0.150 respectively. Furthermore, they obtained the π densities of the boron atom as 0.21 in monomethyl divinylborane and as 0.29 in trivinylborane, while our values are 0.175 in the former and 0.207 in the latter.

The π-conjugation energies were also calculated by Good and Ritter.[7] These values were 4 kcal./mol. in dimethylvinylborane, 8.0 kcal/mol. in monomethyl divinylborane, and 11.8 kcal./mol. in trivinylborane. The results of our calculations are 2.4, 7.4, and 15.0 kcal./mol. respectively (our values are obtained as the differences between the π orbital energy of the isolated ethylene molecule and those in methyl vinylboranes.). These two sets of results seem to be comparable with one other. The π-conjugation energies of the BCl_3, BF_3 and $AlCl_3$ monomers are obtained as 18.2, 6.7, and 7.4 kcal./mol. respectively. In BF_3, the value seems somewhat too small.

The Electronic Structure of the Monomer and the Ion.—Now the change in the electronic structure between the monomer (MX_3) and its ion (MX_4^-) will be discussed. A remarkable difference is indicated in the following two points. One is concerned with the LV orbital energy, and the other, with the $N(z)$ value of the boron and aluminum atoms. The energies of HO and LV orbitals are listed in Table V, while the $N(r)$ values of the boron and aluminum atoms in various compounds are given in Table VI.

TABLE V. THE HO AND LV ORBITAL ENERGIES OF SOME MONOMERS (MX_3) AND CORRESPONDING IONS (MX_4^-)

	HO	LV
BH_3	−13.91	− 8.53
BH_4^-	−13.71	+10.02
BF_3	−20.71	− 6.25
BF_4^-	−20.71	+ 8.82
AlH_3	−13.86	− 6.67
AlH_4^-	−13.71	+ 6.98
$AlCl_3$	−14.94	− 4.73
$AlCl_4^-$	−14.81	+13.21

TABLE VI. THE $N(r)$ VALUES OF BORON AND ALUMINUM ATOMS IN MONOMERS AND IONS

	N(s)	N(x)	N(y)	N(z)
BH_3	0.912	0.825	0.825	0.0
BH_4^-	0.847	0.816	0.816	0.816
BF_3	0.295	0.122	0.122	0.082
BF_4^-	0.298	0.110	0.110	0.110
AlH_3	0.850	0.497	0.497	0.0
AlH_4^-	0.808	0.480	0.480	0.480
$AlCl_3$	0.505	0.206	0.206	0.111
$AlCl_4^-$	0.504	0.202	0.202	0.202

(s: 2s or 3s AO; x, y, z: 2px or 3px, 2py or 3py, 2pz or 3pz AO's)

The difference in HO orbital energy between the monomer and its ion is small, whereas the LV level of ions lies much higher than that of the monomers, corresponding to the weak electron-accepting ability of these ions. The most important change in $N(r)$ value between the monomer and its ion occurs on the pz orbital of the boron and aluminum atoms. The $N(z)$ value of the ions is much larger than that of the corresponding monomers, naturally indicating that the electron-accepting abilities of monomers disappears in ions.

These saturation phenomena can be recognized from the charge migrations. In the $MX_3 + X^- \rightarrow MX_4^-$ (M = boron or aluminum) process, for instance the magnitude of the charge migration from X^- to MX_3 may be roughly estimated by the unit charge in X^- minus the net charge of X

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6) R. S. Mulliken, *Chem. Revs.*, **41**, 207 (1947).

7) C. D. Good and D. M. Ritter, *J. Am. Chem. Soc.*, **84**, 1162 (1962).

* The calculated π overlap values are 0.179 for the B-F bond in BF_3 and 0.124 for B-Cl in BCl_3, but the obtained π charge of the boron atom in BF_3 is smaller than that of BCl_3.

in MX_4^-. This quantity is calculated as 0.824e in BH_3, as 0.157e in BF_3, as 0.561e in AlH_3 and as 0.277e in $AlCl_3$. Many of these transferred electrons enter into the vacant $p\pi$ orbitals of the boron or aluminum atom, as has been shown above.

The Electronic Structures of the Two Configurations of the B_2Cl_4 Molecule.—Two configurations of the tetrachlorodiborine, B_2Cl_4, have been considered.[8] The one is the planar configuration belonging to the symmetry group, D_{2h}, while the other has a D_{2d} configuration in which two BCl_2 planes are perpendicular to each other. These two configurations are shown in Fig. 2. The molecule with the D_{2d} symmetry exists in liquid and gas phases, and the D_{2h} molecule, in the crystal form.[8]

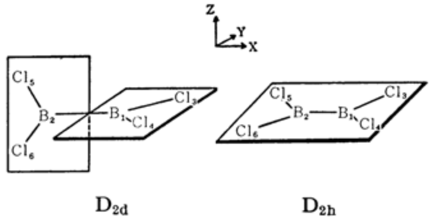

Fig. 2. The D_{2d} and D_{2h} configurations of B_2Cl_4.

TABLE VII. ENERGY (eV.) OF SEVERAL LEVELS AND THEIR IRREDUCIBLE REPRESENTATION OF D_{2d} AND D_{2h} B_2Cl_4 MOLECULES

D_{2d}		D_{2h}	
e*	−6.46	b_{3g}	−4.39
	−6.46	b_{2u}*	−8.03
a_1**	−11.19	a_g**	−11.32
e	−14.54	b_{2g}	−14.47
	−14.54	b_{3u}	−14.60
a_2***	−14.96	a_u***	−14.95
b_1***	−14.99	b_{1g}***	−15.01
b_2	−15.27	b_{1u}	−15.09
e	−15.33	b_{2g}	−15.17
	−15.33	b_{3g}	−15.44
e	−15.55	b_{3u}	−15.56
	−15.55	b_{2u}	−15.58
a_1	−15.74	a_g	−15.85
b_2	−16.52	b_{1u}	−16.52
a_1	−17.39	a_g	−17.39
e	−25.04	b_{2g}	−24.86
	−25.04	b_{3u}	−25.22
b_2	−26.85	b_{1u}	−26.78
a_1	−27.54	a_g	−27.59

* The LV levels.
** The HO levels.
*** The lone pair orbitals of the chlorine atoms.

