A Molecular Orbital Study of Bonding in the Ammonia-Borane & Carbonyl-Borane Complexes

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SCFMO calculations of the CNDO/2 level have been performed for the ground states of the donors NH_3, CO; the acceptor BH_3; and the donor-acceptor complexes $BH_3-NH_3OC-BH_3$. The energetics of the gradual formation of the $N-B$ and $C-B$ bonds over a wide range of distances between the donors and acceptor moieties have been studied. The $N-B$ and $C-B$ bond lengths have been optimized and found to be equal to their experimental values. The molecular orbitals of the H_3N-BH_3 and OC-BH_3 complexes have been transformed by pair-wise unitary transformation to obtain a set localized molecular orbitals.

Introduction

THERE have been considerable interests, both theoretical and experimental, to investigate the nature of bonding in these donor-acceptor complexes[1-10] of BH_3 which acts as a Lewis acid. Theoretical interest here is mainly on the nature of the newly formed 'N—B' and 'C—B' bonds. Molecular orbital studies of both, *ab-initio*[1-3,8-10] as well as semi-empirical[4,7] nature have been performed for these molecules and the bonding have been analysed in terms of Mulliken Population Analysis. But no attempt seems to have been made so far to obtain a set of localized molecular orbitals for these molecules. In this investigation we have attempted to present a detailed analysis of bonding in these molecules in terms of a set of energy localized molecular orbitals, which we have generated from our semi-empirical self-consistent field molecular orbital (SCFMO) wave functions of $H_3N—BH_3$ and OC—BH_3 complexes.

Calculations and Results

The wave functions for the ground states of BH_3, NH_3, CO, $H_3N—BH_3$, OC—BH_3 have been calculated by the well known CNDO/2 formalism of Pople and coworkers[11]. STO basis sets have been used and the core orbitals of C, B, N, O atoms have been neglected. The orbital parameters have been taken from literature[11]. Overlap and coulomb repulsion integrals needed to calculate the elements of the Fock-Roothaan matrices have been evaluated using the explicit equations derived by Roothaan[12]. N—B and C—B bond axis have been made to coincide with the Z-axis of the coordinate system used. A series of calculations over a range of N—B and C—B dis-

tances have been performed to see the gradual fall of potential energy as the molecules are formed through gradual approach of the donor moieties towards the fixed BH_3 acid moiety. The C_3-proper rotational axis has been preserved throughout this approach, and for $H_3N—BH_3$, the staggered form has been found to be the preferred conformation. Both $H_3N—BH_3$ and OC—BH_3 belong to the point group C_{3v} and as such the symmetry classification of the basis atomic orbitals of B, N, C, O atoms are as follows:

$B(2S)$, $B(2P_z)$, $N(2S)$, $N(2P_z)$, $C(2S)$, $C(2P_z)$, $O(2S)$, $O(2P_z)-A$; $[B(2P_x), B(2P_y)]$, $[N(2P_x), N(2P_y)]$, $[C(2P_x), C(2P_y)]$, $[O(2P_x), O(2P_y)]-E$.

The hydrogen atoms of BH_3 and NH_3 moieties span a reducible representation which can be decomposed into the irreducible components conforming to the A_1 and E symmetry through the transformation

$$[H_1H_2H_3]\begin{bmatrix} 1 & 1 & 0 \\ 1 & -1 & 1 \\ 1 & -1 & -1 \end{bmatrix} = [G(A_1)G(E)G(E)]$$

where H_1, H_2, H_3 refer to the three bihydrogens of BH_3 or NH_3. The N—B and C—B bonds are of pivotal importance in these complexes. Hence, we have calculated the wave functions for these over a long range of N—B and C—B distances, keeping all the other bond distances and bond angles at their experimental values[13,14]. The potential energy curve obtained by plotting the total energies against the N—B and C—B distances is shown in Fig. 1. The optimized N—B and C—B distances computed from the curve have been found to be 1·56 Å and 1·54 Å respectively, the same as their experimental values. The wave function of $H_3N—BH_3$ and OC—BH_3 are listed in Tables 1 and 2 respectively.

