Inorg. Chem. **2003**, *42*, 7990–7994

Inorganic Chemistry
Article

Why Is BCl_3 a Stronger Lewis Acid with Respect to Strong Bases than BF_3?[†,‡]

Fabienne Bessac[§,||] **and Gernot Frenking***[,||]

Laboratoire de Physique Quantique, Université Paul Sabatier, 118 Route de Narbonne,
F-31062 Toulouse, France, and Fachbereich Chemie, Philipps-Universität Marburg,
Hans-Meerwein-Strasse, D-35043 Marburg, Germany

Received February 11, 2003

Geometries and bond dissociation energies of the complexes $Cl_3B–NH_3$ and $F_3B–NH_3$ have been calculated using DFT (PW91) and ab initio methods at the MP2 and CCSD(T) levels using large basis sets. The calculations give a larger bond dissociation energy for $Cl_3B–NH_3$ than for $F_3B–NH_3$. Calculations of the deformation energy of the bonded fragments reveal that the distortion of BCl_3 and BF_3 from the equilibrium geometry to the pyramidal form in the complexes requires nearly the same energy. The higher Lewis acid strength of BCl_3 in $X_3B–NH_3$ compared with BF_3 is an intrinsic property of the molecule. The energy partitioning analysis of $Cl_3B–NH_3$ and $F_3B–NH_3$ shows that the stronger bond in the former complex comes from enhanced covalent interactions between the Lewis acid and the Lewis base which can be explained with the energetically lower lying LUMO of BCl_3.

Introduction

Experimental studies have shown that the strength of the Lewis acidity of boron trihalides with respect to strong Lewis bases increases in the order $BF_3 < BCl_3 < BBr_3$.[1] Quantum chemical calculations of Cl_3B-NH_3 and F_3B-NH_3 predict that the bond energy of the former complex is 7.7 kcal/mol higher than for the latter.[2] The increase in the Lewis acid strength of BX_3 for heavier atoms X is opposite to the trend of the electronegativity of the halogens X. Calculations of the atomic partial charges of BX_3 using different charge partitioning methods give larger positive values for the boron atom when X becomes more electronegative.[3] Thus, the electron deficiency at the boron atom does not explain the relative strength of the X_3B-NH_3 donor−acceptor interaction.

It is sometimes stated that the $2p(\pi)$ charge donation of fluorine lone-electron pairs into the formally empty $2p(\pi)$ AO of boron is more efficient and leads to stronger B−X π bonding compared with the $3p(\pi)$ charge donation of chlorine because of poorer overlap of the 3p AOs than 2p AOs. This type of argument has also sometimes been used to explain the putative weakness of π bonds between heavier main-group elements. However, it has been shown that the overlap between the more diffuse $p(\pi)$ orbitals of the heavier main-group elements has a similar size or may even be larger than for the atoms of the first octal row.[4,5] In particular, the overlap between the boron and chlorine $p(\pi)$ orbitals in BCl_3 is larger than the overlap between the boron and fluorine $p(\pi)$ orbitals in BF_3.[4] A recent theoretical study of the π-donor strength of the halogens in AX_3 and BX_3^+ (A = B−Tl; B = C−Pb) showed clearly that the order is always F < Cl < Br < I.[3]

In a theoretical study published in 1993, Brinck and coworkers suggested that the stronger bonding in Cl_3B-NH_3 compared with F_3B-NH_3 comes from the larger charge capacity of Cl_3B.[4] The charge capacity was estimated from the ionization potential and the electron affinity which increases for boron trihalides BX_3 and phosphorus trihalides PX_3 with X = F < Cl < Br.[6] This is because the larger, more polarizable congeners can accommodate an additional

---

* Author to whom correspondence should be addressed. E-mail: frenking@chemie.uni-marburg.de.

[†] Theoretical Studies of Inorganic Compounds. 32. Part 31: Esterhuysen, C.; Frenking, G. *Theor. Chem. Acc.,* in press.

[‡] This paper is dedicated to Professor Manfred T. Reetz on the occasion of his 60th birthday.

[§] Université Paul Sabatier.

