Comparative Theoretical Study of Lewis Acid–Base Complexes of BH_3, BF_3, BCl_3, $AlCl_3$, and SO_2

Volker Jonas,[†,‡] Gernot Frenking,[*,†] and Manfred T. Reetz[§]

Contribution from the Fachbereich Chemie, Universität Marburg, Hans-Meerwein-Strasse, D-35032 Marburg, Germany, and the Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, D-45470 Mülheim an der Ruhr, Germany

Received March 17, 1994[®]

Abstract: Quantum mechanical calculations at the MP2/TZ2P level of theory predict geometries and bond energies of donor–acceptor complexes of the Lewis acids BH_3, BF_3, BCl_3, $AlCl_3$, and SO_2 which are in very good agreement with experimental gas-phase values. Strong donor–acceptor bonds are calculated for the boron complexes OC–BH_3 (D_0(298) = 25.1 kcal/mol), H_3N–BH_3 (D_0(298) = 30.7 kcal/mol), Me_3N–BH_3 (D_0(298) = 41.1 kcal/mol), H_3N–BF_3 (D_0(298) = 22.0 kcal/mol), Me_3N–BF_3 (D_0(298) = 32.9 kcal/mol), H_3N–BCl_3 (D_0(298) = 29.7 kcal/mol), and Me_3N–BCl_3 (D_0(298) = 40.5 kcal/mol). Weakly bound van der Waals complexes are predicted for OC–BF_3 (D_0(298) = 4.7 kcal/mol), HCN–BF_3 (D_0(298) = 7.2 kcal/mol), MeCN–BF_3 (D_0(298) = 9.1 kcal/mol), OC–BCl_3 (D_0(298) = 4.0 kcal/mol), and MeCN–BCl_3 (D_0(298) = 6.4 kcal/mol). Intermediate dissociation energies are calculated for the BF_3 complexes with Me_2O (D_0(298) = 17.3 kcal/mol), benzaldehyde (D_0(298) = 13.0 kcal/mol), and 2-methylacrolein (D_0(298) = 12.8 kcal/mol). The strongest donor–acceptor bond is calculated for Me_3N–$AlCl_3$ (D_0(298) = 49.3 kcal/mol). A strong bond is also predicted for EtCClO–$AlCl_3$ (D_0(298) = 24.8 kcal/mol), while the complex Me_3N–SO_2 is more weakly bound (D_0(298) = 15.5 kcal/mol). The bond lengths of the Lewis acids are longer in the complexes than in the isolated molecules. A good correlation is found between the calculated bond strengths of the BF_3 complexes and the lengthening of the B–F bond. The NBO partitioning scheme suggests that there is no correlation between the charge transfer and the bond strength. The topological analysis of the electron density distribution shows that the donor–acceptor bonds of the strongly bound boron complexes have significant covalent contributions, while the weakly bound boron complexes are characterized by electrostatic interactions between the Lewis acid and base. However, the nature of the strongly bound $AlCl_3$ complexes is different from that of the strongly bound boron complexes. The strongest donor–acceptor bond calculated for Me_3N–$AlCl_3$ is characterized by electrostatic interactions and very little covalent contributions. The bond shortening of the donor acceptor bonds between the gas phase and the solid state is calculated to be mainly due to short-range dipole–dipole interactions. The geometry-optimized dimer and tetramer of H_3N–BH_3 and the dimer of H_3N–BF_3 have significantly shorter B–N bonds than the monomer.

Introduction

Chemical bonds are usually classified as electrostatic, covalent, or metallic.[1] Weakly bound molecules exhibit yet another type of bonding, which is characterized by van der Waals interactions.[2] Most compounds can be identified as belonging to one of these classes by the nature of the chemical bonds in the molecule. There is one type of compound, however, which makes such an assignment difficult. The class of donor–acceptor complexes comprises molecules that may be bound by electrostatic, covalent, or van der Waals interactions. The present understanding of this important class of molecules is based on the epochal work of Lewis,[3] who introduced the concept of electron-pair donor–acceptor complexes. A popular qualitative model for the interpretation of donor–acceptor interactions is the theory of hard and soft acids and bases (HSAB) suggested by Pearson.[4] A quantitative evaluation and prediction of donor–acceptor interactions has been made by Drago,[5] who introduced the so-called *E* and *C* parameters in an attempt to predict the bond strength of new complexes. The *E* and *C* model has been applied to understand solvent effects and the reactivity in chemical and biological systems.[6] Although much work has been done to characterize the intermolecular interactions, there are still many puzzling features of donor–acceptor complexes that are not completely understood.

One difference between the Lewis-type donor–acceptor bond and normal covalent bonds is that the dissociation of the former yields two closed-shell fragments with an electron lone-pair donor and electron-pair acceptor, while the latter gives two open-shell fragments. Haaland[7] defines *dative bonds* as a new bond type on the basis of their bond rupture behavior, which is different from covalent bonds. Another difference is that the bond length of a normal covalent bond is usually not very different in different aggregation states, while donor–acceptor bonds have frequently larger interatomic distances in the gas phase than in the solid state.[8-22] An intringuing example has recently been reported by Dvorak et al.,[21] who found that the B–N bond length in MeCN–

† Philipps-Universität Marburg.
§ Max-Planck-Institut für Kohlenforschung, Mülheim.
‡ Present address: Organisch-Chemisches Institut, Universität Zürich, CH-8057 Zürich, Switzerland.
® Abstract published in *Advance ACS Abstracts*, August 15, 1994.

(1) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.
(2) van Lenthe, J. H.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Duijneveldt, F. B. In *Ab Initio Methods in Quantum Chemistry II*; Lawley, K. P., Ed.; Wiley & Sons Ltd.: London, 1987; p 521.
(3) Lewis G. N. *Valence and the Structure of Atoms and Molecules*; The Chemical Catalog Co., Inc.: New York, 1923.
(4) (a) Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533. (b) Pearson, R. G.; Songstad, J. *J. Am. Chem. Soc.* **1967**, *89*, 1827. (c) Pearson, R. G. *Hard and Soft Acids and Bases*; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1973.
(5) Drago, R. S. *Structure Bonding* **1973**, *15*, 73.
(6) (a) Drago, R. S. *Pure Appl. Chem.* **1980**, *52*, 2261. (b) Drago, R. S. *Coord. Chem. Rev.* **1980**, *33*, 251.
(7) Haaland, A. *Angew. Chem.* **1989**, *101*, 1017; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.
(8) (a) Bühl, M.; Steinke, T.; Schleyer, P. v. R.; Boese, R. *Angew. Chem.* **1991**, *103*, 1179; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1160. (b) Boese, R. Personal communication.
(9) Thorne, L. R.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1983**, *78*, 167.
(10) Iijima, K.; Adachi, N.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 3269.

0002-7863/94/1516-8741$04.50/0 © 1994 American Chemical Society

BF_3 in the gas phase is 2.011 Å, while it is 1.630 Å in the solid state.[20] The value of r_{BN} = 2.011 Å is intermediate between the limits normally observed for van der Waals and covalently bound systems. This makes $MeCN-BF_3$ a particularly interesting molecule. An even larger difference between the interatomic distances in the gas phase and in the solid state has been reported by Burns et al.[19] for $HCN-BF_3$, which has a bond length of 2.473 Å in the gas phase and 1.638 Å in the solid state.

The classical donor-acceptor complex H_3N-BF_3 merits special attention. It is the first known coordination compound of any element, synthesized in 1809 by Gay-Lussac.[23] H_3N-BF_3 was used by Lewis[3] as an example to illustrate the concept of the donor-acceptor bond. However, it has only recently been detected in the gas phase by Legon and Warner.[24] These authors report a B-N equilibrium distance of 1.59 ± 0.03 Å. This has been challenged by quantum mechanical calculations, which predict a longer B-N bond, r_{BN} = 1.68 ± 0.02 Å, for H_3N-BF_3.[25]

There are several reviews and books that have attempted systematic comparisons of calculated and experimental parameters for gas-phase and solid-state donor-acceptor complexes.[7,26] Not only are donor-acceptor complexes interesting from a theoretical point of view, but they have also successfully been utilized for the design of new synthetic methods.[27] Therefore, the knowledge about their structures and properties is important for experimental as well as theoretical chemistry. Several theoretical studies are devoted to donor-acceptor complexes,[28-33] but no systematic comparison of the calculated properties with experimentally observed gas-phase and solid-state structures has been published to date. The goal of this paper is to study systematically the theoretically predicted structures of several donor-acceptor complexes of BH_3, BF_3, BCl_3, $AlCl_3$, and SO_2. The choice of complexes investigated was made with the aim to include all different types of strongly bound molecules and van der Waals complexes. Therefore, the complexes of the five Lewis acids with the strong Lewis base Me_3N have been calculated. The complexes of the three boron Lewis acids BH_3, BF_3, and BCl_3 with CO and NH_3 are also included in this work. Finally, some donor-acceptor complexes with the rather weak Lewis bases Me_2O, HCN, MeCN, benzaldehyde, and 2-methylacrolein were investigated, because experimental data were available for these molecules. The molecules being studied are $OC-BH_3$ (**1**), H_3N-BH_3 (**2**), Me_3N-BH_3 (**3**), $OC-BF_3$ (**4**), H_3N-BF_3 (**5**), Me_3N-BF_3 (**6**), Me_2O-BF_3 (**7**), $HCN-BF_3$ (**8**), $MeCN-BF_3$ (**9**), benzaldehyde-BF_3 (**10**), 2-methylacrolein-BF_3 (**11**), $OC-BCl_3$ (**12**), H_3N-BCl_3 (**13**), Me_3N-BCl_3 (**14**), $MeCN-BCl_3$ (**15**), $EtCClO-AlCl_3$ (**16**), $Me_3N-AlCl_3$ (**17**), and Me_3N-SO_2 (**18**). The properties investigated in this study are the equilibrium geometries and bond energies of the donor-acceptor complexes.

The nature of the dative bond is studied in detail. In order to investigate the electronic structure of the molecules, we use the natural bond orbital (NBO) partitioning scheme developed by Weinhold and co-workers[34] and the topological analysis of the wave function suggested by Bader.[35]

Computational Methods

The ab initio molecular orbital calculations were carried out with the program packages GAUSSIAN90,[36] GAUSSIAN92,[37] and TURBOMOLE.[38] All complexes have been optimized at the HF and MP2 levels of theory.[39,40] Three different basis sets were used for the calculations: the standard 3-21G(d) and 6-31G(d) split valence plus polarization basis sets[41,42] and a TZ2P triple-ζ double-polarized basis set.[43,44] The calculations were carried out with the five spherical components of the respective d functions. Harmonic vibrational frequencies were calculated

(11) Cassoux, P.; Kuczkowski, R. L.; Bryan, P. S.; Taylor, R. C. *Inorg. Chem.* **1975**, *14*, 126.

(12) (a) Geller, S.; Hoard, J. L. *Acta Crystallogr.* **1951**, *4*, 399. (b) Hoard, J. L.; Geller, S.; Owen, T. B. *Acta Crystallogr.* **1951**, *4*, 405.

(13) Iijima, K.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 711.

(14) Hargittai, M.; Hargittai, I. *J. Mol. Struct.* **1977**, *39*, 79.

(15) Clippard, P. H.; Hanson, J. C.; Taylor, R. C. *J. Cryst. Mol. Struct.* **1971**, *1*, 363.

(16) Hess, H. *Acta Crystallogr., Sect. B* **1969**, *25*, 2338.

(17) Iijima, K.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 1908.

(18) Iijima, K.; Shibata, S. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1891.

(19) Burns, W. A.; Leopold, K. R. *J. Am. Chem. Soc.* **1993**, *115*, 11622.

(20) (a) Hoard, J. L.; Owen, T. B.; Buzzell, A.; Salmon, O. N. *Acta Crystallogr.* **1950**, *3*, 130. (b) Swanson, B.; Shriver, D. F.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2182.

(21) Dvorak, M. A.; Ford, R. S.; Suenram, R. D.; Lovas, F. J.; Leopold, K. R. *J. Am. Chem. Soc.* **1992**, *114*, 108.

(22) (a) Burg, A. B. *J. Am. Chem. Soc.* **1943**, *65*, 1629. (b) Moede, J. A.; Curran, C. *J. Am. Chem. Soc.* **1949**, *71*, 852. (c) Christian, S. D.; Grundnes, J. *Nature (London)* **1967**, *214*, 1111. (d) Grundnes, J.; Christian, S. D. *J. Am. Chem. Soc.* **1968**, *90*, 2239. (e) Grundnes, J.; Christian, S. D.; Cheam, V.; Farnham, S. B. *J. Am. Chem. Soc.* **1971**, *93*, 20. (f) Van Der Helm, D.; Childs, J. D.; Christian, S. D. *J. Chem. Soc., Chem. Commun.* **1969**, 887. (g) LaBarge, M. S.; Matos, J.; Hillig, K. W.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1987**, *109*, 7222. (h) Oh, J. J.; LaBarge, M. S.; Matos, J.; Kampf, J. W.; Hillig, K. W.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 4732.

(23) Gay-Lussac, J. L.; Thénard, J. L. *Mem. Phys. Chim. Soc. d'Arcueil* **1809**, *2*, 210.

(24) Legon, A. C.; Warner, H. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1397.

(25) Jonas, V.; Frenking, G. *J. Chem. Soc., Chem. Commun.* **1994**, 1489.

(26) (a) Satchell, D. P. N.; Satchell, R. S. *Q. Rev., Chem. Soc.* **1971**, *25*, 171. (b) Gur'yanova, E. N.; Gol'dshtein, I. P.; Romm, I. P. *The Donor-Acceptor Bond*; Wiley: New York, 1975. (c) Gutmann, V. *The Donor-Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978. (d) Jensen, W. B. *The Lewis Acid-Base Concept—An Overview*; John Wiley & Sons, Inc.: New York, 1980. (e) Shambayati, S.; Crowe, W. E.; Schreiber, S. L. *Angew. Chem.* **1990**, *102*, 273; *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 256.

(27) (a) Reetz, M. T. *Acc. Chem. Res.* **1993**, *26*, 462. (b) Reetz, M. T. *Angew. Chem.* **1984**, *96*, 542; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 556. (c) Schinzer, D., Ed. *Selectivities in Lewis Acid Promoted Reactions*; Kluwer Academic Publishers: Dordrecht, 1989. (d) Shambayati, S.; Schreiber, S. L. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 1, p 283. (e) Yamaguchi, M. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1991; Vol. 1, p 325.

(28) (a) Umeyama, H.; Morokuma, K. *J. Am. Chem. Soc.* **1976**, *98*, 7208. (b) Redmon, L. T.; Purvis, G. D.; Bartlett, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 2856. (c) Zirz, C.; Ahlrichs, R. *J. Chem. Phys.* **1981**, *75*, 4980. (d) Bonaccorsi, R.; Palla, P.; Cimiraglia, R.; Tomasi, J. *Int. J. Quantum. Chem.* **1983**, *24*, 307. (e) Binkley, J. S.; Thorne, L. R. *J. Chem. Phys.* **1983**, *79*, 2932. (f) Bonaccorsi, R.; Cammi, R.; Tomasi, J. *Int. J. Quantum. Chem.* **1986**, *29*, 373. (g) Cammi, R.; Tomasi, J. *Theor. Chim. Acta* **1986**, *69*, 11. (h) McKee, M. L. *Inorg. Chem.* **1988**, *27*, 4241. (i) Cioslowski, J. *J. Am. Chem. Soc.* **1989**, *111*, 8333. (j) Brint, P.; Sangchakr, B.; Fowler, P. W. *J. Chem. Soc., Faraday Trans. 2* **1989**, *85*, 29. (k) Allen, L. C.; Egolf, D. A.; Knight, E. T.; Liang, C. *J. Phys. Chem.* **1990**, *94*, 5602. (l) Sana, M.; Leroy, G.; Wilante, C. *Organometallics* **1992**, *11*, 781. (m) Holme, T. A.; Truong, T. N. *Chem. Phys. Lett.* **1993**, *215*, 53.

(29) (a) Armstrong, D. R. *Inorg. Chim. Acta* **1979**, *33*, 177. (b) Andres, J.; Arnau, A.; Bertran, J.; Silla, E. *J. Mol. Struct. (THEOCHEM)* **1985**, *21*, 315. (c) Hirota, F.; Miyata, K.; Shibata, S. *J. Mol. Struct. (THEOCHEM)* **1989**, *60*, 99. (d) Jurgens-Lutovsky, R.; Almlöf, J. *Chem. Phys. Lett.* **1991**, *176*, 263. (e) Fowler, P. *Nature* **1992**, *355*, 586. (f) Branchadell, V.; Oliva, A. *J. Am. Chem. Soc.* **1991**, *113*, 4132.

(30) (a) LePage, T. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 6642. (b) Gung, B. W. *Tetrahedron Lett.* **1991**, *32*, 2867. (c) Gung, B. W.; Wolf, M. A. *J. Org. Chem.* **1992**, *57*, 1370.

(31) (a) Papatheodorou, G. N.; Curtiss, L. A.; Maroni, V. A. *J. Chem. Phys.* **1983**, *78*, 3303. (b) Chey, J.; Choe, H.-S.; Chook, Y.-M.; Jensen, E.; Seida, P. R.; Francl, M. M. *Organometallics* **1990**, *9*, 2430. (c) Jasien, P. G. *J. Phys. Chem.* **1992**, *96*, 9273.

(32) (a) Lucchese, R. R.; Haber, K.; Schaefer, H. F., *J. Am. Chem. Soc.* **1976**, *98*, 7617. (b) Douglas, J. E.; Kollman, P. A. *J. Am. Chem. Soc.* **1978**, *100*, 5226. (c) Sakaki, S.; Sata, H.; Imai, Y.; Morokuma, K.; Onkubo, K. *Inorg. Chem.* **1985**, *24*, 4538. (d) Pradeep, T.; Sreekanth, C. S.; Hegde, M. S.; Rao, C. N. R. *J. Am. Chem. Soc.* **1989**, *111*, 5058. (e) Pradeep, T.; Rao, C. N. R. *J. Mol. Struct. (THEOCHEM)* **1989**, *59*(200), 339. (f) Wong, M. W.; Wiberg, K. B. *J. Am. Chem. Soc.* **1992**, *114*, 7527.

(33) (a) Røeggen, I. *Chem. Phys.* **1992**, *162*, 271. (b) Glendening, E. D.; Streitwieser, A. *J. Chem. Phys.* **1994**, *100*, 2900.

(34) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(35) (a) Bader, R. F. W. *Acc. Chem. Res.* **1985**, *18*, 9. (b) Bader, R. F. W. *Atoms in Molecules. A Quantum Theory*; Oxford University Press: New York, 1990.

(36) *GUASSIAN 90, Revision J*; Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1990.

(37) *GAUSSIAN 92, Revision C*; Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G. Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A.; Gaussian, Inc., Pittsburgh, PA, 1992.

at the HF/6-31G(d) level. The calculated zero-point vibration energies (ZPE) were scaled by a factor of 0.89 to correct for the overestimation of vibrational frequencies at this level of theory.[45] All structures were verified as minima on the potential energy hypersurface by only positive eigenvalues of the Hessian matrix. Bond energies were calculated at the MP2 level of theory using the energy differences between the complexes and the donor and acceptor moieties. Our best bond energies are given at MP2/TZ2P//MP2/TZ2P. Unless otherwise specified, the results discussed in this paper are based on this level of theory. We did not correct for basis set superposition errors, which should be relatively small with a TZ2P basis set.[46] For computational reasons, the investigation of the electronic structure[34,35] was carried out at the MP2/6-31G(d) level of theory.

Geometries

Table 1 lists the experimental donor–acceptor bond lengths of some complexes for which gas-phase and solid-state data are known.

Table 1. Experimental Donor–Acceptor Bond Lengths (Å)

	X-ray	gas phase
$H_3N{-}BH_3$	1.564 ± 0.006[a]	1.657 ± 0.02[b]
$Me_3N{-}BH_3$	1.616 ± 0.001[a]	1.656 ± 0.002[c]
		1.638 ± 0.01[d]
$Me_3N{-}BF_3$	1.585 ± 0.03[e]	1.674 ± 0.004[f]
		1.664 ± 0.011[g]
$Me_3N{-}BCl_3$	1.610 ± 0.006[h]	1.652 ± 0.009[j]
	1.575 ± 0.011[i]	1.659 ± 0.006[g]
$Me_3N{-}BBr_3$	1.603 ± 0.021[h]	1.663 ± 0.013[j]
$Me_3N{-}BI_3$	1.584 ± 0.025[h]	1.663 ± 0.013[k]
$HCN{-}BF_3$	1.638 ± 0.002[l]	2.473 ± 0.029[l]
$CH_3CN{-}BF_3$	1.630 ± 0.004[m]	2.011 ± 0.007[n]
$Me_3N{-}SO_2$	2.046 ± 0.004[o]	2.26 ± 0.03[o]

[a] Reference 8. [b] Reference 9. [c] Reference 10. [d] Reference 11. [e] Reference 12. [f] Reference 13. [g] Reference 14. [h] Reference 15. [i] Reference 16. [j] Reference 17. [k] Reference 18. [l] Reference 19. [m] Reference 20. [n] Reference 21. [o] Reference 22.

Table 2. Experimental and Calculated Donor–Acceptor Bond Lengths (Å) of BH_3 Complexes

	$OC{-}BH_3$ **1** (C_{3v})	$H_3N{-}BH_3$ **2** (C_{3v})	$Me_3N{-}BH_3$ **3** (C_{3v})
exptl (X-ray)		1.564 ± 0.006[c]	1.616 ± 0.001[c]
		1.56 ± 0.05[d]	
exptl (gas phase)	1.53[a]	1.657 ± 0.02[e]	1.638 ± 0.01[f]
	1.534 ± 0.01[b]		1.656 ± 0.002[g]
HF/321G	1.615[h]	1.740[h]	1.685
HF/6-31G(d)	1.628	1.690	1.679
HF/TZ2P	1.616	1.672	1.662
MP2/6-31G(d)	1.548	1.662	1.647
MP2/TZ2P	1.543	1.648	1.628
MP3/6-31G(d)		1.664[i]	

[a] Reference 49. [b] Reference 50. [c] Reference 8. [d] Reference 51. [e] Reference 9. [f] Reference 11. [g] Reference 10. [h] Reference 39. [i] Reference 28e.

The experimental results show that the donor–acceptor bonds are in all cases longer in the gas phase than in the solid state. The differences are between 0.02 and 0.09 Å for the amine–BX_3 complexes. For the more weakly bound complexes $HCN{-}BF_3$, $CH_3CN{-}BF_3$, and $Me_3N{-}SO_2$ the differences are much larger. The largest difference is reported for $HCN{-}BF_3$, which has a bond length of 2.473 Å in the gas phase and 1.638 Å in the solid state.[19] It follows that geometries of donor–acceptor complexes determined by X-ray crystallography may be used only with caution for comparison with calculated geometries.

Figure 1 shows the optimized structures of the calculated complexes **1–18** and the Lewis acids and bases at the MP2/TZ2P level of theory. Experimental gas-phase values are given in parentheses. Tables 2–4 show the experimental and calculated donor–acceptor bond lengths.

The calculated interatomic distances for the BH_3 complexes **1–3** shown in Table 2 indicate that the donor–acceptor bond is always predicted to be shorter at the MP2 level than at the HF level using the same basis set. The difference between the MP3 and MP2 results for the bond length of **2** is negligible. The theoretically predicted donor–acceptor bond lengths for **1** and **2** at the MP2 level are in good agreement (±0.01 Å) with the experimental gas-phase values (Table 2) and with previous calculations.[28e] Good agreement between theory and experiment

(38) TURBOMOLE: (a) Häser, M.; Ahlrichs, R. *J. Comput. Chem.* **1989**, *10*, 104. (b) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. M. *Chem. Phys. Lett.* **1989**, *162*, 165. (c) Horn, H.; Weiss, H.; Häser, M.; Ehrig, M.; Ahlrichs, R. *J. Comput. Chem.* **1991**, *12*, 1058. (d) Häser, M.; Almlöf, J.; Feyereisen, M. W. *Theor. Chim. Acta* **1991**, *79*, 115. (e) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571. (f) Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455. (g) Haase, F.; Ahlrichs, R. *J. Comput. Chem.* **1993**, *14*, 907.

(39) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(40) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. (b) Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229.

(41) (a) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. (b) Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *J. Am. Chem. Soc.* **1982**, *104*, 2797. (c) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; Defrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. The 3-21G(d) basis set includes d polarization functions only on the second-row elements.

(42) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (c) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. (d) Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921. (e) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654. The 6-31G(d) basis set includes d polarization functions both on the first- and second-row elements.

(43) Huzinaga, S. *Approximate Atomic Wavefunctions*; Department of Chemistry Report, University of Alberta: Edmonton, Alberta, Canada, 1971. TZ2P for B, C, N, O, and F is a (9s5p2d)/[5s3p2d] basis set; TZ2P for H is a (5s2p)/[3s2p] basis set.

(44) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639. TZ2P for Al, S, and Cl is a (12s9p2d)/[6s5p2d] basis set with two sets of d polarization functions from the following: Andzelm, J.; Huzinaga, S.; Klobukowski, M.; Radzio, E.; Sakai, Y.; Tatewaki, H. *Gaussian Basis Sets For Molecular Calculations*; Elsevier: Amsterdam, 1984.

(45) Hout, R. F.; Levi, B. A.; Hehre, W. J. *J. Comput. Chem.* **1982**, *2*, 234.

(46) We did not correct the calculated dissociation energies for basis set superposition errors (BSSE). There are two types of errors in calculations using a truncated basis set, i.e., the BSSE and the basis set incompletion error (BSIE). These two errors have opposite sign. Both errors can, in principle, be corrected by saturating the basis set. Correcting for the BSSE would leave the BSIE uncorrected. We think that, for a comparison with experimental values, directly calculated results should be used rather than estimated data obtained from correction procedures such as the counterpoise[47] method which is not undisputed.[2,48]

(47) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(48) (a) Schwenke, D. W.; Truhlar, D. G. *J. Chem. Phys.* **1985**, *82*, 2418. (b) Frisch, M. J.; DelBene, J. E.; Binkley, J. S.; Schaefer, H. F., III. *J. Chem. Phys.* **1986**, *84*, 2279. (c) Gutowski, M.; van Duijneveldt-van de Rijdt, J. G. C. M.; van Lenthe, J. H.; van Duijneveldt, F. B. *J. Chem. Phys.* **1993**, *98*, 4728. (d) Gutowski, M.; Chalasinski, G. *J. Chem. Phys.* **1993**, *98*, 5540.

(49) Pépin, C.; Lambert, L.; Cabana, A. *J. Mol. Spectrosc.* **1974**, *53*, 120.

(50) Venkatachar, A. C.; Taylor, R. C.; Kuczkowski, R. L. *J. Mol. Struct.* **1977**, *38*, 17.

(51) Hughes, E. W. *J. Am. Chem. Soc.* **1956**, *78*, 502.

(52) Janda, K. J.; Bernstein, L. S.; Steed, J. M.; Novick, S. E.; Klemperer, W. *J. Am. Chem. Soc.* **1978**, *100*, 8074.

(53) Hoard, J. L.; Geller, S.; Cashin, W. M. *Acta Crystallogr.* **1951**, *4*, 396.

(54) Iijima, K.; Yamada, T.; Shibata, S. *J. Mol. Struct.* **1981**, *77*, 271.

(55) Reetz, M. T.; Hüllmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405.

(56) Corey, E. J.; Loh, T.-P.; Sarshar, S.; Azimioara, M. *Tetrahedron Lett.* **1992**, *33*, 6945.

(57) Le Carpentier, J.-M.; Weiss, R. *Acta Crystallogr., Sect. B* **1972**, *28*, 1437.

(58) Grant, D. F.; Killean, R. C. G.; Lawrence, J. L. *Acta Crystallogr. Sect. B* **1969**, *25*, 377.

(59) Almenningen, A.; Haaland, A.; Haugen, T.; Novak, D. P. *Acta Chem. Scand.* **1973**, *27*, 1821.

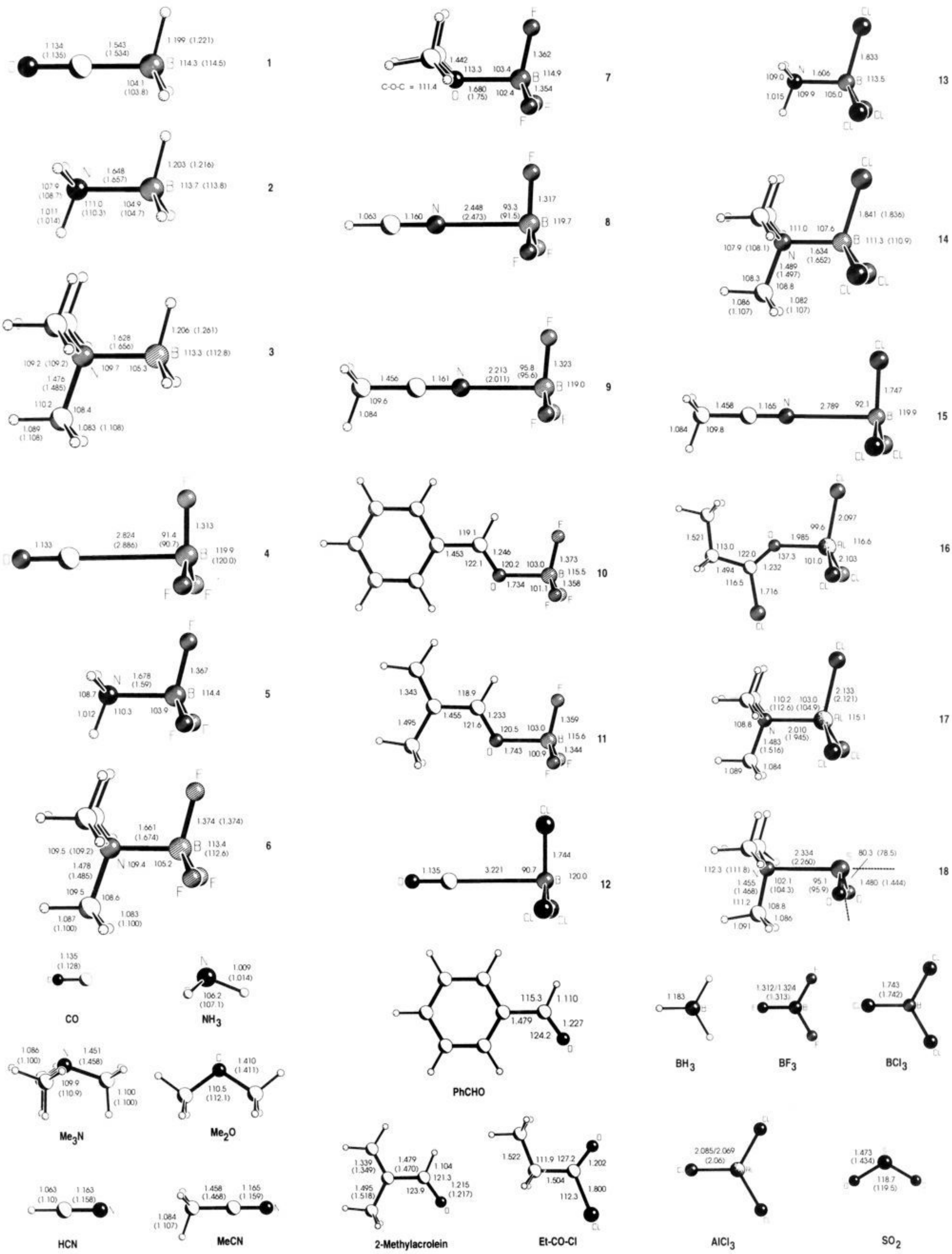


Figure 1. Optimized geometries at MP2/TZ2P. The values for **10**, **16**, PhCHO, and EtCClO are given at MP2/6-31G(d). For BF_3 and $AlCl_3$, the first value is at MP2/TZ2P, and the second value is at MP2/6-31G(d). Experimental gas phase values are given in parentheses.[61] Bond distances are in angströms, and angles are in degrees.

is also found for **3**, if the experimental value of 1.638 Å is used as a reference.[11] The calculations at the MP2 level predict that the N–B bond of $Me_3N–BH_3$ should be 0.02 Å shorter than that of $H_3N–BH_3$, which is reasonable because Me_3N is a stronger

Table 3. Experimental and Calculated Donor-Acceptor Bond Lengths (Å) of BF_3 Complexes

	$OC-BF_3$ **4** (C_{3v})	H_3N-BF_3 **5** (C_{3v})	Me_3N-BF_3 **6** (C_{3v})	Me_2O-BF_3 **7** (C_s)	$HCN-BF_3$ **8** (C_{3v})	CH_3CN-BF_3 **9** (C_{3v})	$PhCHO-BF_3$ **10** (C_s)	$MABF_3$ **11** (C_s)
exptl (X-ray)		1.60 ± 0.02[b]	1.585 ± 0.03[d]		1.638 ± 0.002[h]	1.630 ± 0.004[i]	1.591 ± 0.006[k]	1.587 ± 0.008[l]
exptl (gas phase)	2.886 ± 0.01[a]	1.59 ± 0.03[c]	1.674 ± 0.004[e] 1.664 ± 0.011[f]	1.75 ± 0.02[g]	2.473 ± 0.029[h]	2.011 ± 0.007[j]		
HF/3-21G	2.551	1.683	1.642	1.598	1.839	1.761	1.625	1.633
HF/6-31G(d)	2.956	1.693	1.677	1.703	2.577	2.484	1.691	1.705
HF/TZ2P	3.114	1.687	1.676	1.685	2.687	2.576	1.688	1.703
MP2/6-31G(d)	2.756	1.679	1.665	1.694	2.421	2.214	1.734	1.738
MP2/TZ2P	2.824	1.678	1.661	1.680	2.448	2.213		1.743

[a] Reference 52. [b] Reference 53. [c] Reference 24. [d] Reference 12. [e] Reference 13. [f] Reference 14. [g] Reference 54. [h] Reference 19. [i] Reference 20. [j] Reference 21. [k] Reference 55. [l] Complex of 2-methylacrolein with BF_3, ref 56.

Table 4. Experimental and Calculated Donor-Acceptor Bond Lengths (Å) of Other Complexes

	$OC-BCl_3$ **12** (C_{3v})	H_3N-BCl_3 **13** (C_{3v})	Me_3N-BCl_3 **14** (C_{3v})	$CH_3CN-BCl_3$ **15** (C_{3v})	$EtCClO-AlCl_3$ **16** (C_s)	$Me_3N-AlCl_3$ **17** (C_{3v})	Me_3N-SO_2 **18** (C_s)
exptl (X-ray)			1.575 ± 0.011[a] 1.610 ± 0.006[b]	1.562 ± 0.008[e]	1.847 ± 0.006[f]	1.96 ± 0.01[g]	2.046 ± 0.004[i]
exptl (gas phase)			1.659 ± 0.006[c] 1.652 ± 0.009[d]			1.945 ± 0.035[h]	2.26 ± 0.03[i]
HF/3-21G(d)	3.039	1.646	1.646	2.479	1.871	1.972	2.153
HF/6-31G(d)	3.586	1.628	1.664	3.045	1.948	2.041	2.527
HF/TZ2P	3.811	1.608	1.642	3.225	1.932	2.022	2.599
MP2/6-31G(d)	3.218	1.630	1.664	2.802	1.985	2.029	2.365
MP2/TZ2P	3.221	1.606	1.634	2.793		2.010	2.334

[a] Reference 16. [b] Reference 15. [c] Reference 14. [d] Reference 17. [e] Reference 20b. [f] Reference 57. [g] Reference 58. [h] Reference 59. [i] Reference 22h.

base than H_3N.[60] This is in agreement with the experimental values of 1.638 Å[11] for **3** and 1.657 Å[9] for **2**. It is also possible that the correct B–N bond length of **2** is ca. 1.68 Å, which would be at the upper limit of the experimental error bar,[9] and that r_{BN} in **3** is 1.656 Å.[10] The geometries of **1–3** exhibit a tetrahedral structure around the boron center. The bond angle X–B–H (X being the donor atom) is 104–105°. The B–H bond is slightly longer in complexes **1–3** than in isolated BH_3 (Figure 1). This is reasonable, because the B–H bond in BH_3 at boron is sp^2 hybridized, while the hybridization changes toward sp^3 in the donor–acceptor complexes.

Experimentally determined donor–acceptor bond lengths are available for the BF_3 complexes **4–11**, which are shown in Table 3. The BF_3 complexes **4**, **8**, and **9** are characterized by rather long donor–acceptor bonds. This is in agreement with the calculations, which predict nearly planar BF_3 moieties and long (Figure 1) donor–acceptor bond lengths for **4**, **8**, and **9**. These molecules should therefore be considered as van der Waals complexes. Table 3 shows that the interatomic distances predicted at the HF level for the three complexes exhibit very large alterations when different basis sets are employed. The bond lengths become much longer when larger basis sets are used. The calculated bond lengths for **4**, **8**, and **9** are too short at HF/3-21G and too long at HF/TZ2P compared to the experimental gas-phase values. The bond lengths are calculated shorter at the MP2 level of theory. The theoretically predicted donor–acceptor bond lengths of **4** and **8** at MP2/TZ2P are in good agreement (±0.06 Å) with experiment.

The calculated structure of **9** merits special attention. A recent microwave study[21] showed that $MeCN-BF_3$ is extremely unusual in that the bond length and bond angle are intermediate between the limits normally observed for van der Waals and covalently bound systems. The structure of **9** was interpreted as a "gas-phase snapshot along the reaction path for the formation of the boron–nitrogen dative bond".[21] The calculations predict a B–N bond length which is somewhat longer (2.213 Å) than the experimental value (2.011 ± 0.007 Å).[21] This is puzzling, because the calculated value for $HCN-BF_3$ (2.448 Å) is in excellent agreement with experiment (2.473 ± 0.029 Å).[19] A recent theoretical study at the MP2/DZ+P level predicted a B–N bond length of 2.17 Å for **9**.[29d] Still, the calculated results agree with the interpretation of the gas-phase study that **9** is remarkable because the B–N bond length is truly intermediate between a covalent bond, which is calculated as 1.66–1.68 Å (see **5** and **6**, Table 3), and a van der Waals complex (2.45 Å for **8**). The B–N bonds of **8** and **9** are much shorter in the solid state than in the gas phase.

The calculations predict much shorter donor–acceptor bonds for the complexes **5–7**, **10**, and **11** than for the other BF_3 complexes (Table 3). The BF_3 moieties have a tetrahedral structure with X–B–F bond angles of 103–105°. Unlike **4**, **8**, and **9**, the theoretical donor–acceptor bond lengths of **5–7**, **10**, and **11** calculated at the HF level are not very different from the MP2 values using the same basis set. It follows that bond lengths of donor–acceptor complexes with short (strong) bonds may already be calculated with reasonably accuracy at the HF level. It is interesting to note that the donor–acceptor bonds of the BF_3 complexes **5** and **6** are calculated to be only slightly longer than the corresponding BH_3 complexes **2** and **3**, while the BF_3 complex **4** is found with a much longer bond that the BH_3 complex **1**.

The bond length predicted at the MP2 level for the Me_3N-BF_3 complex (**6**) (1.661 Å at MP2/TZ2P, 1.665 Å at MP2/6-31G(d)) is in excellent agreement with the experimental gas-phase values (Table 3). A disagreement between theory and experiment is found, however, for the classical donor–acceptor complex H_3N-BF_3 (**5**). NH_3 is a weaker base than Me_3N, and the calculations predict a slightly longer (and weaker, see below) donor–acceptor bond for **5**. The experimental value from microwave spectroscopy for **5** is r_{BN} = 1.59 ± 0.03 Å.[24] However, this value was derived with the assumption that the B atom lies close to the center of mass in $H_3{}^{14}N^{11}BF_3$, but probably on the opposite side from the N atom. A value of z_B = –0.03(3) Å was chosen for the position of the B atom relative to the center of mass. The position of the nitrogen atom was obtained as z_N = 1.555 Å. Our calculations predict that the position of the nitrogen atom should be z_N =

(60) The experimental proton affinity of Me_3N is 224.3 kcal/mol, while that of NH_3 is 205.0 kcal/mol: Aue, D. H.; Bowers, M. T. In *Gas Phase Ion Chemistry*; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, p 16.

1.463 Å. For the B atom a value $z_B = -0.216$ Å is calculated (MP2/TZ2P). It seems possible that the estimate of the position of the boron atom, which is used for the analysis of the microwave spectrum of **5**, is too close to the center of mass. In view of the otherwise excellent agreement between theoretical and experimental gas-phase values for the bond distances of the strongly bound donor–acceptor complexes, and because it is difficult to understand why NH_3 should be more strongly bound to BF_3 than Me_3N, we think that the experimentally derived[24] value for the B–N bond length of **5** is too short. The more likely value predicted by our calculations should be 1.68 ± 0.02 Å.[25]

The experimental value for the donor–acceptor bond length of **7** (1.75 ± 0.02 Å)[54] is longer than the calculated value at MP2/TZ2P (1.680 Å). The experimental value was derived assuming local C_{3v} symmetry of the CH_3 and BF_3 groups. The calculations show that the BF_3 moiety is significantly disturbed from C_{3v} symmetry (Figure 1). The calculated B–F bond lengths are 1.354 and 1.362 Å, respectively. Also, the measurements at different temperatures gave values of 1.73 ± 0.05 Å at 16 °C and 1.75 ± 0.02 Å at 70 °C.[54] The former value agrees within the experimental error bar with the calculated equilibrium distance of 1.68 Å.

The calculated donor–acceptor bond lengths for complexes **10** and **11** are very interesting, because the predicted values at the MP2 level are *longer* than the HF results (Table 3). The BF_3 moieties of **10** and **11** show a significant distortion from C_{3v} symmetry. The in-plane B–F bonds are clearly longer than the out-of-plane B–F bonds by 0.015 Å (Figure 1). There are no experimental gas-phase values available for **10** and **11**. The solid-state structures exhibit significantly shorter donor–acceptor bonds than calculated for **10** and **11** at the MP2 level. Although the solid-state structures cannot be compared directly with the calculated geometries, it is noteworthy that the observed conformations[55,56] of **10** and **11** are very similar to the calculated structures.

The B–F bond length is a very sensitive probe for the strength of the donor–acceptor interactions in the complexes. The weakly bound complexes **4**, **8**, and **9** have B–F bond lengths that are only slightly longer than in isolated BF_3 (1.312 Å. Figure 1). The strongly bound BF_3 complexes **5–7**, **10**, and **11**, however, have much longer B–F interatomic distances. A lengthening of the B–F bond of BF_3 in donor–acceptor complexes has been noted before.[13,21,29c] The most strongly bound BF_3 complex, **6**, has the longest calculated B–F bond (1.374 Å). The theoretically predicted bond lengthening of the B–F bond in **6** is in excellent agreement with experiment (Figure 1). The experimentally observed[61g] B–F bond length of BF_3 is 1.313 Å (calculated 1.312 Å), and the observed[13] B–F bond length of $Me_3N–BF_3$ is 1.374 Å (calculated 1.374 Å). Figure 2 shows a plot of the calculated B–F bond lengths of **4–11** with the calculated bond energies D_e (see below and Table 6). There is a correlation between the strength of the donor–acceptor interactions and the lengthening of the B–F bond.

The lengthening of the B–F bonds upon complex formation is much larger than that of the B–H bonds in the BH_3 complexes **1–3** (Figure 1). This is because BF_3 is stabilized by strong π donation of the fluorine lone pairs into the formally empty $p(\pi)$ orbital at boron, which yields shorter B–F bonds. There is no empty valence orbital at boron in the strongly bound donor–acceptor complexes.

(61) (a) CO: Herzberg, G. *Spectra of Diatomic Molecules*, 2nd ed.; Van Nostrand: New York, 1950. (b) NH_3: Helminger, P.; De Lucia, F. C.; Gordy, W. *J. Mol. Spectrosc.* **1971**, *39*, 94. (c) Me_3N: Beagley, B.; Medwid, A. R. *J. Mol. Struct.* **1977**, *38*, 229. (d) Me_2O: see Ref 51. (e) HCN and MeCN: Karakida, K.; Fukuyama, T.; Kuchitsu, K. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 299. (f) 2-Methylacrolein: Durig, J. R.; Qiu, J.; Dehoff, B.; Little, T. S. *Spectrochim. Acta* **1986**, *42A*, 89. (g) BF_3 and BCl_3: Gershikov, A. G.; Spiridonov, V. P.; Zasorin, E. Z. *J. Mol. Struct.* **1983**, *99*, 1. (h) $AlCl_3$: Zasorin, E. Z.; Rambidi, N. G. *Zh. Strukt. Khim.* **1967**, *8*, 391. (i) SO_2: Holder, C. H.; Fink, M. *J. Chem. Phys.* **1981**, *75*, 5323.

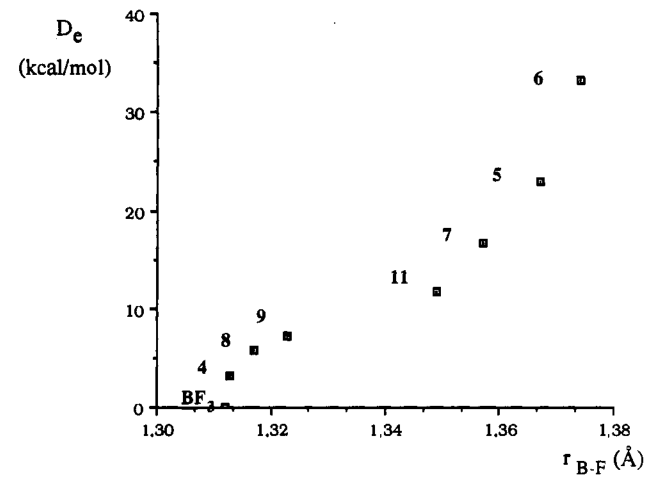


Figure 2. Plot of the calculated B–F bond lengths (Å) in the BF_3 complexes **4–9** and **11** vs the calculated interaction energies D_e (kcal/mol).

Table 5. Experimental and Calculated Bond Energies of the BH_3 Complexes (kcal/mol)[a]

method		$OC–BH_3$ **1**	$H_3N–BH_3$ **2**	$Me_3N–BH_3$ **3**
HF/6-31G(d)	D_e (D_0)	9.2 (5.8)	23.4 (18.0)	25.5 (20.6)
HF/TZ2P	D_e (D_0)	8.4 (5.1)	21.8 (16.4)	25.4 (20.5)
MP2/6-31G(d)	D_e (D_0)	25.6 (22.2)	34.6 (29.2)	41.3 (36.4)
MP2/TZ2P	D_e (D_0)	26.4 (23.0)	33.7 (28.3)	43.6 (38.7)
MP2/TZ2P	D_0(298)[b]	25.1	30.7	41.1
exptl		24.6[c]	31.1[d]	38.3[c]

[a] Values in parentheses include ZPE corrections. [b] Includes thermal corrections (see text). [c] Reference 62. [d] Estimated value, reference 7.

Table 4 shows the calculated and experimental bond lengths for the BCl_3 complexes **12–15**, the $AlCl_3$ complexes **16** and **17**, and the SO_2 complex **18**. Experimental gas-phase geometries are available for **14**, **17**, and **18**. The calculated bond lengths at the MP2 level are in good agreement with the experimental values (Table 4). The solid-state structures of **14** and **18** have shorter donor–acceptor bonds than the isolated molecules. The calculated bond lengths at the MP2 level of theory for **12**, **13**, **15**, and **16** may be used to predict the unknown structures of the molecules in the gas phase. It should be noted that the $OC–BCl_3$ complex (**12**) and the $CH_3CN–BCl_3$ complex (**15**) are predicted with *longer* donor–acceptor bonds than the $OC–BF_3$ complex (**4**) and the $CH_3CN–BF_3$ complex (**9**), while the $H_3N–BCl_3$ and $Me_3N–BCl_3$ complexes (**13** and **14**) are predicted with a *shorter* donor–acceptor bond than the $H_3N–BF_3$ and $Me_3N–BF_3$ complexes (**5** and **6**) (Table 3). Also the BCl_3 complexes are calculated with much longer B–Cl bond lengths than isolated BCl_3 (Figure 1). The bond lengthening of the BCl_3 complexes is even larger than that of the BF_3 complexes. The calculated B–Cl interatomic distance of the most strongly bound BCl_3 complex, $Me_3N–BCl_3$ (**14**), is 0.100 Å longer than in BCl_3. The bond lengths of the Lewis acids $AlCl_3$ and SO_2 become also longer when they are complexed with a base. The calculations predict that the geometry of the Lewis acid changes more than the geometry of the Lewis base upon complex formation (Figure 1).

The calculated B–N bond length of the $CH_3CN–BCl_3$ complex (**15**) is very interesting. The MP2/TZ2P optimized value differs by 1.23 Å from the experimental X-ray structure analysis.[20b] The N–B bond length of **15** in the solid state is even 0.07 Å shorter than that of $CH_3CN–BF_3$ (**9**). The calculations and the X-ray structure indicate a possible record bond length shortening from the gas-phase value to the solid state by more than 1 Å. We encourage experimentalists to investigate the $CH_3CN–BCl_3$ complex both in the solid state and in the gas phase.

The calculated donor–acceptor bond lengths of $AlCl_3$ complexes **16** and **17** are only slightly longer than the experimentally reported

Table 6. Experimental and Calculated Bond Energies of the BF_3 Complexes (kcal/mol)[a]

method		OC–BF$_3$ 4	H$_3$N–BF$_3$ 5	Me$_3$N–BF$_3$ 6	Me$_2$O–BF$_3$ 7	HCN–BF$_3$ 8	CH$_3$CN–BF$_3$ 9	PhCHO–BF$_3$ 10	MA–BF$_3$ 11
HF/6-31G(d)	D_e (D_0)	2.5 (1.9)	20.8 (17.4)	25.0 (22.2)	12.0 (10.2)	5.0 (4.3)	6.1 (5.6)	11.1 (9.8)	10.6 (9.2)
HF/TZ2P	D_e (D_0)	1.6 (1.0)	17.5 (14.1)	21.8 (19.0)	9.0 (7.2)	4.0 (3.4)	5.0 (4.5)	8.3 (7.0)	7.9 (6.5)
MP2/6-31G(d)	D_e (D_0)	4.0 (3.4)	26.8 (23.5)	36.1 (33.3)	19.3 (17.5)	6.6 (5.9)	8.0 (7.5)	14.3 (13.0)	14.3 (12.9)
MP2/TZ2P	D_e (D_0)	3.2 (2.6)	23.0 (19.6)	33.3 (30.5)	16.7 (14.9)	5.8 (5.1)	7.2 (6.7)	11.9 (10.6)[d]	11.8 (10.4)
MP2/TZ2P	D_0(298)[b]	4.7	22.0	32.9	17.3	7.2	9.1	13.0	12.8
exptl				31.0 ± 1.1[c]	17.6 ± 0.8[c]		12.0 ± 0.8[c]	15.5 ± 1.0[c]	

[a] Values in parentheses include ZPE corrections. [b] Thermal corrections included (see text). [c] Reference 64, note that the experimental enthalpies of complexation in methylene chloride are corrected by the value for CH_2Cl_2 (2.4 ± 0.7 kcal/mol). [d] MP2/6-31G(d) geometry.

Table 7. Experimental and Calculated Bond Energies of Other Complexes (kcal/mol)[a]

method		OC–BCl$_3$ 12	H$_3$N–BCl$_3$ 13	Me$_3$N–BCl$_3$ 14	CH$_3$CN–BCl$_3$ 15	EtCClO–AlCl$_3$ 16	Me$_3$N–AlCl$_3$ 17	Me$_3$N–SO$_2$ 18
HF/6-31G(d)	D_e (D_0)	0.7 (0.4)	25.1 (21.0)	21.6 (18.4)	2.6 (2.3)	22.7 (21.7)	40.4 (37.8)	8.2 (6.7)
HF/TZ2P	D_e (D_0)	0.5 (0.2)	23.2 (19.2)	21.3 (18.1)	1.8 (1.4)	19.6 (18.7)	37.6 (35.0)	6.9 (5.4)
MP2/6-31G(d)	D_e (D_0)	2.0 (1.7)	31.4 (27.4)	36.7 (33.6)	4.4 (4.1)	24.9 (24.0)	50.2 (47.6)	13.1 (11.6)
MP2/TZ2P	D_e (D_0)	2.2 (1.9)	31.3 (27.3)	41.3 (38.1)	4.3 (4.0)	23.3 (22.4)[f]	49.5 (46.9)	14.6 (13.1)
MP2/TZ2P	D_0(298)[b]	4.0	29.7	40.5	6.4	24.8	49.3	15.5
exptl				(30.5[c])			47.5 ± 2.0[d]	9.1 ± 0.4[e]

[a] Values in parentheses include ZPE corrections. [b] Thermal corrections included (see text). [c] Estimated value, probably too low (see text), ref 63. [d] Reference 66. [e] Reference 22d. [f] MP2/6-31G(d) geometry.

interatomic distances in the solid state (Table 4). This indicates that **16** and **17** have rather strong donor–acceptor bonds. This is indeed the case (see below). The molecular structure of **17** has also been determined by gas-phase electron diffraction.[59] A bond length of 1.945 ± 0.035 Å was reported for the Al–N bond, which is slightly *shorter* than the value in the solid state (Table 4). However, it was noted that "the value obtained for the Al–N bond distance is...considerably less accurate than the Al–N bond distance determined by X-ray crystallography".[59] We think that the calculated value of 2.010 Å, which is close to the upper bound of the experimental gas-phase value, is probably more reliable.

The $Me_3N–SO_2$ complex (**18**) has been the subject of many experimental[22] and theoretical[32] studies. The gas-phase structure of **18** has recently been given by Oh et al.,[22h] who reported the microwave spectrum of this compound. Figure 1 shows that the calculated structure is in excellent agreement with the experimentally derived geometry. The theoretical value for the N–S donor–acceptor bond is 2.334 Å, and the experimental gas-phase value is 2.26 ± 0.05 Å.[22h] The calculated tilt angle of the SO_2 moiety with respect to the N–S axis is 80.3°. The experimental value is 78.5°.

Bond Energies

Tables 5–7 show the experimental and calculated bond energies for the donor–acceptor complexes **1–18**.

The theoretical dissociation energies D_e are calculated as the energy differences between the complexes and the respective Lewis acid and base. The dissociation energy $D_0(0)$ (which is actually the reaction enthalpy at 0 K) is given by D_e plus the correction for zero-point vibrational energies ZPE. In order to compare the calculated values with the experimental results, we used the empirical correction of $^1/_2RT$ per rotational or translational degree of freedom and RT for the work term pV. This gives a correction at room temperature of –2.4 kcal/mol for the calculated dissociation energies $D_0(298)$ of the donor–acceptor complexes. The temperature correction for the $D_0(298)$ values of **1**, **4**, **8**, and **12** is –2.1 kcal/mol, because CO and HCN are linear molecules, which have only 2 degrees of rotational freedom. The theoretically predicted bond strengths refer to the calculated $D_0(298)$ values at the MP2/TZ2P//MP2/TZ2P + ZPE level of theory, unless otherwise mentioned.

The agreement between the experimentally derived and the theoretically predicted bond energies at the MP2 level of theory for the donor–acceptor complexes is quite good. The calculated bond strengths at the MP2/TZ2P level differ from the experimental values by less than 3 kcal/mol with the exception of **18**. Here the difference is 6 kcal/mol. Also the values at MP2/6-31G(d) are not very different from the experimental results. The calculated dissociation energies may therefore be used to estimate the bond strengths of complexes that have not been determined experimentally. The theoretically predicted dissociation energies at the HF level are too low. This is in agreement with the calculated interatomic distances, which are too long at the HF level.

The donor–acceptor complex $OC–BH_3$ (**1**) is the only known carbonyl complex of a main-group element that is stable at room temperature. **1** is predicted with a rather strong donor–acceptor bond (25.1 kcal/mol), which is in good agreement with the experimental value (24.6 kcal/mol).[62] Higher dissociation energies are predicted for the BH_3 complexes with the stronger bases NH_3 and NMe_3. The classical donor–acceptor complexes $H_3N–BH_3$ (**2**) and $Me_3N–BH_3$ (**3**) are calculated with rather strong donor–acceptor bonds. The experimental value of **2** (31.1 kcal/mol) is an extrapolation, which is based on the measured bond strengths of the set of methyl amine–BH_3 and methyl amine–BMe_3 complexes $Me_nH_{3-n}N–BX_3$.[7] The calculated value for **2** (30.7 kcal/mol) is in excellent agreement with the experimental estimate.[7] Previous calculations of the bond strength of **2** at the MP4/6-311G(d,p)//MP3/6-31G(d) level of theory give a similar value ($D_0(0)$ = 28.7 kcal/mol)[28e] as in our calculations ($D_0(0)$ = 28.3 kcal/mol). The theoretically predicted bond strength of **3** (41.1 kcal/mol) is also in good agreement with the experimental value of 38.3 kcal/mol.[62] Earlier experimental values[63] of the bond strengths of **1** (18.8 kcal/mol) and **3** (31.5 kcal/mol) are much lower. They are probably wrong.

Many experimental values are available for the bond strengths of BF_3 complexes, mainly because of the systematic studies by Gal and Maria.[64] These workers report experimental enthalpies of complexation for complexes **6**, **7**, **9**, and **10**, which are in good agreement with the calculated dissociation energies (Table 6). The calculations predict that the BF_3 complexes with CO, NH_3, and NMe_3, i.e., **4–6**, are more weakly bound than the respective BH_3 complexes **1–3**. Complex **6** is calculated with a bond energy

(62) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.
(63) McCoy, R. E.; Bauer, S. H. *J. Am. Chem. Soc.* **1956**, *78*, 2061.
(64) Gal, J.-F.; Maria, P.-C. *Prog. Phys. Org. Chem.* **1990**, *17*, 159.

of 32.9 kcal/mol, which is in very good agreement with the experimental value of 31.0 ± 1.1 kcal/mol reported by Gal and Maria.[64] An earlier experimental value of 26.6 kcal/mol is probably not correct.[63] The latter experimental study from 1956 reported bond energies of 18.8 kcal/mol for **1** and 31.5 kcal/mol for **3**, which are definitely too low.

The calculated bond strength of **5** is 22.0 kcal/mol. A much weaker bond is predicted for **4**. The very low theoretical dissociation energy of **4** ($D_0(298)$ = 4.7 kcal/mol) is supported by the experimentally determined[52] donor-acceptor bond length of 2.886 Å (calculated 2.824 Å), which is much longer than for **1** (observed[50] 1.534 Å, calculated 1.543 Å). The theoretical dissociation energy of the Me_2O–BF_3 complex (**7**) (17.3 kcal/mol) is in excellent agreement with the experimental value[64] of 17.6 ± 0.8 kcal/mol. An earlier experimental value of 13.7 kcal/mol is probably too low.[65] The aldehyde–BF_3 complexes **10** and **11** are predicted with slightly weaker donor-acceptor bonds than that of **7**. The calculated bond energy of **11** is 12.8 kcal/mol. Structure **10** could only be calculated at MP2/TZ2P//MP2/6-31G(d) because of the size of the molecule. The calculations at the MP2/TZ2P//MP2/6-31G(d) and MP2/6-31G(d)//MP2/6-31G(d) levels indicate that the bond strength of the benzaldehyde–BF_3 complex (**10**) (13.0 kcal/mol), which is in good agreement with the experimental value of 15.5 ± 1.0 kcal/mol,[64] is nearly the same as that of the vinylic aldehyde–BF_3 complex **11**. The nitrile complexes **8** and **9** are predicted to have bond energies of 7.2 and 9.1 kcal/mol, respectively. The latter value is in reasonable agreement with the experimental bond energy of 12.0 ± 0.8 kcal/mol.[64] The calculated donor-acceptor bond strengths of the BF_3 complexes shown in Table 6 indicate that the qualitative order of the Lewis base strength is amine > ether > aldehyde > nitrile > CO.

The BCl_3 complexes with NH_3 (**13**) and NMe_3 (**14**) are calculated (Table 7) to be more strongly bound than the respective BF_3 complexes **5** and **6** (Table 6), but more weakly bound than the BH_3 complexes **2** and **3** (Table 5). The calculations predict that **14** is more strongly bound than **13**. The calculated dissociation energy of **14** ($D_0(298)$ = 40.5 kcal/mol) is higher than the experimental estimate of 30.5 kcal/mol.[63] However, this estimate is based on early experimental values for **1** (18.8 kcal/mol) and **3** (31.5 kcal/mol), which are too low (see above). Therefore, we think that the estimate of 30.5 kcal/mol for the bond strength of **14** is also too low. The carbonyl complex **12** is calculated as a weakly bound ($D_0(298)$ = 4.0 kcal/mol) van der Waals complex. Also the acetonitrile–BCl_3 complex (**15**) is calculated with a weak donor-acceptor bond ($D_0(298)$ = 6.4 kcal/mol). Much higher dissociation energies are calculated for the $AlCl_3$ complexes **16** and **17**. The acyl chloride–$AlCl_3$ structure **16** is predicted to have a bond energy of 24.8 kcal/mol (MP2/TZ2P//MP2/6-31G(d)). The most strongly bound complex investigated in our study is **17**. The theoretical value of $D_0(298)$ = 49.3 kcal/mol is in excellent agreement with the experimental value of 47.5 ± 2.0 kcal/mol.[66] The theoretical dissociation energy of **18** ($D_0(298)$ = 15.5 kcal/mol) is higher than the observed value of 9.7 ± 0.4 kcal/mol.[22d]

The calculated bond energies of the BH_3, BF_3, and BCl_3 complexes establish a trend for the relative strengths of the boron Lewis acids. For the strongly bound donor-acceptor complexes, involving covalent bonding (see below), BH_3 appears a marginally stronger Lewis acid than BCl_3, which is significantly stronger than BF_3. For the weakly bound complexes to CO and RCN, involving large electrostatic interactions, the situation is more complex. The bond strengths of OC–BF_3 and CH_3CN–BF_3 are higher than the bond strengths of the respective BCl_3 complexes. This is because the donor-acceptor interactions in the weakly bound CO and CH_3CN complexes are mainly caused by electrostatic interactions, whereas the amine complexes are covalently bound (see below). BF_3 is a hard acid and BCl_3 is a soft acid in the terminology of hard and soft acids and bases.[67] CO and CH_3CN are hard bases, while NH_3 and NMe_3 are soft bases. The HSAB model makes it plausible that OC–BF_3 is more strongly bound than OC–BCl_3, and that CH_3CN–BF_3 is more strongly bound than CH_3CN–BCl_3.

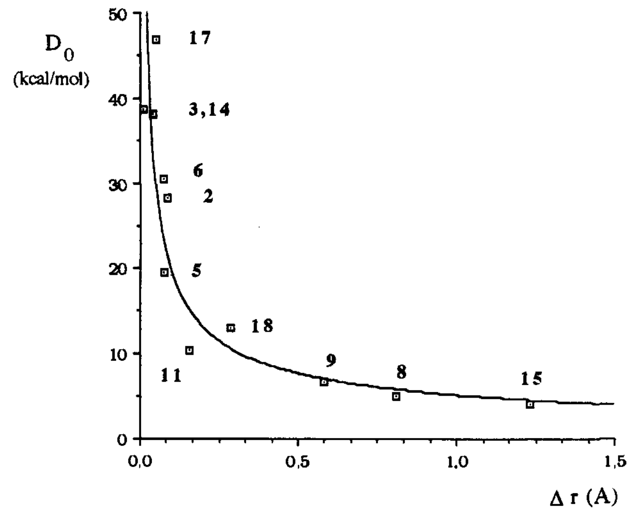


Figure 3. Correlation of the differences Δr between the donor-acceptor bond lengths in the solid state and the calculated values (Å) with the theoretically predicted dissociation energies D_0 (kcal/mol).

The calculated bond strengths of OC–BH_3 (**1**) and OC–BCl_3 (**12**) show that the previous conclusion that "substitution of hydrogen by chlorine at boron in borine complexes seems to have little effect upon the dissociation enthalpy"[7] is not always correct. Substitution of hydrogen by chlorine may even alter the nature of the complex. The calculated bond strength of **1** ($D_0(298)$ = 25.1 kcal/mol) is much higher than that of **12** ($D_0(298)$ = 4.0 kcal/mol).

The calculations predict that the Me_3N–$AlCl_3$ complex (**17**) has the strongest donor-acceptor bond (Table 7). The calculated dissociation energies indicate that $AlCl_3$ is the strongest Lewis acid investigated in our study.[68] This is in agreement with previous conclusions based on experimental values.[7,26b]

A comparison of the experimentally observed donor-acceptor bond lengths in the solid state and in the gas phase with the calculated bond strengths reveals a very interesting trend. Figure 3 shows a plot of the differences Δr between the interatomic distances observed in the solid state and the MP2/TZ2P optimized bond lengths and the predicted dissociation energies D_0. There is clearly a correlation between Δr and the bond strengths of the complexes. Weakly bound complexes have a significantly shorter donor-acceptor bond in the solid state than in the gas phase.

Electronic Structure

The electronic structure of donor-acceptor complexes has been the topic of many theoretical studies.[28a,d-f,i,k,29a,c,32e,f,33a,b] The nature of the dative bond, however, is still controversial. Of particular interest is the question if the donor-acceptor bond is mainly caused by electrostatic interactions, or whether nonelectrostatic (covalent) contributions, which are induced by charge transfer from the donor to the acceptor, are dominant. The HSAB model considers electrostatic and covalent interactions as the principal forces.[4] It is difficult, however, to develop a procedure that transforms the qualitative HSAB model into a quantitative

(65) McLaughlin, D. E.; Tamres, M. *J. Am. Chem. Soc.* **1960**, *82*, 5618.
(66) Andersen, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 1947.

(67) That BF_3 is a harder Lewis acid than BCl_3 becomes obvious by the calculated partial charge at the boron atom in BF_3 and BCl_3; see Table 8.
(68) Theory predicts that the strongest neutral Lewis acid is BeO: Koch, W.; Frenking G. In *Molecules in Natural Science and Medicine—an Enconium for Linus Pauling*; Maksic, Z. B., Eckert-Maksic, M., Eds.; Ellis Horwood: New York, 1991; p 225.

Table 8. MP2/6-31G(d)-NBO Charges for All Complexes

	donor-atom	acceptor atom	Lewis acid	D_e[a]
BH_3		0.33	0	
$OC-BH_3$ **1**	0.76	−0.60	−0.44	26.4
H_3N-BH_3 **2**	−0.94	−0.15	−0.35	33.7
Me_3N-BH_3 **3**	−0.44	−0.16	−0.34	43.6
BF_3		1.49	0	
$OC-BF_3$ **4**	0.44	1.48	−0.03	3.2
H_3N-BF_3 **5**	−1.03	1.38	−0.28	23.0
Me_3N-BF_3 **6**	−0.53	1.40	−0.26	33.3
Me_2O-BF_3 **7**	−0.56	1.44	−0.20	16.7
$HCN-BF_3$ **8**	−0.34	1.49	−0.04	5.8
CH_3CN-BF_3 **9**	−0.35	1.48	−0.08	7.2
$PhCHO-BF_3$ **10**	−0.51	1.43	−0.20	11.9[b]
$MA-BF_3$ **11**	−0.51	1.43	−0.20	11.8
BCl_3		0.32	0	
$OC-BCl_3$ **12**	0.44	0.32	−0.01	2.2
H_3N-BCl_3 **13**	−1.01	0.29	−0.36	31.3
Me_3N-BCl_3 **14**	−0.51	0.32	−0.32	41.3
$CH_3CN-BCl_3$ **15**	−0.34	0.33	−0.03	4.3
$AlCl_3$		1.51	0	
$EtCClO-AlCl_3$ **16**	−0.60	1.49	−0.14	23.3[b]
$Me_3N-AlCl_3$ **17**	−0.64	1.51	−0.14	49.5
SO_2		1.48	0	
Me_3N-SO_2 **18**	−0.49	1.53	−0.16	14.6
OC	0.44			
H_3N	−1.12			
Me_3N	−0.51			

[a] Calculated at MP2/TZ2P. [b] MP2/6-31G(d) geometry.

method.[5] The problem is that the decomposition of the interaction energy between the donor and the acceptor moiety into different terms may lead to qualitatively different answers. The Morokuma analysis[69] of the interactions in H_3N-BH_3 suggests that the stabilization has mainly electrostatic character,[28a] while the extended geminal model of Røeggen[70] emphasizes nonelectrostatic contributions to the bonding.[33a] Both methods find significant nonelectrostatic contributions to the bonding in $OC-BH_3$.[28a,33a] A very recent study by Glendening and Streitwieser[33b] using the natural energy decomposition analysis (NEDA), which is based on the NBO procedure,[34] comes to the conclusion that $OC-BH_3$ and H_3N-BH_3 are significantly stabilized by charge-transfer interactions. In the following we compare the results of the NBO population scheme[34] and the topological analysis[35] of complexes **1–18**. We begin with the calculated charge distribution given by the NBO analysis, which is shown in Table 8.

Before we discuss the calculated atomic partial charges, we want to remind the reader that dividing up the molecular electronic charge into atomic regions is *always* based upon an arbitrary partitioning scheme. The calculated charges have no physical meaning; they should only be used as a model to explain trends and properties of molecules. In particular, the absolute values of the partial charges should not be overinterpreted.[71] Rather, the change in the partial charges upon complex formation should be compared.

Table 9. Electron Density ρ_b (e/Å^3), Laplacian $\nabla^2\rho_b$ (e/Å^5), and Energy Density H_b (hartree/Å^3) at the Bond Critical Points r_b of the Donor-Acceptor Bonds[a]

	ρ_b	$\nabla^2\rho_b$	H_b	r_b
$OC-BH_3$ **1**	0.89	14.85	−0.60	0.32
H_3N-BH_3 **2**	0.66	12.03	−0.35	0.31
Me_3N-BH_3 **3**	0.73	11.41	−0.44	0.31
$OC-BF_3$ **4**	0.08	0.91	0.01	0.44
H_3N-BF_3 **5**	0.71	6.64	−0.50	0.31
Me_3N-BF_3 **6**	0.80	5.19	−0.63	0.31
Me_2O-BF_3 **7**	0.58	5.59	−0.38	0.32
$HCN-BF_3$ **8**	0.13	1.38	0.00	0.43
CH_3CN-BF_3 **9**	0.20	1.62	−0.03	0.40
$PhCHO-BF_3$ **10**	0.52	4.27	−0.34	0.33
$MA-BF_3$ **11**	0.52	4.17	−0.34	0.33
$OC-BCl_3$ **12**	0.04	0.47	0.01	0.47
H_3N-BCl_3 **13**	0.83	7.74	−0.61	0.31
Me_3N-BCl_3 **14**	0.84	4.20	−0.68	0.31
$CH_3CN-BCl_3$ **15**	0.08	0.78	0.00	0.46
$EtCClO-AlCl_3$ **16**	0.30	7.15	0.04	0.42
$Me_3N-AlCl_3$ **17**	0.39	7.22	−0.02	0.40
Me_3N-SO_2 **18**	0.39	2.55	−0.05	0.50

[a] Position of the bond critical point r_b is given by r(CP–A)/r(D–A). All data are at MP2/6-31G(d); CP = coordinate of bond critical point, A = acceptor atom, D = donor atom.

The results show that BH_3 complexes **1–3** have a higher charge transfer from the donor to the acceptor moiety than the complexes of BF_3, $AlCl_3$, and SO_2, although the positive partial charge at the acceptor atom of the Lewis acids BF_3, $AlCl_3$, and SO_2 is much higher than that of BH_3. BH_3 complexes **1–3** differ from the other structures by a much higher change of the partial charge at the acceptor atom boron toward a more negative value, while the hydrogen atoms at boron become less negatively charged. The B atom in BH_3 has a truly empty p orbital, while this orbital is partially occupied in BF_3 and BCl_3 by the charge donation of the halogen lone-pair electrons. The charge transfer to BH_3 is higher for **1** (0.44 e) than for **2** (0.35 e) and **3** (0.34 e), but the bond energy of **1** is lower than for **2** and **3** (Table 5). The higher charge transfer of **1** is consistent with the significantly shorter donor–acceptor bond (1.543 Å) than those of **2** (1.648 Å) and **3** (1.628 Å, Table 2). The very short donor–acceptor bond of **1** can be explained by the fact that the donor atom carbon is sp hybridized, while the donor atom nitrogen is sp^3 hybridized in **2** and **3**. From the NBO analyses it follows that *there is no correlation between charge transfer and bond strength in donor–acceptor complexes*! The most strongly bound donor–acceptor complex, **17**, has only a charge transfer of 0.14 e (Table 8).

More detailed information about the electronic structure of the donor–acceptor complexes is available from the topological analysis of the electron density distribution.[35] Table 9 shows the calculated results. Figure 4 displays the contour line diagrams of the Laplacian distribution of the electronic charge for **1–18** and the most important isolated Lewis acids and bases.

BH_3 complexes **1–3** are characterized by large covalent contributions to the donor–acceptor bond. This is revealed by the strongly negative value of the energy density at the bond critical point H_b (Table 9). It has been shown that covalent bonds have negative H_b values, while ionic bonds and van der Waals complexes have values of $H_b \geq 0$.[73] Typical values of H_b for a covalent single bond are between −1 and −3.[73] The calculations suggest that structure **1** has a more covalent donor–acceptor bond (H_b = −0.60) than **2** (−0.35) and **3** (−0.44). Parts a–c of Figure 4 show that the donor–acceptor bonds of **1**, **2**, and

(69) (a) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236. (b) Morokuma, K.; Iwata, S.; Lathan, W. A. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, 1974. (c) Morokuma, K. *Acc. Chem. Res.* **1977**, *10*, 294. (d) Morokuma, K.; Kitaura, K. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; Wiley: New York, 1980; Vol. 1 and references cited therein.

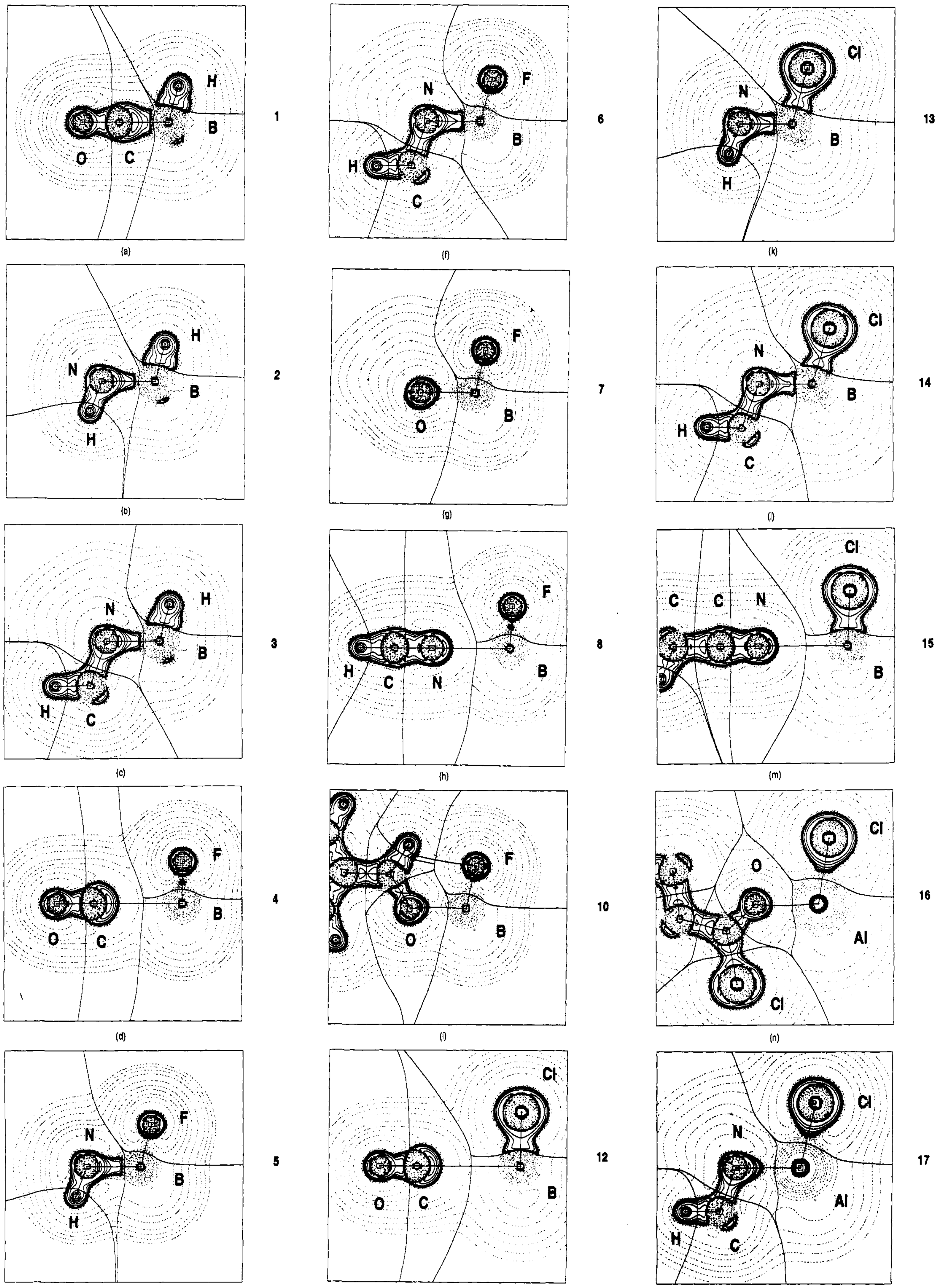
(70) (a) Røeggen, I. *J. Chem. Phys.* **1983**, *79*, 5520. (b) Røeggen, I.; Reza Ahmadi, G.; Wind, P. A. *J. Chem. Phys.* **1993**, *99*, 277 and references cited therein.

(71) An important example is the charge distribution of CO. There is a widespread belief that the measured dipole moment of CO (0.11 D, carbon being the *negative* end of the dipole)[72] necessarily means that the partial charge at the carbon atom must be negative. This assumption ignores the *polarization* of the atomic densities. The atomic charge distribution is *not* spherically symmetric. Therefore, the dipole moment cannot be used as an experimental proof to estimate atomic charges.

(72) Nelson, R. D.; Lide, D. R.; Maryott, A. A. *Natl. Stand. Ref. Data Ser.* (*U.S. Natl. Bur. Stand.*) **1967**, *10*.

(73) Cremer, D.; Kraka, E. *Angew. Chem.* **1984**, *96*, 612; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 627.

(74) (a) Bay, C. M.; Katritzky, A. R.; Sutton, L. E. *J. Chem. Soc.* **1958**, 1258. (b) Romm, I. P.; Sevast'yanova, T. G.; Gur'yanova, E. N.; Kolli, I. D.; Rodionov, R. A. *Zh. Obshch. Khim.* **1968**, *38*, 1938; *J. Gen. Chem. USSR* (Engl. Transl.) **1968**, *38*, 1881.



(a) 1 H O C B
(b) 2 H N H B
(c) 3 N H H C B
(d) 4 F O C B
(e) 5 N F B H
(f) 6 N F H B C
(g) 7 F O B
(h) 8 F H C N B
(i) 10 F O B
(j) 12 Cl O C B
(k) 13 Cl N B H
(l) 14 Cl N B H C
(m) 15 Cl C C N B
(n) 16 Cl O Al Cl
(o) 17 Cl N Al H C

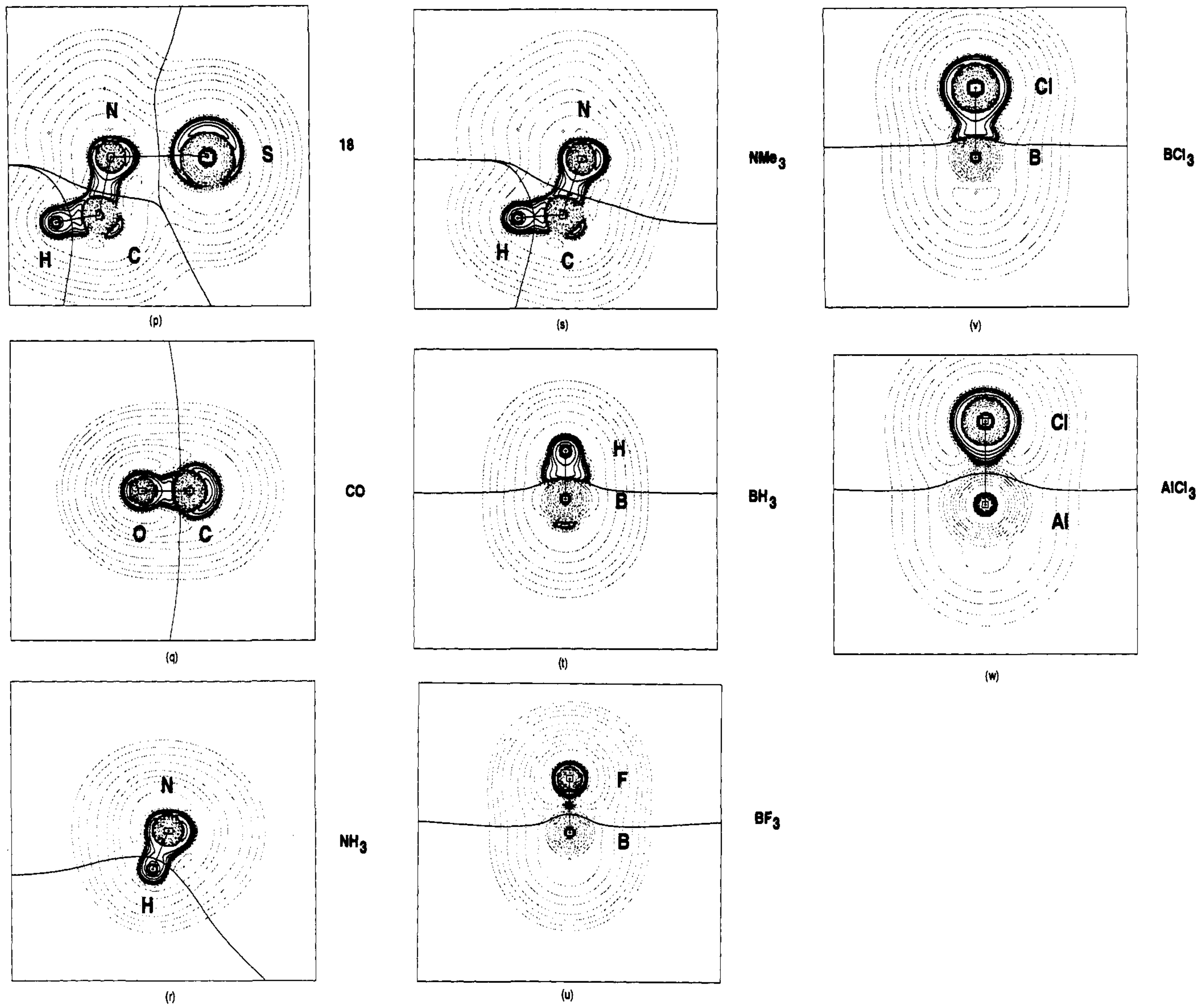


Figure 4. Contour line diagrams of the Laplacian distribution $\nabla^2\rho(\mathbf{r})$ at MP2/6-31G(d). Dashed lines indicate charge depletion ($\nabla^2\rho(\mathbf{r}) > 0$), and solid lines indicate charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$). The solid lines connecting the atomic nuclei are the bond paths, and the solid lines separating the atomic nuclei indicate the zero-flux surfaces in the molecular plane. The bond critical point $\mathbf{r}_b$ is at the crossing of the bond path and the zero-flux surface.

3 are characterized by an area of charge concentration ($\nabla^2\rho(\mathbf{r}) < 0$, solid lines), which is formed by the deformation of the lone-pair electronic charge at the donor atoms (compare the Laplacian distribution of CO, NH_3, and NMe_3). The shape of the Laplacian distribution makes the type of bonding, that is, the donation of electronic charge from the Lewis base toward the Lewis acid, clearly visible. The large area of charge concentration in the donor–acceptor bonding region is in agreement with the calculated H_b values, which predict significant covalent contributions to the bonding. The deformation at the nitrogen atom appears to be larger for **3** than for **2**, which agrees with the higher H_b value of **3** (0.44) than that of **2** (0.35).

The larger negative value $H_b = -0.60$ for the donor–acceptor bond of **1** than those of **2** ($H_b = -0.35$) and **3** ($H_b = -0.44$) indicates stronger covalent interactions in the former complex than in the latter molecules. Yet, the donor–acceptor interactions of **2** ($D_e = 28.3$ kcal/mol) and **3** ($D_e = 38.7$ kcal/mol) are stronger than those of **1** ($D_e = 23.0$ kcal/mol). A similar result has been found in the recent theoretical study by Glendening and Streitwieser[33b] using the natural energy decomposition analysis (NEDA). The NEDA results reveal that the strongest donor–acceptor interactions in **1** and **2** are charge-transfer (CT) interactions, but the calculated CT stabilization of **1** is nearly twice as large as that of **2**. The H_b values of **1** and **2** show a similar ratio. Also the calculated partial charges indicate a larger charge transfer from the donor to the acceptor for **1** than for **2** (Table 8). The NEDA results show that the electrostatic and deformation terms of the donor–acceptor interactions are stronger in **2** than in **1**.[33b] It follows that the stronger donor–acceptor bond of **2** (and probably **3**) than that of **1** is caused by electrostatic and deformation terms.

The comparison of the Laplacian distribution of BH_3 complexes **1–3** with that of the respective BF_3 complexes **4–6** shows striking differences. The Laplacian distribution at CO in **4** is hardly disturbed by the BF_3 acceptor (Figure 4d). The H_b value (0.01, Table 9) indicates that the complex **4** is formed solely by electrostatic interactions. However, the Laplacian distributions of BF_3 complexes **5** and **6** show stronger deformations of the charge concentration at the donor atom than the respective BH_3 complexes **2** and **3** (Figure 4e,f). Also the H_b values for **5** and **6** are more negative than for **2** and **3** (Table 9). Yet, the donor–acceptor bonds of **2** and **3** are stronger than those of **5** and **6** (Tables 5 and 6). This demonstrates that neither the degree of covalency nor the electrostatic interactions alone determine the strength of the donor–acceptor bonds.

The shapes of the Laplacian distribution of the other BF_3

complexes, **7**, **8**, and **10**, show less deformation at the donor atoms than the nitrogen atoms of the amine complexes **5** and **6** (Figure 4g–i). The contour line diagrams of the Laplacian distribution of **9** and **11** in the bonding region are very similar to those of **8** and **10**, respectively. Therefore, they are not shown here. The oxygen atoms of **7** and **10** have only a small droplet-like appendix in the direction of the boron atom. But the H_b values of the O–B bonds in these complexes suggest significant covalent contributions to the bonding (–0.38 for **7**, –0.34 for **10** and **11**, Table 9). The cyano complexes **8** and **9**, however, are only bound by electrostatic interactions. The H_b values for the donor–acceptor bonds are nearly 0.

The Laplacian distribution of BCl_3 complexes **12**–**15** is similar to that of the corresponding BF_3 complexes **4**–**6** and **9** (Figure 4j–m). Structures **12** and **15** are weakly bound complexes held together by electrostatic interactions (see the H_b values in Table 9). There is very little change in the Laplacian distribution between **12** and **15** and the respective Lewis bases and acid. The Laplacian distribution of **13** and **14** shows a strong deformation at the nitrogen atom, which is even stronger than in the respective BF_3 complexes **5** and **6**. The H_b values indicate that **13** and **14** have higher covalent contributions than **5** and **6**, respectively. The higher covalency of the BCl_3 complexes induces stronger bonds for **13** and **14** than for **5** and **6** (Tables 6 and 7).

The topological analyses of the electronic structure of the $AlCl_3$ complexes **16** and **17** demonstrate that *a strong dative bond does not necessarily have a covalent character*! The shape of the Laplacian distribution of **17** reveals that the electronic charge at the nitrogen atom of NMe_3 is much less altered by the presence of the Lewis acid $AlCl_3$ than in the boron complexes **3**, **6**, and **14** (Figure 4o). The calculated H_b value suggests that the donor–acceptor bond of **17** has practically no covalent contributions (H_b = –0.05, Table 9). It follows that **17** is held together mainly by electrostatic interactions. Still, complex **17** is the most strongly bound donor–acceptor complex investigated in our study. Strong dative bonds of donor–acceptor complexes may be formed by electrostatic *or* by covalent interactions!

Also the SO_2 complex **18** is mainly bound by electrostatic interactions (H_b = –0.05, Table 9). The Laplacian distribution of **18** is very interesting (Figure 4p). The area of charge concentration at the nitrogen atom is not directed toward the *hole* in the valence sphere of the electronic charge at the sulfur atom. This is because the oxygen atoms are placed in the direction of the charge depletion above and below the molecular plane. The steric repulsion between the oxygen atoms and the Lewis base prevents the orientation of the nitrogen lone-pair electronic charge toward the area of charge depletion at the sulfur atom.

Dipolar Intermolecular Interactions

The comparison of the donor–acceptor bond lengths observed in the gas phase and in the solid state (Table 1) reveals that the complexes always have shorter bonds in the latter aggregation state. This is attributed to the dipole–dipole interactions in the solid state.[8,19,21] Table 10 shows the theoretically predicted and experimentally observed dipole moments of complexes **1**–**18**. The agreement between the calculated and experimental values is quite good aside for **7**. The calculations show that most complexes have rather large dipole moments, except for carbonyl complexes **1**, **4**, and **12**.

The N–B interatomic distance of $H_3N–BH_3$ (**2**) is 1.657 ± 0.02 Å in the gas phase[9] and 1.564 ± 0.006 Å in the solid state.[8,75] In the weaker crystal field of $H_3N–BH_3$–[18-crown-6] the N–B interatomic distance is only 1.603 ± 0.032 Å.[76] Theoretical calculations of the geometry of **2** with simulating the electric field of a surrounding solvent using the self-consistent reaction field (SCRF) model[77] predict a shortening of the N–B bond from 1.66 Å for the isolated species to 1.62 Å in the presence of hexane and 1.57 Å in the presence of water.[8a]

In order to calculate explicitly the effect of short-range dipolar interactions, we optimized the geometries of the dimer and tetramer of **2**. Monomeric **2** has a dipole moment of 5.22 D.[9] The theoretical value at MP2/TZ2P is 5.44 D. The optimized geometries of the dimer (C_{2h}) and tetramer (C_{3v}) of **2** are shown in Figure 5. Both structures, which are fully optimized within the given point group, are minima on the potential energy

Table 10. Experimental and Calculated (MP2/TZ2P) Dipole Moments for All Complexes

	calcd	exptl
$OC–BH_3$ **1**	2.16	1.70[b]
$H_3N–BH_3$ **2**	5.44	5.22[c]
$Me_3N–BH_3$ **3**	5.06	4.62[d]
$OC–BF_3$ **4**	0.85	0.59[e]
$H_3N–BF_3$ **5**	6.14	
$Me_3N–BF_3$ **6**	6.09	5.63[d]
$Me_2O–BF_3$ **7**	5.49	4.35[f]
$HCN–BF_3$ **8**	4.22	
$CH_3CN–BF_3$ **9**	6.06	
$PhCHO–BF_3$ **10**	8.43[a]	
$MA–BF_3$ **11**	7.45	
$OC–BCl_3$ **12**	0.58	
$H_3N–BCl_3$ **13**	6.17	
$Me_3N–BCl_3$ **14**	6.75	6.31[d]
$CH_3CN–BCl_3$ **15**	4.90	
$EtCClO–AlCl_3$ **16**	8.47[a]	
$Me_3N–AlCl_3$ **17**	6.86	
$Me_3N–SO_2$	4.59	4.80[g]

[a] MP2/6-31G(d) value. [b] Reference 50. [c] Reference 9. [d] Reference 74a. [e] Reference 52. [f] Reference 74b. [g] Reference 22h.

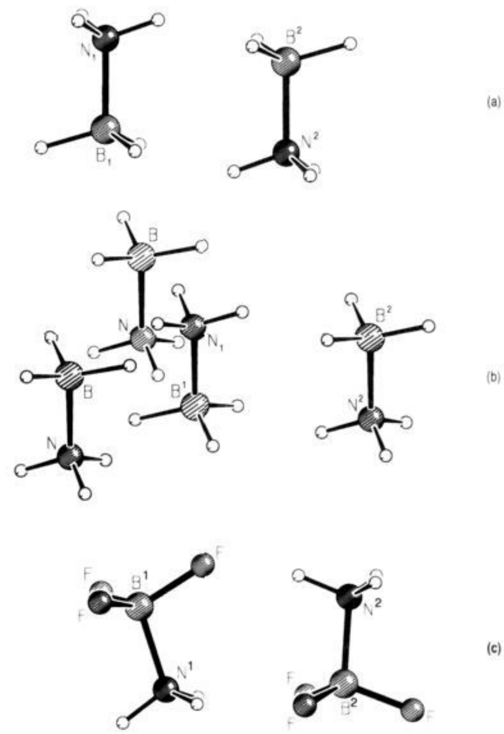


Figure 5. Optimized structures of the dimer and tetramer of **2** and the dimer of **5**.

(75) Boese, R.; Niederprüm, N.; Bläser, D. In *Molecules in Natural Science and Medicine—an Enconium for Linus Pauling*; