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On the Stability of BH_3 and BF_3 Adducts with BF, CO and N_2

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Ab-initio SCF MO calculations have been carried out on the adducts of borane and boron trifluoride with carbon monoxide, dinitrogen, and boron fluoride. The calculations correctly predict that BH_3 forms stronger complexes than BF_3 and that CO forms stronger complexes than N_2. It is predicted that the complexes of BF should be even stronger. These trends can be understood from the energies and wave functions of the HOMO and LUMO orbitals of the components.

INTRODUCTION

BH_3CO is a surprisingly stable species, having a calculated dissociation energy into BH_3 and CO of 75 kJ/mol[1]. The species BF_3N_2 and BF_3CO are known as van der Waals complexes, having been detected spectroscopically in supersonic nozzle beams with binding energies presumably no greater than *ca.* 17 kJ/mol.[2] BH_3N_2 has not been reported but presumably would also exist only as a van der Waals complex. There are two features of interest in this family. Firstly that BH_3 appears to form a stronger complex than BF_3 and secondly that CO forms a stronger complex than N_2. There have been some qualitative explanations of these trends and some MO calculations which support the facts[3–10]. However, the two are not in all respects consistent.

Several different types of study have been previously carried out with some of the adducts analysed in this work. The system that has received most attention is BH_3CO. In one of these studies[4] (non-empirical SCF) it was pointed out that the electron donation is mainly from the 2*s* orbital of the carbon to the empty $2p_z$ orbital of the boron. This gives rise to the major component of the B—C σ bond-order. The authors also point out that electrons migrate from the oxygen *via* the carbon towards the boron. Also, the B—C π-bond interaction is slightly bonding in character, which the authors believe indicates a hyperconjugative effect by the BH_3 group.

Other authors[6,11–13] also discuss the importance of hyperconjugation in BH_3CO, pointing out, amongst other things, the expected shortening of the B—C distance and the increase in the B—H bond distance. Although the first factor does occur (by 0.18 Å), the second one, *i. e.* increase on the B—H bond length, is very small (less than 10^{-2} Å), indicating that the B—H bond length is not influenced by hyperconjugation.

BH_3N_2, BF_3N_2 and BF_3CO have also been studied. In the case of BH_3N_2 one of the groups[1] which have studied this system indicate that no equilibrium geometry could be found, although they observed, that the N—N bond has a smaller electronic loss than the corresponding C—O bond in BH_3CO. Another group[14], using the CNDO/2 method, not only found a minimum but also found that the side-on conformation (in both BH_3N_2 and BF_3N_2) is more stable than the linear. However, CNDO is not an adequate method for studying weakly interacting systems.

Our study has the objective of giving a simple explanation based on good quality *ab-initio* calculations and we have extended the calculations to the isoelectronic species BH_3BF and BF_3BF to predict whether either should have a stability similar to that of BH_3CO.

All calculations were carried out using the GAUSSIAN 76 series of programs[15]. All molecules have singlet ground states and were treated in the RHF model. The split-valence 4-31G basis set supplied by the program was used in all cases.

In the BH_3 adducts the BH bond was fixed at 1.19 Å, and in the BF_3 adducts the BF bond was fixed at 1.31 Å. All other bond lengths and angles were optimised, or varied sequentially.

In Figure 1 we define the nomenclature used here for the parameters of all the molecules, $BX_3L_1L_2$ (where $X = H$, or F, $L_1 = C$, N, or B, and $L_2 = O$, N, or F).

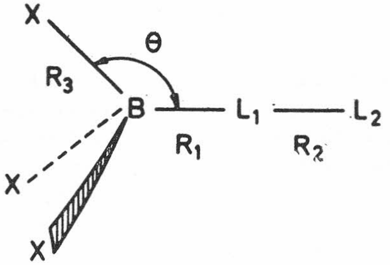

Figure 1. Nomenclature for molecular geometries.

In all the cases it was found that the geometry presented in Figure 1 is energetically more stable than the geometry $BX_3L_2L_1$, or, in the case of the N_2 complexes, the side-on geometry.

RESULTS

The calculated and experimental geometrical parameters, where they are known, are presented in Tables I and II for the BH_3 and BF_3 molecules respectively, the calculated energies are presented in Table III.

The dispersion energy, due to electron correlation between the components of the molecules, cannot be obtained by SCF calculations. However, it should be included to obtain accurate potentials and when the binding energies are very small as in BH_3N_2, it is reasonable to assume that the main part of the binding energy is due to this dispersion energy. Although we are aware of the necessity of including this dispersion energy the methods used to obtain it, configuration interaction or many-body perturbation theory, are outside the scope of this work.

