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New Insights into Factors Influencing B−N Bonding in $X{:}BH_{3-n}F_n$ and $X{:}BH_{3-n}Cl_n$ for $X=N_2$, HCN, LiCN, H_2CNH, NF_3, NH_3 and $n=0$–3: The Importance of Deformation

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Abstract: Understanding the bonding in complexes $X{:}BH_{3-n}F_n$ and $X{:}BH_{3-n}Cl_n$, for $X=N_2$, HCN, LiCN, H_2CNH, NF_3, NH_3 with $n=0$–3, is a challenging task. The trends in calculated binding energies cannot be explained in terms of any of the usual indexes, including π donation from the halogen lone pairs to the p(π) empty orbital on B, deformation energies, charge capacities, or LUMO energies, which are normally invoked to explain the higher Lewis acidity of BCl_3 relative to BF_3. The results of the high-level G3B3 ab initio calculations reported in this study suggest that the interaction energies of these complexes are determined by a combination of at least three factors. These include the decrease in the electron-accepting ability of B as a result of π donation by the halogen atom, the increase in the electron-acceptor capacity of B due to deformation of the acid, and the large increase in the deformation energy of the acid with increasing halogen substitution. The dominant effects are those derived from the electronic effects of acid deformation. Deformation not only has direct energetic consequences, which are reflected in the large differences between dissociation (D_0) and interaction (E_{int}) energies, but also leads to an enhancement of the intrinsic acidities of $BH_{3-n}F_n$ and $BH_{3-n}Cl_n$ moieties by lowering the LUMO energies to very different extents, consistent with the frontier orbital model of chemical reactivity. Although this lowering depends on both the number and the nature of the halogen substituents, binding energies do not systematically increase or decrease as the number of halogen atoms increases.

Keywords: ab initio calculations · acidity · boranes · frontier orbital theory · Lewis acids

Introduction

B−N bonds have attracted the attention of chemists for many years, particularly because they are isoelectronic with C−C bonds. Hence, there has been much interest in answering questions concerning the similarities and differences between them.[1,2] Among the various B−N bonds in different chemical compounds, that in ammonia borane (also called borazane) $H_3B{:}NH_3$, although not unique, is prototypical of a class of bonds known as donor–acceptor or dative bonds. Interest in this bond is reflected in a series of important papers addressing its inelastic neutron scattering[3] and its 225 K phase transition, studied using high-resolution solid-state ^{15}N NMR spectroscopy.[4] In addition, the structures of methylamine borane molecules ($Me_nH_{3-n}N{:}BH_3$, $n=1$–3) have been investigated using X-ray diffraction, gas-phase electron diffraction, and quantum chemical calculations.[5] Plumley and Evanseck have discussed the covalent and ionic nature of the dative bond in ammonia borane based on high-level QCISD(T) calculations,[6] and Anane et al. have carried out a comparison of the B−N with the B−P bond[7] by comparing $H_3N{:}BX_3$ with $H_3P{:}BX_3$ (X = H, F, Cl) at the G2/MP2 level.

Almost as important as ammonia borane is ammonia boron trifluoride ($F_3B{:}NH_3$) and related compounds. $F_3B{:}N(CH_3)_3$ was one of the first donor–acceptor complexes studied by microwave spectroscopy, which determined a B−N bond length of 1.636 ± 0.004 Å.[8] Miller determined the ^{11}B–^{15}N coupling constant for this same complex to be

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−18.70 Hz.[9] The solid-state structure and the structure and dynamics of F_3B:ND_3 in the gas phase have been studied by NMR, neutron diffraction, and ab initio methods.[10] The gas-phase-ion chemistry of BF_3/NH_3 mixtures has also been investigated by the application of mass spectrometric techniques and theoretical methods.[11] The vibrational spectra of the molecular complexes formed by boron trifluoride and NH_3, CH_3NH_2, $(CH_3)_2NH$, and $(CH_3)_3N$ have been investigated theoretically at the MP2/6-311++G(d,p) level of theory.[12] Finally, Plumley and Evanseck carried out a theoretical study of the Lewis acidity of BF_3 and related compounds using NH_3 as a Lewis base.[13]

B−N bonds in borazane and its derivatives are extremely important, both fundamentally in terms of their nature, and for various applications. In particular, borazane might be an efficient and safe molecular system for hydrogen storage (19.6 wt% H_2), able to deliver large amounts of molecular hydrogen through dehydrogenation reactions.[14,15] Thus, the following question has arisen: is ammonia borane a hydrogen source *par excellence*?[16] This possibility has revived interest in borane complexes, but despite the many studies reported in the literature over the last few decades, some intriguing questions about their bonding have not been resolved. For example, it is often argued that as the atoms or groups of atoms bonded to boron become more electronegative, boron becomes a stronger Lewis acid, because it is increasingly more electron deficient in its valence shell.[13] However, this argument contradicts the well-known trend in the Lewis acidities of the boron trihalides: $BF_3 < BCl_3 < BBr_3$.[17] The reasons for this ordering are controversial, and many different explanations have been proposed. These include charge donation of the halogen lone pairs into the empty 2p orbital of B,[18–20] the larger deformation energy of the BF_3 Lewis acid,[21] the greater charge capacity of the BCl_3 acid,[22] and the lower LUMO energy of BCl_3.[23]

Based on a bonding analysis of H_3N:BF_3 versus H_3N:BCl_3, Bessac and Frenking[23] concluded that the higher Lewis acidity of BCl_3 comes from enhanced covalent interactions due to its lower energy LUMO. However, although this argument rationalizes the situation involving these two compounds, the question remains as to whether it can be generalized to explain acidity changes in a related series of boron acids. We decided to address this question by carrying out a systematic investigation of the bonding of X:$BH_{3-n}F_n$ and X:$BH_{3-n}Cl_n$ complexes for X = N_2, HCN, LiCN, H_2CNH, NF_3, and NH_3, with $n = 0$–3. We will attempt to demonstrate that none of the previously proposed bonding models are capable on their own of explaining the bonding complexities in these molecules. Rather, a more complete bonding description requires a combination of several factors. In this work we will offer some new insights into the various factors which influence B−N bonding in order to explain the stability trends along both series of complexes, X:$BH_{3-n}F_n$ and X:$BH_{3-n}Cl_n$.

