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Articles

A Computational Analysis of the Bonding in Boron Trifluoride and Boron Trichloride and Their Complexes with Ammonia

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Complexation energies for the interactions of BF_3 and BCl_3 with NH_3 have been calculated at the *ab initio* Hartree–Fock and MP2 levels of theory, using large polarized basis sets. The formation of $H_3N\cdot BCl_3$ is found to be favored by 4.27 kcal/mol over $H_3N\cdot BF_3$ at the MP2 level. This is in agreement with the experimental observation that the Lewis acidities of the boron trihalides increase in the order $BF_3 < BCl_3 < BBr_3$. Calculated atomic charges and molecular electrostatic potentials show the boron to be much more positive in BF_3 than in BCl_3, as would be expected from the respective electronegativities of fluorine and chlorine. These results and the relevant $p\pi$–$p\pi$ overlap integrals do not support using the concept of back-bonding and consequent stabilization to explain the trend in Lewis acidities. As an alternative explanation, it is suggested that this trend reflects the importance of Lewis base $\rightarrow$ BX_3 charge transfer in these complexes and the fact that the ability to accept the charge, as indicated by charge capacities, increases in the order $BF_3 < BCl_3 < BBr_3$.

Introduction

It is well-known that the Lewis acidities of boron trihalides increase in the order $BF_3 < BCl_3 < BBr_3$.[1–5] This is opposite to what would be expected from the electronegativities of the halogens, which decrease in the order F > Cl > Br; the more electronegative species would be expected to withdraw charge more effectively from the boron and thereby favor its interaction with the lone pair of a Lewis base. The anomalous behavior of boron trihalides has often been attributed to back-donation of charge from the $p\pi$ orbitals of the halogens to that of the boron.[1–3,5,6] The back-donation is viewed as being stronger for the smaller halogens, especially fluorine, due to a greater degree of $p\pi$–$p\pi$ overlap. It has also been argued that the back-donation results in a resonance stabilization of the ground states,[1–3,5,6] which would decrease in the order $BF_3 > BCl_3 > BBr_3$ and would oppose the formation of Lewis complexes, in which the boron trihalides become pyramidal. The objective of this study has been to examine these interpretations of the bonding in Lewis complexes with boron trihalides.

Methods

We have computed the complexation energies of BF_3 and BCl_3 with NH_3, using Gaussian 92[7] at the *ab initio* HF/6-31+G(2d,p)//HF/6-31+G(2d,p), HF/6-311+G(2d,p)//HF/6-311+G(2d,p), and MP2/6-31+G(2d,p)//MP2/6-31+G(2d,p) levels of theory.[8] The sizes of these basis sets should hold the basis set superposition error to an acceptable magnitude and allow quantitative comparisons of complexation energies.[9] Corrections for zero-point vibrational energies have been made from HF/6-31G* harmonic frequencies scaled by 0.89.[10]

Results and Discussion

Our optimized geometries for BF_3, BCl_3, and their complexes with NH_3 are in Table I, and the calculated interaction energies are in Table II. Our highest level calculation (MP2) shows the binding to be stronger in $H_3N\cdot BCl_3$ by 4.97 kcal/mol (4.27 kcal/mol with the inclusion of zero-point energies). We have found no experimentally-determined interaction energies for these ammonia complexes, but for the corresponding trimethylamine systems, gas-phase calorimetric measurements give a difference of 3.9 kcal/mol;[11] on the other hand, an estimate based on NMR shifts was 18 kcal/mol.[12] Solution measurements for BF_3 and BCl_3 complexes with pyridine indicate the latter interaction energy to be more negative by about 8 kcal/mol,[1] and pyridine has usually been found to bind more strongly to Lewis acids than does ammonia.[13]

Additional evidence that the B–N bond is stronger in the BCl_3 complex is provided by the calculated B–N force constants, which are 2.5 and 1.8 mdyn/Å, respectively (HF/6-31G*), in the BCl_3 and BF_3 systems. Similarly, experimentally-determined B–N force constants for $CH_3CN\cdot BX_3$ complexes increase in the order $BF_3 < BCl_3 < BBr_3$.[2] Finally, the photoelectron spectra of the trimethylamine·BX_3 systems also indicate that the binding is weakest in the case of BF_3.[4]