TABLE I

Equilibrium Geometries of the $BH_3L_1L_2$ Molecules

Molecule	R_1/Å	R_2/Å	R_3 / Å (fixed)	Θ / degrees
BH_3BF calc.	1.646	1.294	1.19	105.8
BH_3CO exp. (12)	1.54	1.31	1.194	104.6
exp. (16)	1.53	1.14	1.25	103.0
exp. (13)	1.53	1.14	1.22	103.7
calc. (1)	1.611	1.136	1.209	104.0
calc.	1.61	1.131	1.19	104.0
BH_3N_2 calc.	2.644	1.085	1.19	92.5

TABLE II

Equilibrium Geometries of the $BF_3L_1L_2$ Molecules

Molecule	R_1/Å	R_2/Å	R_3 / Å (fixed)	Θ / degrees
BF_3BF calc.	2.683	1.287	1.31	93.8
BF_3CO exp. (2)	2.89			90.7
calc. (8)	2.886			ca. 91.0
calc.	2.678	1.132	1.31	92.5
BF_3N_2 exp. (2)	2.88			90.5
calc. (8)	2.864			ca. 91.0
calc.	2.523	1.085	1.31	91.6

TABLE III

Corrected Total Energy, Binding Energy, Distortion Energy and Binding Energy of the Distorted Fragments

Molecule	Corrected Total Energy $E^*(AB)$ / E_h	Binding Energy ΔE / kJ/mol	Distortion Energy D / kJ/mol	Binding Energy of the Distorted Fragments ΔE^* / kJ/mol
BH_3BF	—150.325	—101.780	54.516	—156.296
BH_3CO	—138.912	—27.423	54.308	—81.732
BH_3N_2	—135.104	—2.450	1.602	—4.051
BF_3BF	—446.729	—14.524	5.986	—20.510
BF_3CO	—435.339	—2.009	5.779	—7.787
BF_3N_2	—431.540	0.649	5.779	—5.130

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* 1 Å = 10^{-10} m, 1 E_h = hartree = 2626 kJ/mol

It is also necessary to correct the total energy of the molecules to take into account the fact that the basis is overgenerous to the molecules in comparison to the fragments, that is, we have to consider the basis set superposition error. If AB is the molecule with fully optimized geometry, A^{∞} and B^{∞} are the optimized fragments at infinity and AB^0 and A^0B represent the molecule with no electrons on B or A, respectively, then the energy gained by the molecule from basis set extesion can be taken as,

$$\Delta = [E\,(AB^0) - E\,(A)] + [E\,(A^0B) - E\,(B)]$$

The corrected total energy is

$$E^*\,(AB) = E\,(AB) - \Delta$$

The value of Δ in our calculations varies from -2.78 kJ/mol for BH_3N_2 to -19.19 kJ/mol for BH_3CO. Table III gives both the values of $E^*\,(AB)$ and the binding energy of the complex defined as,

$$\Delta E = E^*\,(AB) - E\,(A\,\infty) - E\,(B\,\infty)$$

This binding energy contains the distortion energy of the fragments, which is the energy required by the BX_3 groups to change from D_{3h} to C_{3v} geometries and the change in bond length, which is small, for the other fragment. The distortion energy, D, is given by

$$D = E\,(A) - E\,(A\,\infty) + E\,(B) - E\,(B\,\infty)$$

and for these distorted fragments there is a binding energy, ΔE^*, given by,

$$\Delta E^* = \Delta E - D$$

Both of these quantities are also given in Table III.

In Table IV we present the charge distribution for all the molecules and the fragments, at the optimum geometries for the former and the distorted geometries for the latter. The last column shows the amount of charge donated from each of the atoms when the complexes are formed. A positive sign indicates that electrons have been donated from the respective atom.

DISCUSSION

The better bonding of CO compared with N_2 to transition metals has been attributed[17] to the fact that the highest occupied σ orbital of CO ($IP = 0.52\ E_h$) is non-bonding with its greatest component on the carbon, whereas that of the N_2 ($IP = 0.57\ E_h$) is bonding with equal weighting on both atoms. The electrons in this orbital are therefore more readily available for σ- bonding to another species in the case of CO. The non-bonding orbitals of N_2 are of very low energy and derived from the *s*-atomic orbitals. There is much more *sp* mixing in CO than in N_2 and the difference in the energies of the non-bonding orbitals in N_2 and CO is a reflection of this. It has been suggested that the properties of N_2 are a reflection of a unique electronic structure.[17]