The energies of all of the occupied orbitals and lowest-unoccupied orbitals of the molecules in these two configurations are listed in Table VII, together with their irreducible representations. The correspondence of irreducible representations between these two groups is as follows:

D_{2d} (perpendicular)	D_{2h} (planar)
a_1	a_g
b_2	b_{1u}
e	b_{2g}, b_{3g}, b_{2u}, b_{3u}

The differences between the corresponding orbital energies of these two groups are seen to be very small. (The same values of the bond distances are adopted for these two forms as is shown in Table II.) The energy of the e orbital in the D_{2d} may be compared with the sum of the two split orbital energies in the D_{2h}. The LV orbital is the e orbital in the D_{2d}, while the lowest is b_{2u} and the next is b_{3g} in the D_{2h} molecule. The difference in the LV orbital energy between these two forms will be discussed later, again from the point of view of the electronic structrue.

The $M(X)$, $N(r)$ and $M(X\text{–}Y)$ values for the two forms are collected in Table VIII. The corresponding data for these two are almost equal to each other. The atomic orbital bond population between the rth and sth AO's is here denoted by $N(r\text{–}s)$. The $N(z(B_1)\text{–}z(B_2))$ value is -0.001 in the D_{2d} form and $+0.002$ in the D_{2h}, while the $N(y(B_1)\text{–}y(B_2))$ value is -0.001 in the D_{2d} form and -0.009 in the D_{2h} form. Accordingly, the B–B bond in these two configurations is almost purely of a σ type and does not exhibit the double-bond character. This result leads to the conclusion that the rotation about the B–B bond is very easy and that the conversion between two forms may be carried out without a great hindrance.

However, as was discussed above, the situation is remarkably different in the LV orbitals. That is, the LV e orbital of the D_{2d} molecule splits into b_{2u} and b_{3g} in the D_{2h} molecule, where b_{2u} is the lowest. The calculated coefficients of the AO's in these orbitals are collected in Table IX, together with those of the HO orbitals. It may be seen from the table that the LV orbitals in the D_{2d} molecule, which is twofold degenerate, are nonbonding orbitals localized on the B_1 and

TABLE VIII. THE $M(X)$, $N(r)$ AND $M(X\text{–}Y)$ VALUES OF THE D_{2d} AND D_{2h} MOLECULES

	$M(B_1)$	$N(r)$ of B_1				M(B–B)	M(B–Cl)	M(Cl)
		s	x	y	z			
D_{2d}	2.137	0.815	0.744	0.400	0.178	0.836	0.708	7.432
D_{2h}	2.133	0.819	0.739	0.397	0.178	0.830	0.712	7.433

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[8] E. g., "Progress in Boron Chemistry," Ed. by H. Steinberg and A. L. McClossey, Vol. I, Pergamon Press, New York (1964).

TABLE IX. THE HO AND LV ORBITALS IN THE D_{2d} AND D_{2h} B_2Cl_4 MOLECULES

(a) The D_{2d} molecule		
LV	e	$1.03z_{B1}+0.02z_{B2}-0.33(z_{C13}+z_{C14})-0.06(s_{C15}-s_{C16})-0.09(x_{C15}-x_{C16})+0.04(z_{C15}+z_{C16})$
	e	$1.03y_{B2}+0.02y_{B1}-0.33(y_{C15}+y_{C16})-0.06(s_{C12}-s_{C14})+0.09(x_{C12}-x_{C14})+0.04(y_{C12}+y_{C14})$
HO	a_1	$0.23(s_{B1}+s_{B2})-0.44(x_{B1}-x_{B2})+0.32(x_{C13}+x_{C14}-x_{C15}-x_{C16})-0.07(s_{C13}+s_{C14}+s_{C15}+s_{C16})$ $+0.05(y_{C13}-y_{C14}+y_{C15}-y_{C16})$
(b) The D_{2h} molecule		
	b_{3g}	$0.84(z_{B1}-z_{B2})-0.23(z_{C13}+z_{C14}-z_{C15}-z_{C16})$
LV	b_{2u}	$0.65(z_{B1}+z_{B2})-0.25(z_{C13}+z_{C14}+z_{C15}+z_{C16})$
HO	a_g	$0.24(s_{B1}+s_{B2})-0.44(x_{B1}-x_{B2})+0.31(x_{C13}+x_{C14}-x_{C15}-x_{C16})-0.07(s_{C13}+s_{C14}+s_{C15}+s_{C16})$ $+0.07(y_{C13}-y_{C14}+y_{C15}-y_{C16})$

B_2 atoms respectively, whereas the LV orbital of the D_{2h} molecule is a π type B–B bonding and the next LV is a π type B–B anti-bonding. Thus, if a D_{2d} molecule receives two electrons, these will enter into the LV orbitals, localizing on the 2pz orbital of the B_1 atom and on the 2py orbital of the B_2 atom, so that this compound will behave like a biradical. In the D_{2h} molecule, these added electrons will serve to strengthen the B–B π conjugation, behaving like tetrachloroethylene.

It is hoped that these results will be examined by future experiments.

The calculations have been carried out on an IBM 7090 computer at Japan IBM Co., with the permission of the UNICON committee, whom the authors wish to thank.

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