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A set of localized molecular orbitals has been obtained from the delocalized set for H_3N-BH_3 and OC—BH_3 by carrying out successive sequences of unitary transformations over orbital pairs following the method of Ruedenberg and coworkers[15]. That such a transformation over a set of semi-empirically determined approximate molecular orbitals leads to meaningful localization has been demonstrated by Sinanogli and coworkers[16]. The localized molecular orbitals (LMO) for BH_3—NH_3 and BH_3—CO are listed in Tables 3 and 4 respectively. Mulliken Population Analysis[17] for the donors and acceptor

TABLE 1 — EIGEN VECTORS AND EIGEN VALUES OF BH_3—NH_3 AT THE EQUILIBRIUM GEOMETRIES

AOS / MOS	$1a_1$	$2a_1$	$1e$	$2e$	$3a_1$	$3e$	$4e$
B(2S)	0·277	0·502	0·0	−0·204	−0·249	0·0	−0·017
B($2P_x$)	0·001	0·094	−0·0	0·247	0·035	0·0	−0·603
B($2P_y$)	0·0	−0·0	0·265	0·0	0·0	−0·603	−0·0
B($2P_z$)	−0·219	0·065	0·0	0·004	−0·566	0·0	−0·013
H(B)	0·083	0·316	0·113	−0·031	−0·262	−0·524	−0·309
H(B)	0·083	0·250	0·0	−0·213	−0·296	−0·0	0·598
H(B)	0·083	0·316	−0·113	−0·031	−0·262	0·524	−0·308
N(2S)	0·752	−0·104	−0·0	0·027	0·156	−0·0	0·004
N($2P_x$)	0·006	0·289	−0·0	0·669	0·035	−0·0	0·197
N($2P_y$)	0·0	−0·0	0·730	0·0	0·0	0·197	0·0
N2Pz	0·030	0·513	0·0	−0·263	0·656	−0·0	0·009
H(N)	0·312	0·035	−0·0	0·528	−0·065	−0·0	0·179
H(N)	0·309	−0·239	0·431	−0·164	−0·132	0·156	−0·092
H(N)	0·309	−0·239	−0·431	−0·164	−0·132	−0·156	−0·092
Eigen values (a.u.)	−1·652	−0·974	−0·933	−0·928	−0·723	−0·553	−0·5513

TABLE 2 — EIGEN VECTORS AND EIGEN VALUES OF BH_3—CO AT EQUILIBRIUM GEOMETRIES

AOS / MOS*	$1a_1$	$2a_1$	$3a_1$	$1e$	$2e$	$4a_1$	ϵ	$4e$
B(2S)	0·085	0·518	−0·240	0·0	−0·102	−0·299	−0·004	0·0
B($2P_x$)	0·0	0·008	−0·082	−0·0	0·227	0·238	−0·626	0·0
B($2P_y$)	0·0	0·0	0·0	0·244	0·0	−0·0	−0·0	−0·627
B($2P_z$)	0·092	0·188	0·102	0·0	−0·023	0·529	0·003	−0·0
H(B)	0·023	0·230	−0·203	−0·0	0·093	−0·276	−0·576	0·0
H(B)	0·025	0·225	−0·143	0·110	−0·085	−0·323	0·279	−0·493
H(B)	0·025	0·225	−0·143	−0·110	−0·085	−0·323	0·279	0·493
C(2S)	0·468	0·509	0·203	−0·0	0·015	0·320	0·005	−0·0
C($2P_x$)	0·002	0·041	−0·216	−0·0	0·523	0·008	−0·012	0·0
C($2P_y$)	0·0	−0·0	0·0	0·568	0·0	0·0	−0·0	−0·010
C($2P_z$)	0·306	−0·407	0·251	−0·0	0·165	−0·385	−0·002	0·0
O(2S)	0·800	−0·280	−0·340	0·0	−0·121	0·018	−0·001	0·0
O($2P_x$)	−0·0	0·028	−0·267	−0·0	0·715	0·117	0·348	−0·0
O($2P_y$)	−0·0	0·0	0·0	0·771	0·001	0·0	0·0	0·347
O($2P_z$)	−0·173	−0·192	−0·711	0·0	−0·295	0·283	0·0	−0·0
Eigen values (a.u.)	−1·789	−1·264	−0·957	−0·916	−0·915	−0·691	−0·617	−0·615

*Only the occupied MO's are shown here.