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Table I. Calculated and Experimental Structures^{a}

molecule	method	dist (Å)			ang (deg)	
		B–N	B–X	N–H	X–B–X	H–N–H
BF_3	HF/6-31+G(2d,p)		1.297		120	
	HF/6-311+G(2d,p)		1.293		120	
	MP2/6-31+G(2d,p)^{b}		1.320		120	
	expt		1.29,^{c} 1.307^{d}		120^{c,d}	
$H_3N{\cdot}BF_3$	HF/6-31+G(2d,p)	1.670	1.353	1.003	114.3	108.7
	HF/6-311+G(2d,p)	1.676	1.350	1.003	114.2	108.7
	MP2/6-31+G(2d,p)^{b}	1.667	1.377	1.017	114.2	108.6
	expt^{e}	1.60	1.36		111	107.0
BCl_3	HF/6-31+G(2d,p)		1.750		120	
	HF/6-311+G(2d,p)		1.746		120	
	MP2/6-31+G(2d,p)^{b}		1.749		120	
	expt		1.72,^{c} 1.742^{d}		120^{c,d}	
$H_3N{\cdot}BCl_3$	HF/6-31+G(2d,p)	1.611	1.844	1.005	113.2	108.8
	HF/6-311+G(2d,p)	1.608	1.843	1.005	113.2	108.6
	MP2/6-31+G(2d,p)^{b}	1.618	1.839	1.020	113.5	108.7

^{a} C_{3v} symmetry has been assumed. For the complexes, the staggered conformation invariably has been found to have the lowest energy. ^{b} MP2 calculations performed with frozen-core approximation. ^{c} Reference 15. ^{d} Reference 10; gas-phase structure. ^{e} Reference 35; crystal structure.

Table II. Calculated Complexation Energies^{a}

	ΔE(kcal/mol)^{b}		
	HF/6-31+G(2d,p)// HF/6-31+G(2d,p)	HF/6-311+G(2d,p)// HF/6-311+G(2d,p)	MP2/6-31+G(2d,p)// MP2/6-31+G(2d,p)^{c}
$H_3N{\cdot}BF_3$	−17.51 (−14.12)	−17.38 (−13.99)	−23.20 (−19.81)
$H_3N{\cdot}BCl_3$	−21.64 (−17.55)	−21.40 (−17.31)	−28.17 (−24.08)

^{a} Values in parentheses have been corrected for zero-point vibrational energies from frequencies calculated at the HF/6-31G* level and scaled by 0.89. ^{b} $\Delta E = E(H_3N{\cdot}BX_3) - E(H_3N) - E(BX_3)$. ^{c} MP2 calculations performed with the frozen-core approximation.

To investigate the validity of the back-bonding theory, we have calculated the actual overlap integrals,

$$\int (2\mathrm{p}\pi_{\mathrm{B}})(n\mathrm{p}\pi_{\mathrm{X}})\mathrm{d}\tau \qquad n = 2\text{–}4 \qquad \mathrm{X = F, Cl, Br}$$

between pπ orbitals of the halogens and those of the boron, using Slater-type orbitals with optimized exponents[14] and the experimental B–X bond lengths.[15] The largest overlap is for BCl_3, 0.220, with B–Br being slightly smaller, 0.211, and the smallest overlap is found for BF_3, 0.187. The calculated overlap integrals are clearly in contradiction with the back-bonding theory.

Another way to test the back-bonding hypothesis is to look at the boron contributions to the π molecular orbitals of these molecules. At the HF/6-31G*//HF/6-31G* level, the π orbitals of BCl_3 and BF_3 have the following form:

BF_3

$$\phi_\pi = [0.19(2\mathrm{p}_{\pi,3\mathrm{G}}) + 0.08(2\mathrm{p}_{\pi,1\mathrm{G}})]_{\mathrm{B}} + [0.34(2\mathrm{p}_{\pi,3\mathrm{G}}) + 0.23(2\mathrm{p}_{\pi,1\mathrm{G}})]_{\mathrm{F}_1} + \ldots$$

BCl_3

$$\phi_\pi = [0.20(2\mathrm{p}_{\pi,3\mathrm{G}}) + 0.12(2\mathrm{p}_{\pi,1\mathrm{G}})]_{\mathrm{B}} + [-0.14(2\mathrm{p}_{\pi,3\mathrm{G}}) + 0.37(3\mathrm{p}_{\pi,3\mathrm{G}}) + 0.17(3\mathrm{p}_{\pi,1\mathrm{G}})]_{\mathrm{Cl}_1} + \ldots$$

The B 2pπ contribution is slightly bigger for BCl_3 than for BF_3, contrary to what is expected for back-bonding.

We have further calculated the atomic charges in BF_3 and BCl_3. Since charges obtained by the Mulliken population analysis procedure[16] have been criticized for being very basis set dependent and sometimes unrealistic,[17-19] we have also used two other approaches that are available in Gaussian 92: natural bond orbital population analysis (NBO)[20] and the Merz–Singh–Kollman scheme for calculating charges from electrostatic potentials.[21] The NBO method has been shown to be less basis-set sensitive than the usual population analysis,[19] while charges obtained from electrostatic potentials are only indirectly dependent upon the basis set through the electron distribution and reproduce well the multipole moments computed from the same wave function.[17] Table III shows that all three methods, at all of the levels of theory, find boron to be significantly more positive in BF_3 than in BCl_3. Furthermore, both population analysis procedures find the boron 2pπ orbital to be more populated in BCl_3 than in BF_3.