It has also been suggested[18], from an analysis of the properties of complexes of CO and N_2, that N_2 is a poorer ($\sigma + \pi$) ligand than CO but π-acceptance relative to σ-donation is more important in N_2 than in CO. By comparison with CO and RCN it can be said that N_2 is a moderate π-acceptor but a weak

TABLE IV

Charge Distribution in the Complexes and Fragments

Molecules						Charge Donated
BH_3		BF		BH_3BF		
B	0.2028	B	0.4302	B	—0.1525	—0.3553
H	—0.0676	F	—0.4302	B	0.7319	0.3017
				F	—0.4105	0.0197
				H	—0.0563	0.0113
BH_3		CO		BH_3CO		
B	0.2028	C	0.3955	B	0.0327	—0.1701
H	—0.0676	O	—0.3955	C	0.5339	0.1384
				O	—0.4140	—0.0185
				H	—0.0507	0.0169
BH_3		NN		BH_3N_2		
B	0.2322	N	0.0	B	0.2364	0.0042
H	—0.0774	N	0.0	N	0.0178	0.0178
				N	—0.0031	—0.0031
				H	—0.0858	—0.0084
BF_3		BF		BF_3BF		
B	1.2985	B	0.4302	B	1.3001	0.0016
F	—0.4328	F	—0.4302	B	0.4828	0.0526
				F	—0.4168	0.0160
				F	—0.4554	—0.0252
BF_3		CO		BF_3CO		
B	1.2985	C	0.3955	B	1.3201	0.0216
F	—0.4328	O	—0.3955	C	0.4510	0.0555
				O	—0.4086	—0.0131
				F	—0.4542	—0.0214
BF_3		NN		BF_3N_2		
B	1.2985	N	0.0	B	1.3452	0.0467
F	—0.4328	N	0.0	N	0.0069	0.0069
				N	0.0045	0.0045
				F	—0.4522	—0.0194

σ-donor.[18] CO normally can displace N_2 from its complexes, but the converse is not true.[19]

To find out if our results show this behaviour for CO, N_2 and BF, we used Koopmans' theorem[20], to equate the eigenvalue of an orbital to the negative of the ionization potential of an electron in that orbital. The σ *IP*'s for BF, CO and N_2 produced by our calculations are 0.4022, 0.5490 and 0.6295 E_h, respectively, which can be compared with the experimental values, 0.4085[21], 0.5150[21] and 0.5725 E_h[22], respectively. Approximate Hartree-Fock calculations[23] show that the highest occupied orbital for all three molecules has σ symmetry. Our calculations for N_2 lead to the occupied π orbital being just above the σ but for comparison we have used the σ orbital energies for all three species. The lowest vacant orbital in these molecules is a π orbital with energies 0.1216, 0.1487 and 0.1590 E_h for BF, CO and N_2, respectively.

However, one cannot explain the bonding just in terms of orbital energies because CO does not bond through the oxygen atom nor BF through the fluorine. The distribution of the σ-donor and π-acceptor electrons must be equally important. Our calculations give the σ- and π-MO Mulliken populations shown in Table V. We note that the atom through which bonding occurs is that having the greatest σ and π populations. Moreover, the order of the populations suggests both a σ and a π bond strength increasing from N_2 to CO to BF. If the overlap populations are ignored (they contribute equally to both atoms in the Mulliken scheme used for Table V) then the π populations for N_2 and CO are increased (because the π overlap population is negative) and all other populations are decreased.

TABLE V

σ- and π-MO Mulliken Populations for BF, CO and N_2

		σ	π
BF	B	0.88	0.80
	F	0.12	0.20
CO	C	0.83	0.70
	O	0.17	0.30
N_2	N	0.50	0.50

Cl and F atoms withdraw negative charge from the B atom and so increase the electron affinity associated with the boron vacant $2p$ orbital, thus increasing acid strength relative to BH_3. It has also been said[3] that halogens and similar atoms in BX_3, also feed some negative charge into the vacant orbital by a resonance effect, thus tending to decrease its energy, but, apparently, the net effect is usually to increase acid strength. The incomplete octet in BX_3 compounds makes them behave as Lewis acids (acceptors), with the boron obtaining its maximum coordination with an approximately sp^3 hybridization.[24]

Using Koopmans' theorem we predict ionization potentials of 0.4966 E_h and 0.6671 E_h for BH_3 and BF_3 respectively. The HOMO for BH_3 is E' in D_{3h} and hence will overlap with vacant π orbitals of the diatomic fragment. For BF_3, the HOMO is A' but localised almost entirely in the F atoms. There is, however, an E' orbital just below this A', giving an ionization potential of 0.6882 E_h and it is this which will act as the electron donor orbital to the diatomic fragment. BH_3 is, we see, a much stronger donor than BF_3.

The LUMO's of BH_3 and BF_3 have energies 0.0937 E_h and 0.1733 E_h respectively. In both cases these are A'' for the planar boron ligand, largely p orbitals on the boron, and these accept electrons from the donor σ orbitals of the diatomic ligand. BH_3 is a stronger acceptor than BF_3.

It has been said that BH_3 is a stronger Lewis acceptor than BF_3 because in BF_3 (and the other boron trihalides) the boron $2p$ orbital is not fully vacant due to hyperconjugation with the halogen lone pair orbitals. The energy of this orbital is raised by this interaction[11]. Also deformation of the BH_3 or BF_3 structures from D_{3h} to C_{3v} in the complexes is necessary to minimise the repulsion of filled orbitals in the two components and to maximise the availability of the boron vacant orbital, and hyperconjugation would lead to a greater deformation energy for BF_3 than for BH_3. This was suggested as the reason for the nonexistence (at the time) of BF_3CO.[25]

The energy required to distort BF_3 or BH_3 by the same angle is always greater for BF_3. However, in the stronger complexes the distortion of the BH_3 is always larger than of the BF_3, so the distortion energy is actually larger in BH_3CO and BH_3BF than in the corresponding BF_3 complexes. The distortion of the BH_3 and BF_3 fragments in the nitrogen complexes are, however, very similar and hence BF_3N_2 has the larger distortion energy (Table III).

It is, however, necessary to compare these energies of deformation with the binding energies of the complexes (Tables I and III). In some of the cases shown in Table IV the differences between these two energies are so small that there is a competition between the formation of the complex, with the distortion of the BH_3 or BF_3, or the non-formation of the complex.

As can be seen from the table, BH_3N_2 and BF_3CO have very small binding energies and will therefore only exist as van der Waals complexes in very low temperature beams. We find no binding energy for BF_3N_2 but the dispersion energy would provide for small stabilization of a van der Waals complex.

In the case of the complex between BF_3 and BF one has to consider the possibility of forming the species B_2F_4. It has been reported[26] that B_2F_4 can be prepared by passing BF_3 over crystalline B at 2233—2273 K under 1 mm pressure, conditions which give high yields of BF. BF condenses to a green polymer at 77 K from which small amounts of volatile boron fluorides containing up to 14 boron atoms are released on warming. Amongst the products obtained were BF_3, B_2F_4, and possibly B_3F_5. The amount of B_2F_4 obtained depended very strongly on the amount of BF_3 condensed along with the BF.

From experimental evidence[27] it is known that B_2F_4 is planar in the gas phase with $r(B—B) = 1.720^4$ Å $r(B—F) = 1.317^2$ Å and $\langle BFF = 121.4^0$ [1]. However, *ab-initio* SCF calculations using contracted Gaussian basis sets show the staggered form to be more stable but with essentially free rotation about the B—B bond.[28] We have calculated B_2F_4 using the parameters obtained in Ref. 28 and compared the energies obtained with those obtained for BF_3BF. The total energies are: B_2F_4, D_{2d} — 446.796923 E_h, D_{2h} — 446.796841 E_h, BF_3BF — 446.733005 E_h. Also we have calculated the total energies for B_2H_3F in D_{2d} and D_{2h} (in this case, we have optimized the three bond lengths keeping the angles fixed at 120^0) and compared them with the energy obtained for BH_3BF. The values are: B_2H_3F, D_{2d} — 150.363396 E_h, D_{2h} — 150.353426 E_h, BH_3BF — 150.328358 E_h. As can be seen from this results, both B_2F_4 and B_2H_3F in the D_{2d} conformation seem to be more stable than the corresponding BX_3BF molecules.

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SAŽETAK

O stabilnosti adukata BH_3 i BF_3 s dvoatomskim molekulama BF, CO i N_2

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Ispitana je mogućnost vezanja fragmenata BH_3 i BF_3 na dvoatomske molekule BF, CO i N_2 primjenom *ab initio* SCF MO postupka. Računi ispravno reproduciraju činjenicu da BH_3 stvara stabilnije komplekse od BF_3. Isto tako proizlazi da su kompleksi s molekulom CO jači od onih koje stvara molekula dušika N_2. Predviđa se, također, da BF daje najstabilnije komplekse. Spomenuti trendovi mogu se racionalizirati s pomoću oblika HOMO i LUMO orbitala fragmenata i njihovih orbitalnih energija.