TABLE 3 — LOCALIZED MOLECULAR ORBITALS FOR BH_3—NH_3

AO / MO	$\sigma(B-H_1)$	$\sigma(B-H_2)$	$\sigma(B-H_3)$	$\sigma(N-B)$	$\sigma(N-H_1)$	$\sigma(N-H_2)$	$\sigma(N-H_3)$
B(2S)	−0·354	−0·358	0·355	−0·224	−0·009	−0·028	0·028
B($2P_x$)	−0·269	0·531	0·267	0·0	−0·072	0·036	−0·036
B($2P_y$)	−0·461	−0·001	−0·461	0·0	0·0	−0·062	−0·062
B($2P_z$)	−0·171	−0·173	0·171	0·418	0·051	0·037	−0·037
H_1(B)	−0·746	0·004	−0·009	0·006	0·012	0·020	0·032
H_2(B)	0·015	−0·747	−0·013	0·006	−0·039	0·020	−0·020
H_3(B)	0·010	0·006	0·746	0·006	0·012	−0·032	−0·020
N(2S)	0·013	0·013	−0·013	−0·457	−0·365	−0·359	0·359
N($2P_x$)	−0·017	−0·001	0·017	−0·009	−0·616	0·308	−0·308
N($2P_y$)	−0·009	0·0	−0·009	0·0	0·0	−0·534	−0·534
N($2P_z$)	−0·004	−0·004	0·004	−0·751	0·253	0·259	−0·259
H_1(N)	0·013	−0·030	−0·013	−0·009	−0·642	0·004	−0·004
H_2(N)	0·002	0·002	0·040	−0·009	0·004	−0·643	−0·004
H_3(N)	−0·040	0·002	−0·002	−0·009	0·004	0·004	0·643

TABLE 4 — LOCALIZED MOLECULAR ORBITALS FOR BH₃-CO

AO / MO	$\sigma(B-H_1)$	$\sigma(B-H_2)$	$\sigma(B-H_3)$	$\sigma(C-B)$	$\sigma(C-O)$	$\pi_x(C-O)$	$\pi_y(C-O)$	i.p (O)
B(2S)	−0·338	−0·356	−0·356	−0·253	−0·009	−0·023	0·0	−0·009
B(2P$_x$)	−0·552	0·270	0·271	0·006	0·003	0·029	0·0	0·0
B(2P$_y$)	0·0	−0·475	0·475	0·0	0·0	0·0	0·031	0·0
B(2P$_z$)	0·173	0·192	0·192	−0·479	−0·020	0·023	0·0	−0·017
H$_1$(B)	−0·712	−0·003	−0·003	0·0	0·002	−0·059	0·0	0·0
H$_2$(B)	−0·002	−0·716	−0·005	0·0	0·007	0·033	−0·054	0·0
H$_3$(B)	−0·002	−0·005	−0·716	0·0	0·007	0·033	0·053	0·0
C(2S)	0·007	0·014	0·014	−0·689	0·383	−0·007	0·0	0·011
C(2P$_x$)	−0·194	0·039	0·039	0·032	0·036	0·528	−0·002	0·0
C(2P$_y$)	0·0	0·135	0·135	0·0	0·0	0·002	0·534	0·0
C(2P$_z$)	0·023	0·018	0·018	0·480	0·513	−0·032	0·0	−0·009
O(2S)	−0·007	−0·008	−0·008	0·002	0·463	−0·032	0·0	−0·796
O(2P$_x$)	0·077	−0·021	−0·021	−0·001	0·039	0·842	−0·003	−0·008
O(2P$_y$)	0·0	0·058	−0·058	0·0	0·0	0·003	0·841	0·0
O(2P$_z$)	0·008	0·011	0·011	−0·005	−0·609	0·030	0·0	−0·605

molecules as well as the donor-acceptor complexes have been carried out and the results are listed in Table 5.

Discussion

From Tables 1 and 2 it is evident that the electronic structure of the ground states of the complexes are

$H_3N—BH_3$: $(1a_1)^2(2a_1)^2(1e)^2(2e)^2(3a_1)^2(3e)^2(4e)^2$
$OC—BH_3$: $(1a_1)^2(2a_1)^2(3a_1)^2(1e)^2(2e)^2(4a_1)^2(3e)^2(4e)^2$
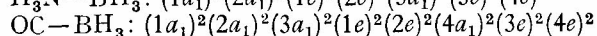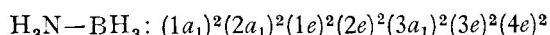
The $(1e, 2e)$ MO pair as well as the $(3e, 4e)$ pair in $H_3N—BH_3$ is found to satisfy the degeneracy requirements of molecular orbitals of this symmetry remarkably well. Similar is the situation for $OC—BH_3$ MOS. The highest occupied MOS for both these compounds are of e-symmetry. The same result was obtained by Veillard *et al.*[2] for the $BH_3—NH_3$ molecule in their *ab-initio* Gaussian basis set calculation, excepting that they found $2a_1$ MO (in their case, $4a_1$) higher in energy than the lowest e-type MO pair.