Table III. Calculated Atomic Charges for Boron

method	BF_3	BCl_3
	HF/6-31G*//HF/6-31G*	
pop. anal.^{a}	0.931	0.276
ESP^{b}	1.076	0.434
NBO^{c}	1.642	0.483
	HF/6-31+G(2d,p)//HF/6-31+G(2d,p)	
pop. anal.^{a}	1.806	0.467
ESP^{b}	1.095	0.323
NBO^{c}	1.654	0.467
	MP2/6-31+G(2d,p)//MP2/6-31+G(2d,p)^{d}	
pop. anal.^{a}	1.556	0.310
ESP^{b}	0.955	0.251
NBO^{c}	1.491	0.291

^{a} Reference 16. ^{b} Electrostatic-potential-derived charges.[21] ^{c} Natural bond orbital analysis.[19] ^{d} MP2 calculations performed with the frozen-core approximation.

A more rigorously-based property for monitoring electrostatic interactions is the molecular electrostatic potential, $V(\mathbf{r})$.[22,23] This represents the interaction energy between the unperturbed charge

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Table IV. Electrostatic Potentials above Boron, in kcal/mol, Computed at the HF/6-31+G(2d,p)//HF/6-31+G(2d,p) Level

	dist (Å)			
	1.0	1.5	2.0	2.5
BF_3	221.4	76.8	34.9	18.5
BCl_3	210.9	66.4	27.0	13.0

Table V. Computed Pyramidalization Energies (kcal/mol) for XBX Angles of 113.5°

	BF_3	BCl_3
HF/6-31G*//HF/6-31G* [a]	25.4	21.5
MP2/6-31G*//HF/6-31G* [a]	23.5	20.6
HF/6-31+G(2d,p)//HF/6-31+G(2d,p)	25.4	21.6
MP2/6-31+G(2d,p)//MP2/6-31+G(2d,p) [b]	24.1	19.7

[a] Reference 24. [b] MP2 calculations performed with the frozen-core approximation.

Table VI. Electron Affinities and Charge Capacities[a]

molecule	electron affinity (eV)	charge capacity (eV^{-1})	molecule	electron affinity (eV)	charge capacity (eV^{-1})
BF_3	<0 (–0.78[b])	<0.063	PF_3	<0	<0.081
BCl_3	0.33 ± 0.2	0.089	PCl_3	0.82 ± 0.1	0.11
BBr_3	0.82 ± 0.2	0.103	PBr_3	1.59 ± 0.1	0.12

[a] The electron affinities are experimentally-determined values (except as indicated) and are taken from ref 12 for the boron trihalides and ref 36 for the phosphorus trihalides. The charge capacities were calculated with eq 1 using these electron affinities and ionization potentials from ref 37. [b] Calculated in this work, at MP4/6-31+G(2d,p)//MP2/6-31+G(2d,p) level with HF/6-31+G* zero-point energy correction scaled by 0.89.

Table VII. Calculated Geometry of the BF_3^- Anion

	B–F (Å)	F–B–F (deg)
HF/6-311+G(2d,p)	1.380	110.6
MP2/6-31+G(2d,p)[a]	1.405	111.2

[a] MP2 calculations performed with the frozen-core approximation.

Table VIII. Calculated Charge Transfer from NH_3 to BF_3 and BCl_3

	BF_3	BCl_3
HF/6-31+G(2d,p)//HF/6-31+G(2d,p)		
pop. anal.[a]	0.256	0.346
ESP[b]	0.279	0.311
NBO[c]	0.288	0.362
MP2/6-31+G(2d,p)//MP2/6-31+G(2d,p)[d]		
pop. anal.[a]	0.299	0.369
ESP[b]	0.293	0.382
NBO[c]	0.311	0.377

[a] Reference 16. [b] Electrostatic-potential derived charges.[21] [c] Natural bond orbital analysis.[19] [d] MP2 calculations performed with the frozen-core approximation.

distribution of the molecule and a positive point charge located at the point **r**. In Table IV are the values of *V*(**r**) computed at several distances above the boron atoms in BF_3 and BCl_3. It is seen that the electrostatic potential above the boron in BF_3 is considerably more positive than in BCl_3. Thus, both the atomic charges and the electrostatic potentials are consistent with the electronegativities of the halogens rather than the back-bonding concept.