[||] Philipps-Universität Marburg.

(1) (a) Cotton, F. A.; Wilkinson, G.; Murillo, C. A.; Bochmann, M. *Advanced Inorganic Chemistry*, 6th ed; Wiley: New York, 1999; p 165. (b) Gur'yanova, E. N.; Gol'dshtein, I. P.; Romm, I. P. *Donor−Acceptor Bond*; Wiley: New York, 1975; p 100.

(2) Jonas, V.; Frenking, G.; Reetz, M. T. *J. Am. Chem. Soc.* **1994**, *116*, 8741.

(3) Frenking, G.; Fau, S.; Marchand, C. M.; Grützmacher, H. *J. Am. Chem. Soc.* **1997**, *119*, 6648.

(4) Brinck, T.; Murray, J. S.; Politzer, P. *Inorg. Chem.* **1993**, *32*, 2622.

(5) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 272.

10.1021/ic034141o CCC: $25.00

electron more easily. However, this explanation is at variance with systematic theoretical studies of donor−acceptor complexes using the NBO partitioning scheme which show that there is no correlation between charge donation and bond strength.[2,7]

Very recently, Gillespie and co-workers presented a simple explanation of the Lewis acid strength of the boron halides using the so-called ligand close-shell (LCP) model.[8] According to the LCP model, the geometry of a molecule AX_n is mainly determined by the repulsion between the atoms or groups X rather than by the nature of the A−X bonding.[9,10] It was suggested that BF_3 is an *intrinsically* stronger Lewis acid than BCl_3 because of the larger electron deficiency of boron in the former molecule. The weaker bond in F_3B-NH_3 compared with Cl_3B-NH_3 was explained with the larger distortion energy of the former complex which is necessary to bring the BX_3 acceptor moiety from its D_{3h} equilibrium geometry to the pyramidal C_{3v} structure. The authors presented results of DFT calculations which suggest that it takes more energy to distort the planar structure of BF_3 toward a pyramidal form with a fixed bond angle than BCl_3.[8] This is in agreement with an earlier study by Branchadell and Oliva who calculated a pyramidalization energy for BCl_3 and BF_3 by optimizing the geometries with the XBX angle distorted to 113.5° and comparing the energies to the ground states.[11] However, it was already shown by Brinck et al.[4] that the distortion energy is 0.5 kcal/mol *smaller* for BF_3 *if the actual geometries of BCl_3 and BF_3 in the complexes X_3B-NH_3 are taken*. The latter result was obtained only at the HF level, however.

Gillespie et al.[8] present the calculation of the distortion energy as a function of only the angles of the BX_3 moieties but not the B−X bond lengths. In addition, Gillespie and co-workers do not report the calculated bond energies of the Cl_3B-D and F_3B-D (D being a strong donor) complexes. The relative strength of the Lewis acidity of BF_3 and BCl_3 was only derived from the calculated interatomic distances B−D although it is known that the bond lengths of donor−acceptor complexes often do not even qualitatively correlate with bond energies.[12] In order to state that the distortion energy of the BX_3 acceptor unit is responsible for the stronger bond of Cl_3B-D compared with F_3B-D, it is necessary to give the calculated bond energies. In the following we give the relevant energy data for the complexes Cl_3B-NH_3 and F_3B-NH_3 which have been used as model compounds. We provide an explanation more consistent with the computational results than that given by Gillespie et al.[8] We also give an explanation for the larger Lewis acid strength of BCl_3 which is in agreement with the nature of the donor−acceptor interaction.