The LMOs listed in Tables 3 and 4 reveal many interesting aspects of the nature of bonding in these compounds.

First, it is observed that each LMO very nearly represents a bond in the conventional sense, i.e. two-centre bonds, lone pairs, etc. For $H_3N—BH_3$, there are three B—H sigma type bonds designated as σ (B—H$_i$) in each of which baron atom uses 2S and 2p type atomic orbitals. Similarly, three N—H sigma bonds, σ (N—H$_i$) are easily discernible. The newly formed N—B bond, which imparts stability to the complex can be clearly seen to be purely σ-type and involves only the B(2S, 2p_σ) and N(2S, 2p_σ) atomic orbitals. Similarly, in the OC—BH₃ molecule, there are three σ(B—H$_i$) bonds, one σ(C—O) bond, and two π(C—O) bonds. Here there is also a lone pair on the O atom which is seen to be formed by O(2S, 2p_σ) atomic orbitals. The newly formed C—B bond is again found to be exclusively σ type and is composed of C(2S, 2p_σ) and B(2S, 2p_σ) atomic orbitals, the off-centre contributions being nearly zero.

Second interesting feature of the bonding in these compounds is the nature of the atomic hybrids used in such bonding. To examine the hybridization,

we have neglected the vanishingly small off-centre contributions and renormalized each bond MOS and then expressed an atomic hybrid (normalized) as

ϕ(hybrid) $= a(2S) + b(2p)$; (with $a^2 + b^2 = 1$) where $2p = b_1(2P_x) + b_2(2P_y) + b_3(2P_z)$ (with $b_1^2 + b_2^2 + b_1^2 = 1$)

Then the nature of hybridization is simply estimated from the coefficients a and b.

In $H_3N—BH_3$ molecule, the boron atom hybrid is computed to be $Sp^{2.5}$-type in B—H sigma bonds while in the N—B bond it is $sp^{3.8}$-type. But the hybrids used by N atom in N—H and N—B bonds are $sp^{3.4}$ and $sp^{2.7}$-types respectively. Such types of non-conventional hybrids are rather common and have been observed in boron compounds by Lipscomb *et al.*[18] and Baird and Datta[19]. In the OC—BH₃ molecule the hybrid type for boron in B—H bonds is $sp^{2.9}$ and in C—B bond $sp^{3.6}$, while that for carbon atom in C—B bond is s^2p. The lone pair on the oxygen atom is found to be a $s^{1.8}p$-type hybrid. In the C—O sigma bond, however, the C-hybrid is $sp^{1.8}$ and O-hybrid is $sp^{1.7}$. Some interesting trend may be observed in these cases. The nature of B-hybrid in the B—H sigma bonds are very similar in $H_3N—BH_3$ ($sp^{2.5}$) and OC—BH₃ ($sp^{2.9}$), thus exhibiting the expected "near transferability" of hybrids in similar compounds[15]. In the newly formed N—B and C—B sigma bonds, the hybridization status of boron is $sp^{3.8}$ and $sp^{3.6}$ respectively. The relatively higher proportion of P-character in the former bond is to be expected on the basis of a principle, introduced by Bent[20], that higher S-character hybrid is generally used in bonding with atoms of lower electronegativity. This trend in the hybridization pattern is also found to be nicely exhibited on comparing B-hybrids in B—H ($sp^{2.5}$) with B—N ($sp^{3.8}$) in the $H_3N—BH_3$ complex as well as on comparing the C hybrids in the C—B (s^2p) and C—O ($sp^{1.8}$) in the OC—BH₃ complex. It is also interesting to note that in the N—B sigma bond, the contribution of nitrogen is about 78% and that of boron is 22% and in C—B sigma bond, the contribution of carbon is about 70% and that of boron is 30%.

The changes in the total energy with gradual approach of the donor and the acceptor moieties,

conserving all the while the C_3, and σ_v-elements are shown in Figs. 1 and 2. The total energy is seen to be slowly falling, without encountering any activation hill. In Figs. 1 and 2 are also plotted the total overlap charge densities, ρ, of the bonds N—B and C—B. The ρ-values at each distance is computed from the equation

$$\rho = \sum_{i<j} P_{ij}\, S_{ij}\, (i,\ j \text{ run over relevant orbitals})$$

where

$$P_{ij} = 2\Sigma_\mu C_{i\mu} C_{j\mu}\ (\mu \text{ goes up to the number of occupied orbitals})$$

The charge density is found to be slowly building up initially and then gradually picks up and the rate becomes quite high as the N—B or C—B distance approaches the equilibrium value.

The distribution of electronic charge in the complexes can be analysed from the Table 5, where the orbital populations[17] in these complexes as well as those in the free donor and acceptor moieties are shown. The gross atomic populations in all these molecules, computed from Table 5 are shown in Scheme 1.

It can be observed that a total of about 0·50e charge is transferred from NH$_3$ moiety to BH$_3$ in the H$_3$N—BH$_3$ complex. This transfer of charge causes interesting redistribution of electronic charges in the BH$_3$ moiety. Each H atom now acquires 0·12e charge, i.e. about 0·06e more than in the free BH$_3$. A part of this total of 0·18e for the three hydrogen may have been taken from the B(2S) orbital which has now a population about 0·16e less than in free BH$_3$.

TABLE 5 — ELECTRONIC POPULATION ANALYSIS

AO	BH$_3$	NH$_3$	CO	BH$_3$—NH$_3$	BH$_3$—CO
B(2S)	1·027			0·864	0·866
B(2P$_x$)	0·887			0·869	0·903
B(2P$_y$)	0·887			0·867	0·905
B(2P$_z$)	0·0			0·538	0·669
H$_1$(B)	1·066			1·117	1·021
H$_2$(B)	1·066			1·121	1·033
H$_3$(B)	1·066			1·117	1·033
N(2S)		1·433		1·202	
N(2P$_x$)		1·074		1·141	
N(2P$_y$)		1·074		1·142	
N(2P$_z$)		1·653		1·528	
H$_1$(N)		0·922		0·828	
H$_2$(N)		0·922		0·831	
H$_3$(N)		0·922		0·831	
C(2S)			1·689		1·244
C(2P$_x$)			0·591		0·644
C2P$_y$)			0·591		0·644
C(2P$_z$)			1·086		0·993
O2S			1·700		1·698
O(2P$_x$)			1·409		1·437
O(2P$_y$)			1·409		1·429
O(2P$_z$)			1·524		1·477
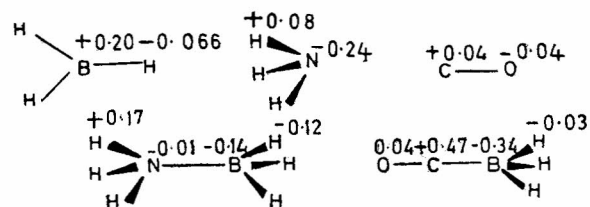
Scheme 1 — Gross atomic population in BH$_3$, CO, NH$_3$, BH$_3$—NH$_3$ and BH$_3$—CO
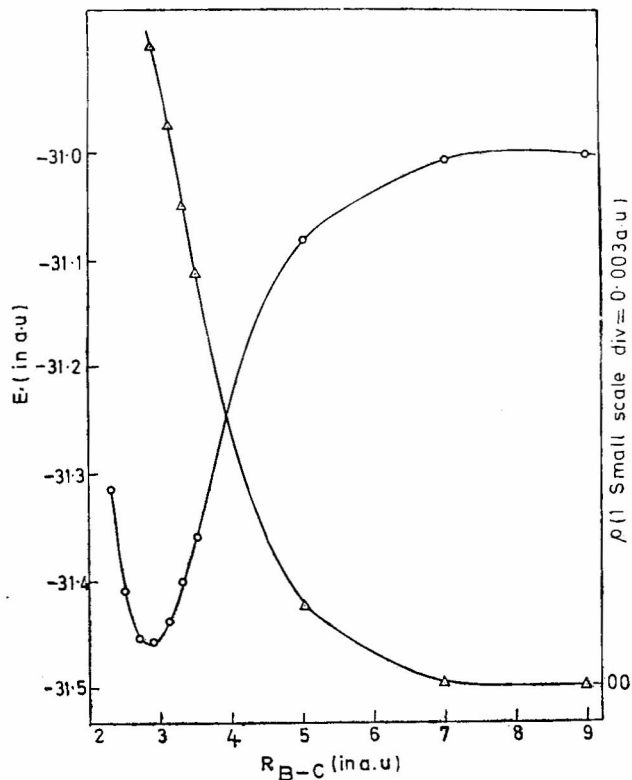
Fig. 1 — B—C distance versus total energy (○—○, E in a.u.) and overlap density (△—△, ρ in a.u.)
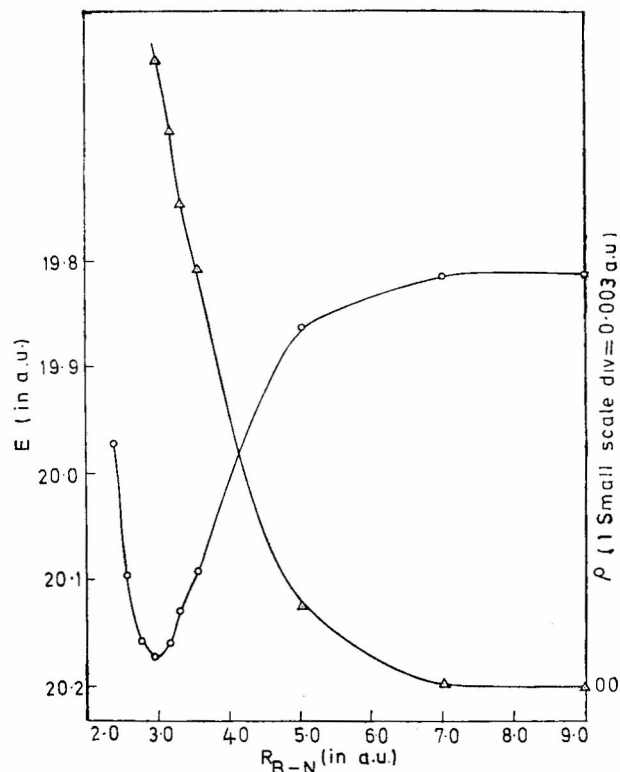
Fig. 2 — B—N distance versus total energy (○—○, E in a.u.) and overlap density (△—△, ρ in a.u.)

It is interesting to note that the (P_x, P_y) orbitals on boron has now slightly less (0·02e each) charge than in free BH_3. This amount must have been transferred to the three hydrogen on boron through π-type interaction with $G_x(E)$, $G_y(E)$ pseudo π-orbitals. The principal acceptor orbital $B(2P_z)$ has acquired 0·54e charge, 0·50 from the donor, NH_3 and the rest coming from the $B(2S)$. The final result of all these redistribution is that boron atom is negatively charged, to the extent of $-0·14$e. Of the total charge of 0·50e donated by NH_3, a significant amount, 0·27e may be seen to be coming from the three hydrogen on NH_3. The $N(2S)$ and $N(2P_z)$ donate 0·23 and 0·12e respectively. Again, it is interesting to note that $N(2P_x)$, $N(2P_y)$ orbitals have gained 0·07e each, after complex formation. This gain must have been taken place from the three hydrogens on N atom through π-type interaction of the $N(P_x, P_y)$ and the $G_x(E)$, $G_y(E)$ orbitals composed from the three hydrogen atoms. The possibility of $B(2P_\pi)$ orbitals back donating to $N(2P_\pi)$ may be discounted on the basis that the $B(2P_\pi)$ orbitals have lost only 0·08e and is thus insufficient to account for a total gain of 0·14e by the $N(2P_\pi)$ orbitals.

In the $OC-BH_3$ complex, the gross charge on oxygen atom is found to be same before and after complex formation. Although there is a small drift of charge (0·04e) through $O(2P_z)$ but the $O(2P_\pi)$ orbitals has gained an equal amount. The carbon atom, however, is found to be strongly positive ($+0·47$e) and boron atom is much more negative ($-0·34$e) than in NH_3-BH_3. The charge donation from carbon is seen to be mainly through the $C(2S)$ orbital (0·45e). The principal acceptor $B(2P_z)$ orbital has gained 0·67e. The H atoms on boron in this complex have lost some charge (0·03e each) instead of gaining, as was observed in H_3N-BH_3 complex. The effects of fluorine substitution in

the acidic moiety on the nature of bonding and charge redistribution are currently being investigated in our laboratory.

Acknowledgement

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