Computational Methods

To obtain good energetics for the evaluation of the relative stabilities of complexes with B−N bonds, we employed the high-level G3B3 approach,[24] as implemented in the Gaussian 03 code.[25] In this approach, B3LYP/6-31G(d) optimized geometries and vibrational frequencies were used, instead of the MP2 geometries and HF frequencies normally used in the standard G3 theory.[26] Because a recent theoretical study of CH_3CN:BF_3 found two minima along the B−N bonding coordinate,[27] potential curves as a function of the B−N distance were also generated at MP2/aug-cc-pVTZ and QCISD/6-311++G(d,p) for complexes HCN:$BH_{3-n}F_n$.

The stability of complexes X:$BH_{3-n}F_n$ and X:$BH_{3-n}Cl_n$ can be measured by their dissociation (D_0) and interaction (E_{int}) energies. The former is the energy difference between the complex X:$BH_{3-n}F_n$ or X:$BH_{3-n}Cl_n$ and the corresponding monomers X and $BH_{3-n}F_n$ or $BH_{3-n}Cl_n$ in their electronic ground states, including zero-point vibrational corrections, separated at infinite distance. The latter is the energy difference between the complex and the corresponding monomers at the same geometries that they have in the complexes. Interaction energies E_{int} were calculated by adding to the D_0 dissociation energies the sum of the relaxation energies of the fragments, that is, the energy difference between the fragments at their equilibrium geometries and at their relaxed geometries in the complexes, evaluated at the G3B3 level.[28]

B−N bonding in these complexes was analyzed by means of three different approaches: the atoms in molecules (AIM) theory;[29] the natural bond orbital (NBO) approach;[30] and the electron localization function (ELF).[31,32] In the framework of the AIM theory, the electron density at the B−N bond critical point (BCP) provides a quantitative estimate of the strength of the B−N bond. This analysis was carried out using the AIMPAC and AIM2000 programs.[33] The NBO approach describes B−N bonding in terms of localized hybrids and lone pairs, which are obtained as local block eigenvectors of the one-particle density matrix. In addition, the Wiberg bond orders (BO) were computed, and second-order perturbation analyses were carried out to detect and quantify the electron-transfer process from the halogen lone pairs into the empty p(π) orbital of B. These analyses were carried out using the NBO-5.G program package.[34] The ELF analysis measures the probability of finding an electron pair in a given region of space. When this function is confined in a [0,1] interval by an appropriate Lorentz transformation, the molecular space can be partitioned into polysynaptic basins (generally disynaptic) with the participation of two or more atomic valence shells, and monosynaptic basins which correspond to electron lone pairs or core electrons. ELF grids and basin integrations were evaluated with the TopMod package.[35] For the three-dimensional plots an ELF value of 0.8 was used.

Results and Discussion

Structures, binding energies, and bonding of complexes X:$BH_{3-n}F_n$ and X:$BH_{3-n}Cl_n$: The calculated dissociation and interaction energies, deformation energies, and internuclear B−N distances of the X:$BH_{3-n}F_n$ and X:$BH_{3-n}Cl_n$ complexes are summarized in Table 1. Total energies are given in Table S1 of the Supporting Information. Equilibrium electronic dissociation energies D_e are summarized in Table S2 of the Supporting Information. Although D_e dissociation energies without zero-point vibrational corrections are greater than D_0, both follow similar trends. Subsequent discussion of dissociation energies is based on D_0 energies. Experimental gas-phase geometries are available for four of these complexes, and are also reported in Table 1. These experimental values are reproduced by the calculations.

Table 1. Dissociation (D_0) and interaction (E_{int}) energies, deformation energies E_{def}[a] [kJ mol^{-1}], and B–N bond lengths R_{BN} [Å] for X:$BH_{3-n}F_n$ and X:$BH_{3-n}Cl_n$ complexes.

	BH_3			BH_2F			BHF_2			BF_3		
	D_0 [E_{int}]	R_{BN}	E_{def}	D_0 [E_{int}]	R_{BN}	E_{def}	D_0 [E_{int}]	R_{BN}	E_{def}	D_0 [E_{int}]	R_{BN}	E_{def}
N_2	11.1 [54.9]	1.555	43.8	4.2 [4.4]	2.994	0.2	5.6 [5.7]	3.060	0.1	9.5 [9.6]	2.807 *(2.875)*[c]	0.1
NF_3	37.3 [71.4]	1.617	34.1	6.2 [6.7]	2.660	0.5	7.6 [7.7]	2.953	0.1	11.9 [12.4]	2.630	0.5
HCN	65.2 [121.0]	1.545	55.8	13.1 [18.4]	2.311	5.3	14.6 [16.2]	2.676	1.6	22.9 [27.4]	2.472 *(2.473)*[d]	4.5
NH_3	109.3 [162.3]	1.669 *(1.66)*[b]	53.0	75.4 [137.5]	1.698	62.1	62.2 [139.5]	1.719	77.3	81.1 [183.8]	1.711 *(1.673)*[e]	102.7
LiCN	116.5 [183.8]	1.544	67.3	72.2 [144.0]	1.601	71.8	54.9 [132.5]	1.671	77.6	77.1 [179.6]	1.673	102.5
H_2CNH	126.6 [188.1]	1.578	61.5	91.1 [161.3]	1.604	70.2	64.2 [136.3]	1.683	72.1	84.8 [184.3]	1.680	99.5

	BH_3			BH_2Cl			$BHCl_2$			BCl_3		
	D_0 [E_{int}]	R_{BN}	E_{def}	D_0 [E_{int}]	R_{BN}	E_{def}	D_0 [E_{int}]	R_{BN}	E_{def}	D_0 [E_{int}]	R_{BN}	E_{def}
N_2	11.1 [54.9]	1.555	43.8	3.7 [3.8]	3.108	0.1	4.4 [4.5]	3.456	0.1	6.0 [6.0]	2.807	0.0
NF_3	37.3 [71.4]	1.617	34.1	4.0 [42.9]	1.712	38.9	7.8 [7.9]	3.201	0.1	8.1 [8.1]	2.630	0.0
HCN	65.2 [121.0]	1.545	55.8	35.3 [105.8]	1.571	70.5	16.6 [97.5]	1.597	80.9	8.7 [100.5]	1.617	91.8
NH_3	109.3 [162.3]	1.669 *(1.66)*[b]	53.0	101.4 [166.9]	1.646	65.5	97.7 [180.9]	1.638	83.2	98.5 [194.0]	1.711	95.5
LiCN	116.5 [183.8]	1.544	67.3	103.7 [194.7]	1.545	91.0	96.7 [204.7]	1.548	108.0	96.6 [220.3]	1.673	123.7
H_2CNH	126.6 [188.1]	1.578	61.5	117.2 [199.7]	1.581	82.5	104.9 [196.6]	1.590	91.7	106.7 [216.3]	1.680	109.6

[a] Deformation energies are obtained as the difference between the energies of the monomer equilibrium structure and the structure in the complex, both evaluated at the G3B3 level. [b] Experimental value taken from reference [36]. [c] Experimental value taken from reference [37]. [d] Experimental value taken from reference [38]. [e] Experimental value taken from reference [39].

One of the most striking features of Table 1 is the large variation in dissociation energies from 3.7 to 126.6 kJ mol^{-1}, and in B–N bond lengths from 1.544 to 3.456 Å. These large ranges are indicative of significant bonding differences. Based solely on these two properties these complexes can be divided into two groups, one consisting of van der Waals complexes with small dissociation energies and long B–N distances, and the other containing covalently bound species with strong and short B–N bonds.

There are three other important observations that can be made from the data of Table 1. First, BH_3 always forms covalently bound complexes, whereas BF_3 does so only with the three strongest Lewis bases. Second, the first F or Cl substitution at B leads to a systematic decrease in the dissociation energies D_0. This is not in agreement with arguments reported in the literature, which suggest that as the groups bonded to B become more electronegative, B should become a stronger acid.[13] Third, the deformation energy (E_{def}) can be very similar to, or even much greater than, the dissociation energy D_0, as exemplified by the N_2:BH_3 complex, for which E_{def} is approximately four times greater than D_0. On the basis of the D_0 dissociation energy, N_2:BH_3 would be considered a van der Waals complex, whereas the E_{int} interaction energy suggests that it is a covalently bound species.

Nevertheless, it is clear from the data of Table 1 that the remaining complexes between N_2 and the other Lewis acids are truly van der Waals complexes, as both dissociation and interaction energies are small. The change in the nature of the B–N bond in going from N_2:BH_3 to N_2:BH_2F is nicely reflected in the electron densities at the B–N bond critical points, which decrease by more than an order of magnitude (0.081 to 0.007 a.u.). The B–N bonding change is consistent with the increase in the B–N distance from 1.55 to 2.99 Å, and with the ELF renderings in Figure 1. These show a disynaptic basin between B and N typical of a covalent bond (V(BN) in Figure 1) for N_2:BH_3 with a population of 3.13 e$^-$, whereas N_2:BH_2F has a much expanded basin corresponding to an N lone pair (V(N) in Figure 1), consistent with a typical van der Waals interaction. Such dramatic differences in bonding characteristics are also observed when the Lewis base is NF_3.

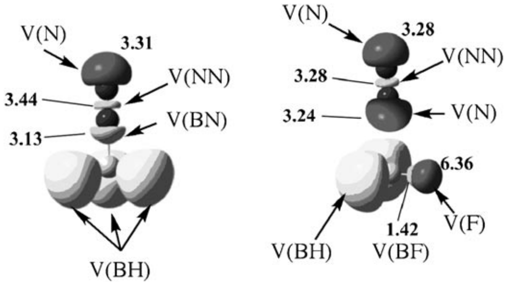

Figure 1. Three-dimensional plots of the ELFs for N_2:BH_3 and N_2:BH_2F. Lobes labeled V(BH) denote disynaptic B–H basins; lobes labeled V(N) and V(F) correspond to lone-pair monosynaptic basins; lobes V(BN), V(BF), and V(NN) denote disynaptic basins involving non-hydrogen atoms (B–N, B–F, N–N). Electron populations are given in e$^-$.

The NBO description of the B–N bond in covalently bound complexes does not change dramatically from one complex to another. In all cases, N lone-pair donation occurs from the Lewis base into the empty p(π) orbital of B. This leads to a bonding molecular orbital composed of approximately 17 % boron sp-type hybrid (16 % s + 84 % p) and 83 % nitrogen sp^3-like hybrid (34 % s + 66 % p). However, a second-order perturbation analysis shows that there is also significant charge transfer from the halogen lone pairs into the empty B p(π) orbital in X:$BH_{3-n}F_n$ and X:$BH_{3-n}Cl_n$ complexes, a reflection of the well-known ability of F and Cl to behave as π-donating atoms. This donation results in reinforcement of the B−F and B−Cl bonds and a decrease in binding energy when the first halogen atom is substituted in BH_3, as illustrated in Figure 2. It may also explain the very strong B−F bond in BF($^1\Sigma^+$), which is estimated to be 752.7 kJ mol^{-1} from high-level ab initio calculations,[40] and the decrease in the electron-acceptor character of the B atom. The latter is consistent with the decrease in the binding energy when the first halogen atom is substituted in BH_3.

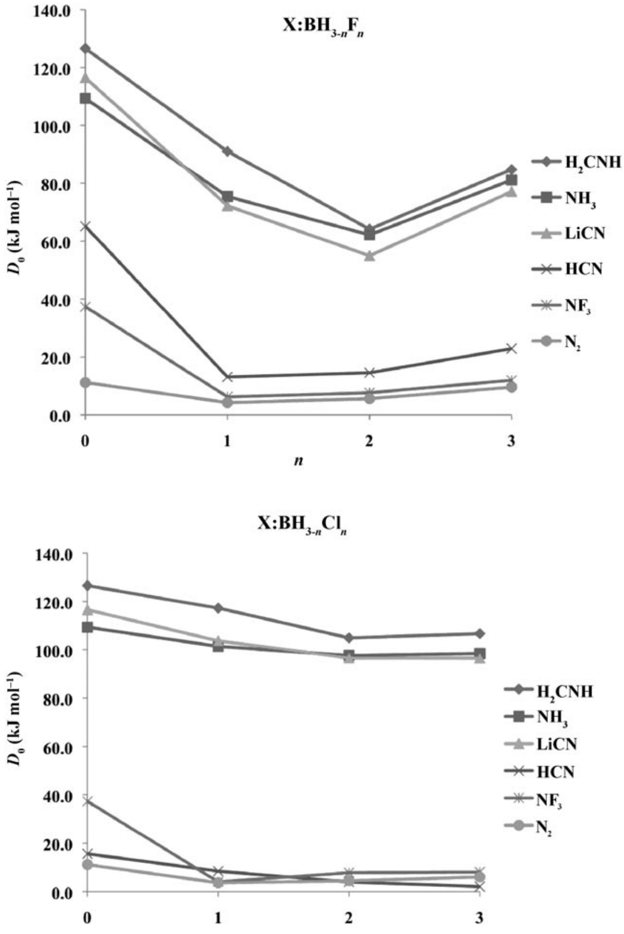

Figure 2. Dissociation energies for X:$BH_{3-n}F_n$ (top) and X:$BH_{3-n}Cl_n$ (bottom) complexes with a given base as a function of the number of halogen atoms in the acid.

It is also interesting to note that the various descriptors, including the electron density at the bond critical point, the population of the disynaptic basin, the Wiberg bond order, the B−N bond length, and the B−N stretching frequency, which are often used to analyze the bonding between two atoms, yield contradictory views for the complexes X:$BH_{3-n}F_n$ and X:$BH_{3-n}Cl_n$. This is evident from the data shown in Table 2, which reports these descriptors for the complexes between NH_3 and the Lewis acids $BH_{3-n}F_n$. Both the electron density at the B−N bond critical point and the population at the B−N disynaptic basin increase with F substitution, an observation in agreement with the argument that the Lewis acidity should increase as the number of electronegative substituents increases. However, B−N bond lengths, bond orders, stretching frequencies, and dissociation energies do not change accordingly. How can these apparent contradictions be explained, and how can such bonding trends be understood?

Table 2. Electron densities at BN bond critical points (ρ_{BCP}, [a.u.]), electron populations at the disynaptic V_{BN} basins (Pop (V_{BN}) [e$^-$]), Wiberg bond orders (BO), BN internuclear distances (R_{BN} [Å]), BN stretching frequencies (ν_{BN} [cm^{-1}]), and dissociation and interaction energies (D_0 and E_{int} [kJ mol^{-1}]) of complexes NH_3:$BH_{3-n}F_n$.

	NH_3:BH_3	NH_3:BH_2F	NH_3:BHF_2	NH_3:BF_3
ρ_{BCP}(BN)	0.099	0.102	0.105	0.111
Pop (V_{BN})	1.88	1.91	1.95	1.98
BO (BN)	0.600	0.574	0.539	0.524
R_{BN}	1.663	1.675	1.686	1.677
ν_{BN}	636	580	566	667
D_0	109.3 (*53.0*)[a]	75.4 (*62.1*)[a]	62.2 (*77.3*)[a]	81.1 (*102.7*)[a]
E_{int}	162.3	137.5	139.5	183.8

[a] Values in italic are the deformation energies of BH_nF_{3-n}.

π-Electron donation: One factor which must play an important role in BN bonding in these complexes is electron donation from the halogen lone pairs into the empty B p(π) orbital.[18–20,41] However, this effect alone cannot explain the evolution of the binding energies with the number of halogen substituents. Moreover, the second-order perturbation energies associated with π donation by F and Cl indicate that this effect increases almost linearly with the number of halogen atoms, but, as shown in Table 1, neither the dissociation nor the interaction energies decrease monotonically as the number of halogens increases. Thus, one of the more surprising results is that, independent of the nature of the Lewis base and therefore independent of the van der Waals or covalent character of the complex, the largest dissociation energies D_0 for complexes X:$BH_{3-n}F_n$ and X:$BH_{3-n}Cl_n$ are found when BH_3 is the acid. Furthermore, for covalently bound complexes, the minimum value of D_0 for both series of complexes is found when the acid has two halogen substituents. Except for HCN:$BH_{3-n}Cl_n$, the minimum for the van der Waals complexes occurs when the acid has only one halogen, as illustrated in Figure 2. This may be due to an increase in dispersion interactions as the number of halogen atoms of the Lewis acid increases. Whereas dispersion contributions to bonding may by relatively small for covalently bound complexes, they are more significant for the weakly bound van der Waals complexes.

Charge capacity: As indicated above, acidity trends cannot be explained in terms of π donation from the halogen lone pairs to the 2p(π) empty orbital of B. Can they be explained in terms of the charge capacity[22] of the Lewis acid? The charge capacity κ is defined[22] in terms of the ionization energy (IE) and the electron affinity (EA) of the system, as given in Equation (1).

$$\kappa = \frac{1}{\mathrm{IE} - \mathrm{EA}} \tag{1}$$

G3B3 values of κ are summarized in Table 3. As the number of halogen atoms increases, κ decreases in the F-substituted acids, but increases in the Cl-substituted acids. These changes suggest that upon successive halogen substitution, the binding energies of complexes with the F-substituted acids should decrease and those for the Cl-substituted acids should increase, but neither is the case.

Frontier orbital model: Previous studies have attributed the greater acidity of BCl_3 relative to BF_3 to the lower energy LUMO of BCl_3. As a result, the interaction of this orbital with the occupied orbital of the N electron donor should be stronger for BCl_3, leading to a stronger covalent interaction.[23] Trends in LUMO energies evident in Figure 3 include the higher energies of the halogen-substituted acids compared to BH_3, the almost linear increase in the LUMO energies with increasing halogen substitution, and the higher LUMO energies for the fluoro-substituted acids compared to the chloro-substituted acids. These trends suggest that complexes of BH_3 with a given base should have the greatest values of D_0, and that covalent complexes $X{:}BH_{3-n}Cl_n$ should have greater D_0 values than corresponding $X{:}BH_{3-n}F_n$ complexes, consistent with the data of Table 1. However, the increasing energy of the LUMO with increasing halogen substitution *cannot* explain the minimum in the binding energy curves for $X{:}BH_{3-n}F_n$ and $X{:}BH_{3-n}Cl_n$ shown in Figure 2.

Table 3. G3B3 charge capacities (κ).

$BH_{3-n}F_n$	κ [eV^{-1}]	$BH_{3-n}Cl_n$	κ [eV^{-1}]
BH_3	0.083	BH_3	0.083
BH_2F	0.081	BH_2Cl	0.090
BHF_2	0.072	$BHCl_2$	0.090
BF_3	0.064	BCl_3	0.094

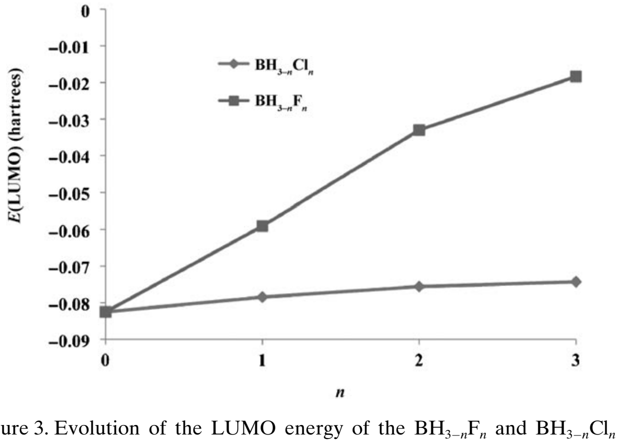

Figure 3. Evolution of the LUMO energy of the $BH_{3-n}F_n$ and $BH_{3-n}Cl_n$ acids in their equilibrium conformations as a function of the number of halogen atoms.

How can these seemingly contradictory observations be resolved? Perhaps the problem arises from the use of the dissociation energies (D_0) rather than the interaction energies (E_{int}) as a measure of the strength of the B−N bond. As reported in Table 1, the deformation energies of $BH_{3-n}F_n$ in covalently bound complexes are significant, being about 50 % of the interaction energy. The interaction energies (E_{int}) of complexes $X{:}BH_{3-n}F_n$ and $X{:}BH_{3-n}Cl_n$ are plotted against the number of halogen substituents in Figure 4 (top and bottom, respectively). A comparison of Figures 2 (top) and 4 (top) shows that for $X{:}BH_{3-n}F_n$ complexes, both E_{int} and D_0 exhibit minima for covalent complexes when BHF_2 is the acid and for van der Waals complexes when BH_2F is the acid. Despite this, there are some significant differences between these two plots. For example, although $H_2CNH{:}BH_3$ has a much higher D_0 than $H_2CNH{:}BF_3$, the

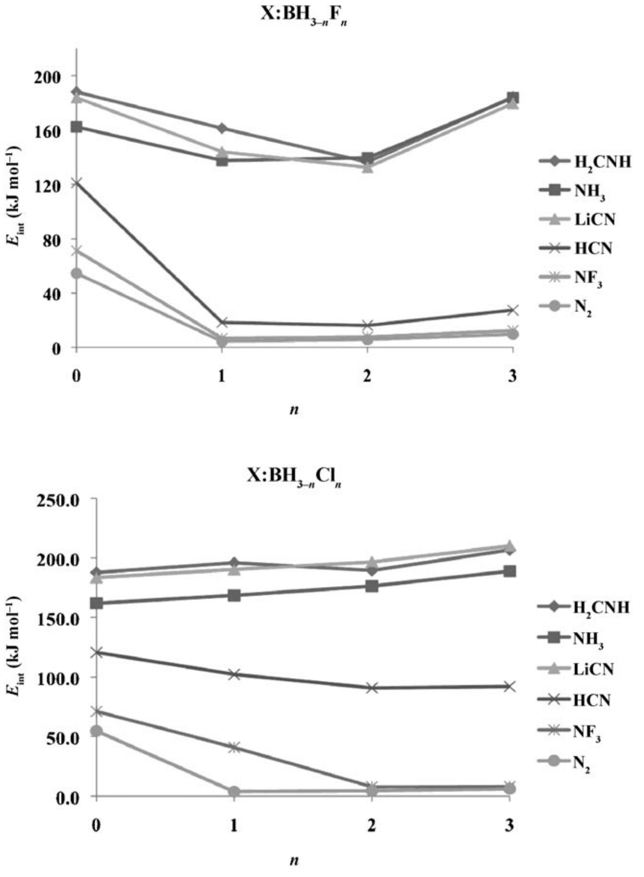

Figure 4. Interaction energies for $X{:}BH_{3-n}F_n$ (top) and $X{:}BH_{3-n}Cl_n$ (bottom) complexes with a given base as a function of the number of halogen atoms.

corresponding interaction energies are nearly equal. Moreover, D_0 of NH_3:BH_3 is larger than that of NH_3:BF_3, but the reverse is found for the interaction energies. The differences between D_0 and E_{int} are even more significant for the X:$BH_{3-n}Cl_n$ complexes. For the covalently bound complexes with H_2CNH, NH_3 and LiCN as the bases, D_0 decreases in going from X:BH_2Cl to X:$BHCl_2$ and then levels off (Figure 2, bottom). In contrast, E_{int} increases upon successive Cl substitution (Figure 4, bottom), except for a small decrease in going from H_2CNH:BH_2Cl to H_2CNH:$BHCl_2$. These significant differences illustrate unambiguously the crucial role played by deformation, which means that acidity trends should be analyzed in terms of interaction energies rather than dissociation energies. However, even if interaction energies are used to describe the strength of the B−N bond, there is no correlation between E_{int} values and the LUMO energies of the Lewis acids. As the number of halogen atoms increases, the LUMO energies increase steadily (Figure 3), whereas values of E_{int} exhibit minima for X:$BH_{3-n}F_n$ complexes (Figure 4, top) or increase rather than decrease for X:$BH_{3-n}Cl_n$ covalent complexes (Figure 4, bottom).

Electronic effects of deformation: The deformation of the Lewis acid not only influences B−N dissociation energies, but also changes the electron distribution of the acid as it triggers changes in the boron hybridization. These electronic changes are clearly mirrored by the LUMO energies. For the covalently bound complexes NH_3:$BH_{3-n}F_n$ and NH_3:$BH_{3-n}Cl_n$, the evolution of the LUMO energies in the complexes with an increasing number of halogen atoms, as shown in Figure 5, is completely different from the evolution with the Lewis acids in their equilibrium conformations, as illustrated in Figure 3. Plots for covalently bound complexes with HCN, LiCN, and H_2CNH, shown in Figure S1 of the Supporting Information, show similar trends. Because weakly bound van der Waals complexes have Lewis acid deformation energies that are negligibly small, the LUMO energies in the complexes and at equilibrium are similar, as illustrated in Figure S2 of the Supporting Information.

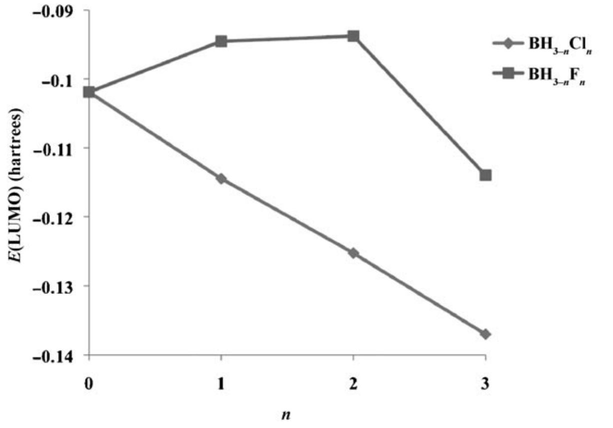

Figure 5. Evolution of the LUMO energies of complexes of the Lewis bases with NH_3 as a function of the number of halogen atoms.

Another striking feature of Figure 5 is that the LUMO energies of BH_3 and BF_3 are significantly lower than those of BH_2F and BHF_2, consistent with the significantly greater interaction energies of covalent complexes X:BH_3 and X:BF_3 compared to complexes X:BH_2F and X:BHF_2, independent of the nature of the base. However, although BF_3 has a lower energy LUMO than BH_3, E_{int} is greater only for NH_3:BF_3. Along the $BH_{3-n}Cl_n$ coordinate in Figure 5, the LUMO energy decreases linearly, consistent with a linear increase in E_{int} for covalent complexes with the three strongest bases, as shown in Figure 4 (bottom). The single exception, which will be explained below, is for H_2CNH:BH_2Cl, which has a slightly greater E_{int} than H_2CNH:$BHCl_2$.

Correlations found between LUMO energies of the deformed Lewis acids and the E_{int} interaction energies are consistent with the frontier orbital model of chemical reactivity, in the sense that the lower the LUMO energy of the Lewis acid, the stronger the covalent interaction with the Lewis base. However, this cannot be the only factor governing the acidity trends. If this were the case, the curve associated with the complexes of H_2CNH in Figure 4 (bottom) should be parallel to and lie above that for complexes with LiCN. However, the two curves cross, and the values of E_{int} for the complexes of H_2CNH with $BHCl_2$ and BCl_3 are slightly lower than those for the corresponding LiCN complexes. It is also interesting to note that the B−N distances are longer in the complexes with H_2CNH compared to the LiCN analogues. This result is not unprecedented, as anomalously short distances have also been reported for complexes involving N_2 compared to stronger bases such as NH_3. Such short distances have been explained in terms of the spatial extent of the sp versus the sp^3 N lone pairs.[42] The same argument would also explain the longer distances in complexes with H_2CNH, which has a more extended sp^2 lone pair, relative to corresponding complexes with LiCN with a more contracted sp lone pair. The shorter distances may also be related to the greater deformation energies of LiCN complexes with a given acid compared to the H_2CNH complexes with the same acid.

A crucial question still remains. Why do the LUMO energies of the Lewis acids change so dramatically upon deformation? To answer this question we evaluated the LUMO energies of the $BH_{3-n}F_n$ and $BH_{3-n}Cl_n$ Lewis acids as a function of the dihedral angle (α) defined by the four atoms of the acid, starting from the planar equilibrium structure ($\alpha = 180°$) and decreasing α in steps of 10° to 120°. Figure 6 shows the variation of the LUMO energy as the structure of the acid changes from planar to pyramidal. As expected, the pure p LUMO on B in the equilibrium planar conformation of the Lewis acid is stabilized by pyramidalization through mixing with the s orbital. What is most significant is the curvature shown in Figure 6, which increases as the number of halogen atoms increases. This occurs because the presence of additional electronegative substituents increases the s-orbital contribution to the sp hybrid, so that BF_3 or BCl_3 have

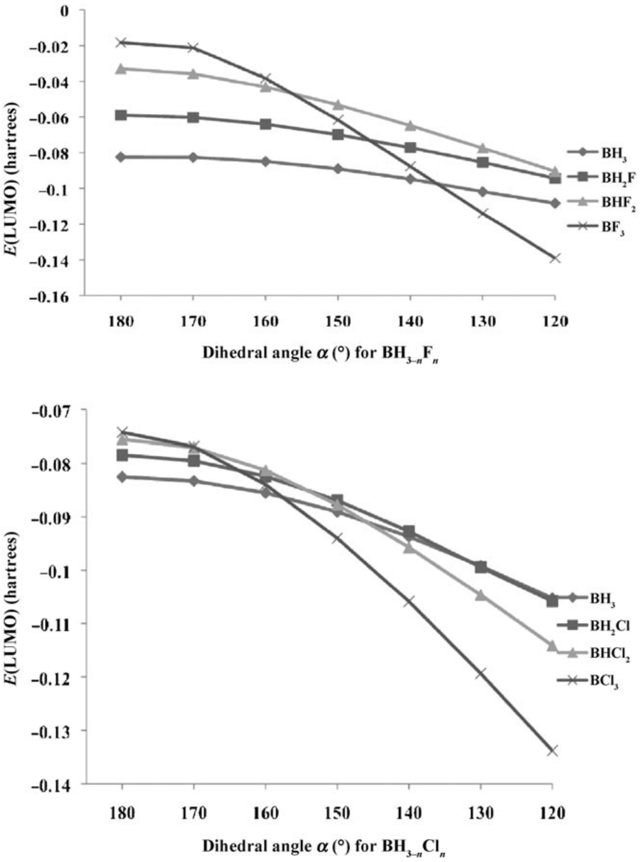

Figure 6. LUMO energies as a function of the pyramidalization of the Lewis acids $BH_{3-n}F_n$ (top) and $BH_{3-n}Cl_n$ (bottom).

the largest s contributions, as illustrated in Figure S3 of the Supporting Information. This effect is qualitatively similar, but quantitatively different for the two series of Lewis acids. For the fluoro-substituted acids, the LUMO energy gap between BH_3 and BF_3 at $\alpha = 180°$ is significant, but decreases as α decreases. When BH_3 approaches the conformation it has in covalent complexes with $\alpha \approx 130°$, its LUMO is still lower than those of BH_2F and BHF_2, but higher than that of BF_3. For the chloro-substituted Lewis acids, the LUMO energy gap at $\alpha = 180°$ is much smaller than for the fluoro derivatives. When the Lewis acid is close to the conformation it has in complexes, the LUMO energies of the three halogen derivatives BH_2Cl, $BHCl_2$, and BCl_3 are now lower than the LUMO of BH_3. Thus, the structural changes which occur as the boron acids make the transition from planar to pyramidal influence the electron distribution in the acids, and this influences the LUMO energies. The extent of electron redistribution depends on both the number and the nature of the substituents, and occurs even in the absence of the base.

Finally, it should be noted that electrostatic interactions must certainly play a role in B−N bonding, as the deformation of the acid is triggered initially by electrostatics. For example, when the geometry of the $H_3N{:}BCl_3$ complex is optimized as a function of the B−N distance, pyramidalization of the BCl_3 moiety begins at B−N distances greater than 4.0 Å, even though at this distance the overlap between the N lone pair and the empty p(π) orbital of B, and the amount of charge transfer from the base to the Lewis acid, are negligible, as illustrated in Figure S4. The molecular electrostatic potential illustrated in Figure 7 shows a positive potential (blue zone) coinciding with the C_3 axis surrounded by a negative potential (red zones) for BCl_3, whereas the negative potential of NH_3 is very strong along the C_3 axis. These potentials lead to B⋯N attraction and Cl⋯N repulsion as the acid and base approach each other to form a complex.

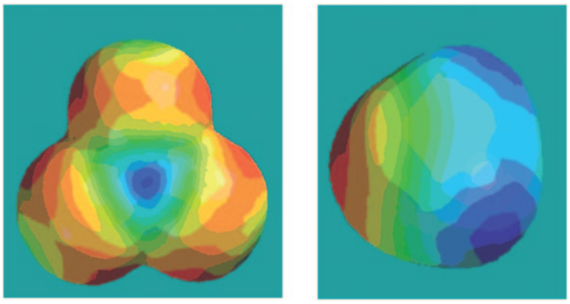

Figure 7. Molecular electrostatic potentials of isolated BCl_3 and NH_3 in their equilibrium conformations. Blue and red areas correspond to positive and negative potentials, respectively.

In summary, explaining B−N bonding along the two series of complexes $X{:}BH_{3-n}F_n$ and $X{:}BH_{3-n}Cl_n$ requires an appropriate combination of factors which address various influences on the acidities of the boron acids. Some of these factors have been proposed previously and discussed in the literature, but not one of these can alone explain the complexities of the acidities of BH_3 and its halogen-substituted derivatives. It is well established that the intrinsic acidities of $BH_{3-n}F_n$ and $BH_{3-n}Cl_n$ in their equilibrium conformations decrease upon halogen substitution due to π-donation from the halogen lone pairs to the empty p(π) orbital of B. However, it is also critical to note that the intrinsic acidities exhibited by the Lewis acids are also *strongly modified* indirectly by the deformation of the acids. Deformation not only has direct energetic consequences, which are reflected in the large differences between dissociation and interaction energies, but also leads to electron redistribution and an enhancement of the intrinsic acidities of the $BH_{3-n}F_n$ and $BH_{3-n}Cl_n$ moieties in part by lowering the LUMO energies, consistent with the frontier orbital model of chemical reactivity. Although this lowering depends on both the number and the nature of the halogen substituents, binding energies do not systematically increase or decrease as the number of halogens increases.

Existence of double minima: As noted in previous sections, a theoretical study of $CH_3CN{:}BF_3$ found two minima along the B−N bonding coordinate, with B−N distances of 1.8 and 2.3 Å.[27] An experimental microwave structure reported an intermediate value of 2.011 Å for this distance.[43] Perhaps the experimental distance is the vibrationally averaged ground-state distance in a complex with double minima and a small barrier between them. We have pursued this question in complexes of the four $BH_{3-n}F_n$ boron acids with the Lewis base HCN. For this purpose, geometries were optimized at MP2/aug-cc-pVTZ and QCISD/6-311++G(d,p), using starting B–N distances of 1.8 and 2.3 Å. Table S3 of the Supporting Information shows that, except for $HCN:BH_2F$, only a single minimum exists along the B–N bonding coordinate, independent of the method of optimization. Moreover, the $HCN:BH_3$ complex is always predicted to be covalently bound, whereas $HCN:BHF_2$ and $HCN:BF_3$ are van der Waals complexes. In contrast, at QCISD/6-311++G(d,p), the $HCN:BH_2F$ potential energy curve (PEC) as a function of the B–N distance exhibits two minima, one at a distance of 1.7 Å and the other at 2.5 Å. However, as evident from Figure S5 a of the Supporting Information, the PEC in this region is very flat, and the barrier between the two minima is less than 2 kJ mol^{-1}. Furthermore, when triple excitations are included and the optimization is carried out at QCISD(T)/6-311+G(d,p), the MP2/6-311++G(d,p) description is recovered, and a single minimum is found at the shorter B–N distance. In contrast, at QCISD/6-311+G(d,p), $HCN:BHF_2$ exhibits only a single minimum, but this corresponds to a van der Waals complex with a B–N distance of 2.7 Å, as shown in Figure S5 b. It is apparent that the potential surfaces must be very flat in this region, and are sensitive to both the wavefunction and the basis set used for the calculations.

Conclusion

High-level ab initio G3B3 calculations have been carried out to investigate B–N bonding in complexes $X:BH_{3-n}F_n$ and $X:BH_{3-n}Cl_n$ for X = N_2, HCN, LiCN, H_2CNH, NF_3, and NH_3 with $n = 0$–3. These complexes can be classified as either covalently bound or van der Waals complexes on the basis of their binding energies and B–N distances. None of the usual indexes, such as π-donation from the halogen lone pairs to the p(π) empty orbital on B, deformation energies, charge capacities, or LUMO energies used previously to explain the higher Lewis acidity of BCl_3 compared to BF_3, can independently explain the acidity trends along the two series of complexes $X:BH_{3-n}F_n$ and $X:BH_{3-n}Cl_n$. The binding energies of these complexes result from a combination of at least three factors. These include the decrease in the electron-accepting ability of B as a result of π-donation by the halogen atom, the increase in the electron-acceptor capacity of B due to deformation, and the large increase in the deformation energy of the acid with increasing halogen substitution. The dominant effects that determine the bonding properties are those derived from electronic changes due to deformation. Deformation not only has direct energetic consequences, which are reflected in the large differences between the dissociation (D_0) and interaction energies (E_{int}), but also leads to an enhancement of the intrinsic acidities of the $BH_{3-n}F_n$ and $BH_{3-n}Cl_n$ moieties by lowering LUMO energies, consistent with the frontier orbital model of chemical reactivity. Although this lowering depends on both the number and the nature of the halogen substituents, the binding energies do not systematically increase or decrease as the number of halogens increases.

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