Methods

In order to be sure that the conclusion of this work does not depend on the level of theory, we used different theoretical methods for the calculations. The geometries of the molecules have first been optimized using Møller−Plesset second-order perturbation theory (MP2)[13] in conjunction with the Pople basis sets 6-311G(2d)[14] and with Dunning's correlation consistent basis sets cc-pVTZ.[15] Improved energies were calculated at MP2/Aug-cc-pVTZ and using coupled-cluster theory with doubles and triples and a perturbative treatment of the triple excitation CCSD(T)[16] in conjunction with cc-pVTZ basis sets at MP2/cc-pVTZ optimized geometries. The vibrational frequencies have been calculated at MP2/cc-pVTZ. All optimized structures are energy minima on the potential energy surface. The geometries and energies have also been calculated with gradient-corrected density functional theory (DFT) using the PW91 exchange-correlation functional by Perdew and Wang.[17] Uncontracted Slater-type orbitals (STOs) were employed as basis functions for the PW91 calculations.[18] The basis sets have quadruple-ζ quality augmented by four sets of polarization functions. This level of theory is denoted PW91/QZ4P. An auxiliary set of s, p, d, f, and g STOs was used to fit the molecular densities and to represent the Coulomb and exchange potentials accurately in each SCF cycle.[19] The ab initio calculations described in this work were performed with the program packages Gaussian 98.[20] The DFT calculations were carried out with ADF 2.3.[21]

The nature of the donor−acceptor bonds of the complexes has been investigated with an energy partitioning analysis (EPA) in order to explain why Cl_3B-NH_3 has a stronger bond than F_3B-NH_3. It is our goal to give an explanation that is derived from data which give insight into the physical origin of the chemical bonding rather than from correlating numbers. The EPA method was developed by Morokuma[22] in the framework of Hartree−Fock theory and later by Ziegler and Rauk[23] in the framework of DFT using Kohn−Sham orbitals. The latter has been used in the present work. The bond dissociation energy D_e between two fragments A and B (in the present case: X_3B and NH_3) is partitioned into several contributions which can be identified as physically meaningful

---

(6) (a) Rothe, G. W.; Mathur, B. P.; Reck, G. P. *Inorg. Chem.* **1980**, *19*, 829. (b) Mathur, B. P.; Rothe, G. W.; Tang, S. Y.; Reck, G. P. *J. Chem. Phys.* **1976**, *65*, 565.

(7) Beste, A.; Krämer, O.; Gerhard, A.; Frenking, G. *Eur. J. Inorg. Chem.* **1999**, 2037.

(8) Rowsell, B. D.; Gillespie, R. J.; Heard, G. L. *Inorg. Chem.* **1999**, *38*, 4659.

(9) (a) Robinson, E. A.; Heard, G. L.; Gillespie, R. J. *J. Mol. Struct.* **1999**, *305*, 485. (b) Gillespie, R. J.; Robinson, E. A. *Adv. Mol. Struct. Res.* **1998**, *4*, 1.

(10) Gillespie, R. J.; Popelier, P. L. A. *Chemical Bonding and Molecular Geometry*; Oxford University Press: New York, 2001; p 191.

(11) Branchadell, V.; Olivia, A. *J. Mol. Struct. (THEOCHEM)* **1991**, *236*, 75.

(12) (a) Bowmaker, G. A.; Schmidbaur, H.; Krüger, S.; Rösch, N. *Inorg. Chem.* **1997**, *36*, 1754−1757. (b) Ernst, R. D.; Freeman, J. W.; Stahl, L.; Wilson, D. R.; Arif, A. M.; Nuber, B.; Ziegler, M. L. *J. Am. Chem. Soc.* **1995**, *117*, 5075−5081. (c) Fischer, R. A.; Schulte, M. M.; Weiss, J.; Zsolnai, L.; Jacobi, A.; Huttner, G.; Frenking, G.; Boehme, C.; Vyboishchikov, S. F. *J. Am. Chem. Soc.* **1998**, *120*, 1237. (d) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Le Van, D.; Krebs, B.; Läge, M. *Organometallics* **2002**, *21*, 2921.

(13) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*. 618.

(14) (a) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. (b) Raghavachari, K.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(15) Kendal, R. A.; Dunning, T. H., Jr.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796.

(16) (a) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479. (b) Watts, J. D.; Gauss, J.; Bartlett, R. J. *J. Chem. Phys.* **1993**, *98*, 8718.

(17) Perdew, J. W.; Wang, Y. In *Electronic Structure of Solids '91*; Ziesche, P., Eschrig, H., Eds.; Akademie-Verlag: Berlin, 1991; p 11.

(18) Snijders, J. G.; Baerends, E. J.; Vernooijs, P. *At. Nucl. Data Tables* **1982**, *26*, 483.

(19) Krijn, J.; Baerends, E. J. *Fit Functions in the HFS-Method*; Internal Report (in Dutch); Vrije Universiteit: Amsterdam, The Netherlands, 1984.

entities. First, D_e is separated into two major components ΔE_{prep} and ΔE_{int}:

$$-D_e = \Delta E_{prep} + \Delta E_{int} \tag{1}$$

ΔE_{prep} (also called deformation energy) is the energy necessary to promote the fragments A and B from their equilibrium geometry and electronic ground state to the geometry and electronic state in the compound AB. The focus of the bonding analysis is the instantaneous interaction energy ΔE_{int} between the donor and acceptor molecules. It is the energy difference between the fragments A and B which are calculated in the frozen geometry of the molecule AB. The interaction energy ΔE_{int} can be divided into three main components which can be interpreted in a physically meaningful way:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb} \tag{2}$$

ΔE_{elstat} gives the electrostatic interaction energy in the promolecule, which is calculated as the energy difference between the donor and acceptor moieties and the juxtaposition of BX_3 and NH_3 at the equilibrium distance of the complex. The second term in eq 2, ΔE_{Pauli}, refers to the repulsive interactions between BX_3 and NH_3 which are caused by the fact that two electrons with the same spin cannot occupy the same region in space. ΔE_{Pauli} is calculated by enforcing the Kohn–Sham determinant of the promolecule to obey the Pauli principle by antisymmetrization and renormalization. The stabilizing orbital interaction term, ΔE_{orb}, is calculated in the final step of the EPA when the Kohn–Sham orbitals relax to their optimal form. This term which may be identified with covalent bonding can be further partitioned into contributions of orbitals having σ, π, δ, etc. symmetry. Further details of method can be found in the literature.[21b] The EPA method has recently been used by us[24,25] and other groups[26] in systematic investigations of the nature of the chemical bond in main-group and transition metal compounds.

Table 1. Calculated Interaction Energies ΔE_{int} between the Frozen Fragments, Preparation Energies ΔE_{prep} of the Fragments, Bond Dissociation Energies D_e, and ZPE Corrected Values D_o[a]

method	$-\Delta E_{int}$	ΔE_{prep}		D_e	D_o
		X_3B	NH_3		
		Cl_3B-NH_3			
MP2/6-311G(2d)	58.0	24.4	0.7	32.9	29.0
MP2/cc-pVTZ	53.0	23.5	0.4	29.1	25.1
MP2/Aug-cc-pVTZ[b]	52.8	23.1	0.2	29.5	25.5
CCSD(T)/cc-pVTZ[b]	49.9	22.4	0.4	27.1	23.1
PW91/QZ4P	45.6	21.9	0.3	23.4	19.4
		F_3B-NH_3			
MP2/6-311G(2d)	48.1	23.3	0.5	24.3	20.9
MP2/cc-pVTZ	46.7	23.1	0.3	23.3	19.8
MP2/Aug-cc-pVTZ[b]	45.7	22.3	0.1	23.3	19.8
CCSD(T)/cc-pVTZ[b]	46.6	23.4	0.3	22.9	19.6
PW91/QZ4P	42.9	21.8	0.2	20.9	17.6

[a] All values are given in kcal/mol. [b] Using MP2/cc-pVTZ optimized geometries.

Table 2. Theoretically Predicted Bond Lengths A–B [Å] and Angles A–B–C [deg] of X_3B-NH_3 and BX_3

variable	method	Cl_3B-NH_3 C_{3v}	F_3B-NH_3 C_{3v}	BCl_3 D_{3h}	BF_3 D_{3h}
X–B	MP2/6-311G(2d)	1.835	1.370	1.745	1.314
	MP2/cc-pVTZ	1.827	1.367	1.740	1.315
	PW91/QZ4P	1.838	1.380	1.746	1.322
B–N	MP2/6-311G(2d)	1.611	1.678		
	MP2/cc-pVTZ	1.617	1.681		
	PW91/QZ4P	1.628	1.692		
X–B–N	MP2/6-311G(2d)	105.2	103.9		
	MP2/cc-pVTZ	104.9	103.9		
	PW91/QZ4P	105.1	104.1		
B–N–H	MP2/6-311G(2d)	110.5	110.6		
	MP2/cc-pVTZ	110.0	110.3		
	PW91/QZ4P	109.9	110.3		

Results

Table 1 gives calculated energies of Cl_3B-NH_3 and F_3B-NH_3 which are relevant for the discussion. The MP2 values are given with three different basis sets in order to show the changes which are given when the basis set becomes augmented with addition polarization functions and diffuse functions. We will discuss the MP2/Aug-cc-pVTZ results because they have been obtained with the largest basis set that has been employed in the ab initio calculations. The most important bond lengths and bond angles are shown in Table 2.

The calculated bond dissociation energy (BDE) of Cl_3B-NH_3 is predicted at all levels of theory to be higher than for F_3B-NH_3. The difference between the D_e values is slightly larger at the ab initio levels (6.2 kcal/mol at MP2/Aug-cc-pVTZ, 4.2 kcal/mol at CCSD(T)/cc-pVTZ) than at DFT (2.5 kcal/mol at PW91/QZ4P), but the order is the same. Table 1 gives also the preparation energies ΔE_{prep} of BX_3 and NH_3, i.e., the energy difference between the acceptor and donor moieties in the equilibrium geometries of the free species and in the complexes. The preparation

---

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.3; Gaussian, Inc.: Pittsburgh, PA, 1998.

(21) (a) Bickelhaupt, F. M.; Baerends, E. J. In *Reviews in Computational Chemistry* Lipkowitz, K. B., Boyd, D. B., Eds.; Wiley-VCH: New York, 2000; Vol. 15, p 1. (b) te Velde, G.; Bickelhaupt, F. M.; Baerends, E. J.; van Gisbergen, S. J. A.; Fonseca Guerra, C.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931.

(22) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236.

(23) Ziegler, T.; Rauk, A. *Theor. Chim. Acta* **1977**, *46*, 1.

(24) (a) Diefenbach, A.; Bickelhaupt, F. M.; Frenking, G. *J. Am. Chem. Soc.* **2000**, *122*, 6449. (b) Chen, Y.; Frenking, G. *J. Chem. Soc., Dalton Trans.* **2001**, 434. (c) Lein, M.; Frunzke, J.; Timoshkin, A.; Frenking, G. *Chem. Eur. J.* **2001**, *7*, 4155. (d) Uddin, J.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 1683. (e) Doerr, M.; Frenking, G. *Z. Allg. Anorg. Chem.* **2002**, *628*, 843. (f) Frenking, G.; Wichmann, K.; Fröhlich, N.; Grobe, J.; Golla, W.; Le Van, D.; Krebs, B.; Läge, M. *Organometallics* **2002**, *21*, 2921. (g) Frunzke, J.; Lein, M.; Frenking, G. *Organometallics* **2002**, *21*, 3351. (h) Loschen, C.; Voigt, K.; Frunzke, J.; Diefenbach, A.; Diedenhofen, M.; Frenking, G. *Z. Allg. Anorg. Chem.* **2002**, *628*, 1294. (i) Rayón, V. M.; Frenking, G. *Chem. Eur. J.* **2002**, *8*, 4693. (j) Cases, M.; Frenking, G.; Duran, M.; Solà, M. *Organometallics* **2002**, *21*, 4182.

(25) Review: Frenking, G.; Wichmann, K.; Fröhlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayón, V. M. *Coord. Chem. Rev.* **2003**, *238–239*, 55.

(26) (a) Bickelhaupt, F. M.; Radius, U.; Ehlers, A. W.; Hoffmann, R.; Baerends, E. J. *New J. Chem.* **1998**, *22*, 1. (b) Radius, U.; Bickelhaupt, F. M.; Ehlers, A. W.; Goldberg, N.; Hoffmann, R. *Inorg. Chem.* **1998**, *37*, 1080. (c) Ehlers, A. W.; Baerends, E. J.; Bickelhaupt, F. M.; Radius, U. *Chem. Eur. J.* **1998**, *4*, 210. (d) Dickinson, A. A.; Willock, D. J.; Calder, R. J.; Aldridge, S. *Organometallics* **2002**, *21*, 1146.

Table 3. Energy Partitioning Analysis of Cl_3B-NH_3 and F_3B-NH_3 at PW91/QZ4P[a]

term	Cl_3B-NH_3		F_3B-NH_3	
ΔE_{int}	−45.6		−42.9	
ΔE_{pauli}	190.1		125.9	
ΔE_{elstat}[b]	−118.6	(50.3%)	−91.4	(54.1%)
ΔE_{orb}[b]	−117.1	(49.7%)	−77.4	(45.9%)
ΔE_{σ}[c]	−105.9	(90.4%)	−69.4	(89.7%)
ΔE_{π}[c]	−11.2	(9.6%)	−8.0	(10.3%)

[a] All values in kcal/mol. [b] The percentage values in parentheses give the contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$. [c] The percentage values in parentheses give the contribution to the orbital interactions ΔE_{orb}.

energies of BX_3 are quite large while the ΔE_{prep} values for NH_3 are negligible. The differences between the calculated data for BCl_3 and BF_3 are crucial for answering the title question. The theoretical preparation energies for BCl_3 at MP2/Aug-cc-pVTZ (23.1 kcal/mol) and PW91/QZ4P (21.9 kcal/mol) are a bit *larger* than for BF_3 (22.3 kcal/mol at MP2/Aug-cc-pVTZ, 21.8 kcal/mol at PW91/QZ4P). This is in agreement with the HF calculations of Brinck et al.[4] The calculations at CCSD(T)/cc-pVTZ give a slightly smaller value for BCl_3 (22.4 kcal/mol) than for BF_3 (23.4 kcal/mol), but the energy difference of 1.0 kcal/mol is not enough to compensate for the larger BDE of Cl_3B-NH_3. The calculated interaction energy ΔE_{int} is always higher for Cl_3B-NH_3 than for F_3B-NH_3. Thus, *BCl_3 is also an intrinsically stronger Lewis acid with respect to NH_3 than BF_3*. This result is predicted at all three levels of theory.

Table 3 gives the EPA results of Cl_3B-NH_3 and F_3B-NH_3. The largest contribution to the interaction energy comes in both complexes from ΔE_{Pauli}. Note that the Pauli repulsion in Cl_3B-NH_3 is larger than in F_3B-NH_3 although the former compound has a stronger bond. It follows that the larger ΔE_{int} value of Cl_3B-NH_3 results from the stronger attraction between the donor and acceptor species. But which component of the attractive interaction is responsible for the stronger bond? According to the calculated data, the electrostatic contribution to the Cl_3B-NH_3 bond is −118.6 kcal/mol (50.3%), which is only 1.5 kcal/mol more than the orbital interactions, which contribute −117.1 kcal/mol (49.7%). A comparison with the EPA data of F_3B-NH_3 shows that the electrostatic interactions to the latter donor−acceptor bond are −91.4 kcal/mol (54.1%), which is 14.0 kcal/mol more than the covalent bonding, which contributes 77.4 kcal/mol (45.7%). Thus, *the reason why Cl_3B-NH_3 has a stronger bond than F_3B-NH_3 is the stronger covalent attraction in the former complex*.

Why are the covalent interactions in Cl_3B-NH_3 larger than in F_3B-NH_3? Table 3 shows that the ΔE_{orb} term comes as expected mainly from the σ interactions. Because the donor component in the two complexes is the same, we inspected the orbitals of the acceptor moieties BCl_3 and BF_3. Table 4 gives the energy levels of the lowest unoccupied molecular orbital (LUMO) of the boron trihalides at the planar equilibrium geometry and at the pyramidal geometry in the complex at three levels of theory. The DFT energy values of the LUMO are, as expected, much lower lying than the ab initio data. However, both sets of data show that the LUMO of BCl_3 is always lower in energy than the LUMO of BF_3. According to the frontier orbital model of chemical reactivity,[27] a lower lying LUMO indicates stronger interactions with an occupied orbital of a donor species. *Thus, the higher Lewis acid strength of BCl_3 than that of BF_3 in complexes X_3B-NH_3 arises from stronger covalent interactions in Cl_3B-NH_3 which come from the lower lying LUMO of BCl_3.*

Table 4. Energy Levels of the Lowest Unoccupied Molecular Orbitals (LUMO) of BCl_3 and BF_3 [eV]

method	BCl_3	BCl_3[a]	BF_3	BF_3[a]
MP2/Aug-cc-pVTZ[b]	1.091	0.076	1.234	0.405
PW91/QZ4P	−2.817	−4.302	−0.799	−3.625

[a] Calculated using the frozen geometry in the complex. [b] The energy levels refer to Hartree−Fock orbitals.

The results indicate that a careful analysis of the nature of the donor−acceptor interactions should be carried out before the question about the strength of the Lewis acidity and basicity may become addressed. At the same time it becomes obvious why it is not possible to establish an absolute scale for the donor or acceptor strength of a Lewis base or acid because the strength depends on the nature of the bonding interactions and, thus, on the bonding partner. For example, the bond strength of Cl_3B-OH_2 has been calculated to be slightly lower (D_e = 9.5 kcal/mol) than for F_3B-OH_2 (11.0 kcal/mol).[3] Another striking case is the calculated bond energy of H_3B-CO (D_e = 26.4 kcal/mol), which is much higher than the theoretically predicted value for Cl_3B-CO (D_e = 2.2 kcal/mol), while the bond energy of H_3B-NH_3, which was calculated at the MP2/TZ2P level (D_e = 33.7 kcal/mol), is nearly the same as the bond energy of Cl_3B-NH_3 at MP2/6-311G(2d) (D_e = 32.9 kcal/mol).[2] Other examples have been reported in the literature.[7] We also wish to point out that the atomic partial charge is not very reliable for estimating the strength of electrostatic interactions. The electron density distribution of an atom in a molecule is in most cases highly anisotropic. Atoms which carry a positive partial charge may attract a positive charge stronger than a negatively charged atom if there is an area of local electronic charge density pointing toward the positive charge. An example is CO, where the positively charged carbon atom has a lone electron pair which yields stronger electrostatic attraction with a positive point charge than negatively charged oxygen atom.[28]

Summary

The results of this work can be summarized as follows: High-level DFT and ab initio calculations of Cl_3B-NH_3 and F_3B-NH_3 give larger bond dissociation energies for the

---

(27) Fukui, K. *Acc. Chem. Res.* **1971**, *4*, 57. (b) Fukui, K. *Theory of Orientation and Stereoselection*; Springer-Verlag: Berlin, 1975. (c) Fleming, I. *Frontier Orbitals and Organic Chemical Reactions*; Wiley: New York, 1976.

(28) Lupinetti, A.; Fau, S.; Frenking, G.; Strauss, S. H. *J. Phys. Chem.* **1997**, *101*, 9551.

former complex. Calculations of the deformation energy of the bonded fragments reveal that the distortion of BCl_3 and BF_3 from the equilibrium geometry to the pyramidal form in the complexes requires nearly the same energy. The higher Lewis acid strength of BCl_3 in $X_3B{-}NH_3$ compared with BF_3 is an intrinsic property of the molecule. The energy partitioning analysis of $Cl_3B{-}NH_3$ and $F_3B{-}NH_3$ shows that the stronger bond in the former complex comes from the enhanced covalent interactions which can be explained with the energetically lower lying LUMO of BCl_3.

Acknowledgment. We want to express our gratitude to a referee who patiently and kindly helped us to express our results with the right wording. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. Excellent service by the Hochschulrechenzentrum of the Philipps-Universität Marburg is gratefully acknowledged. Additional computer time was provided by the HLRS Stuttgart and HHLRZ Darmstadt.

IC034141O