Branchadell and Olivia have calculated a pyramidalization energy for BF_3 and BCl_3 by optimizing the geometries with the XBX angle distorted to 113.5° and comparing the energies to the ground states.[24] Their values, together with ours for the same degree of distortion, are presented in Table V. Depending upon the computational level, the energy requirement for BF_3 is found to be 2.9–4.4 kcal/mol higher than for BCl_3. This might be an indication that the B–X bond is indeed stronger in BF_3; however it could also reflect a greater repulsive interaction between the fluorines, which have more negative charges than do the chlorines in BCl_3 (Table III). Our calculated structures for the $H_3N–BX_3$ complexes show that BCl_3 is more pyramidal than is BF_3; the XBX angles are 113.5 and 114.3°, respectively. If we use the same geometries for BF_3 and BCl_3 as they have in the complexes, the distortion energy is greater for BCl_3, by 0.5 kcal/mol [HF/6-31+G(2d,p)]. Overall, the computed pyramidalization energies do not seem to clarify the back-bonding/resonance stabilization issue.

The experimentally-determined electron affinities of the boron trihalides increase in the same order as their complexation energies, $BF_3 < BCl_3 < BBr_3$ (Table VI). This trend has also been explained in terms of back-bonding and the resulting resistance to becoming pyramidal upon anion formation.[6] (See Table VII.) However there is actually nothing unusual about electron affinities increasing for heavier congeners within the same column of the periodic table; an example is the phosphorus trihalides (Table VI), in which no extra stabilization is expected.[5] Indeed most small closed-shell molecules containing mainly first-row atoms have negative electron affinities.[6]

These observations can be understood in terms of the concept of charge capacity,[25–28] which refers to the ability of an atom or group to accept or donate electronic charge. Consideration of charge capacities has made it possible to explain a number of seemingly anomalous aspects of chemical behavior,[28] such as the relatively low electron affinity of the fluorine atom and the fact that the gas-phase acidity of fluoroacetic acid is less than that of chloroacetic acid. The charge capacity κ can be estimated from the ionization potential *I* and electron affinity *A*,[27]

$$\kappa = \frac{1}{I-A} \qquad (1)$$

The values of κ for the boron and phosphorus trihalides are given in Table VI and are seen to vary in the same direction as their electron affinities. Thus the trends in the latter can be understood in terms of the increasing ability of the larger, more polarizable congeners to accommodate the additional electron.

We believe that the charge capacity concept also explains the trends in the interaction energies of the boron trihalides with Lewis bases. Our calculated atomic charges for $H_3N{\cdot}BF_3$ and $H_3N{\cdot}BCl_3$ indicate that there is a significant amount of charge transfer from ammonia to the boron trihalide and that this is greater for BCl_3 than for BF_3 (Table VIII). This is in agreement with the results of earlier computational studies of boron trihalide complexes with Lewis bases.[4,29–31] The same conclusion was reached for trimethylamine·BX_3 systems on the basis of proton NMR;[32] the fact that the methyl proton shifts increase in the order $BF_3 < BCl_3 < BBr_3$ is attributed to increasing donation of charge from the methyl groups to the nitrogen to compensate for charge transfer from nitrogen to boron. Supporting evidence was found in the measured dipole moments of these complexes,[33]

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which increase in the order $BF_3 < BCl_3 < BBr_3$ (as do those of the corresponding pyridine systems). It has also been found that the shift in the carbonyl stretching frequency of ethyl acetate upon complexation with boron trihalides increases in the order $BF_3 < BCl_3 < BBr_3$.[34] The shift is interpreted as reflecting transfer of electron density from the carbonyl bond to the acid.

If it is accepted that significant charge transfer occurs in the interactions of boron trihalides with Lewis bases, then it is understandable that the relative tendencies to form these complexes cannot be explained in terms of electrostatic considerations alone. The ability of the BX_3 molecule to accommodate this extra charge (i.e. its charge capacity) then becomes a key factor, and Table VI shows that this increases in the order $BF_3 < BCl_3 < BBr_3$.

Summary

Our computational analyses of the interactions of BF_3 and BCl_3 with NH_3 are in agreement with the experimental observation that the Lewis acidities of the boron trihalides increase in the order $BF_3 < BCl_3 < BBr_3$. This is opposite to the variation in the positive charge on the boron that is predicted by electronegativity considerations and is confirmed by our calculated atomic charges and molecular electrostatic potentials. The latter results (as well as the relevant overlap integrals) accordingly do not support using the concept of back-bonding and consequent stabilization to explain the trend in Lewis acidities. As an alternative explanation, we suggest that this trend reflects the importance of Lewis base → BX_3 charge transfer in these complexes and the fact that the ability to accept the charge, as indicated by charge capacities, increases in the order $BF_3 < BCl_3 < BBr_3$.

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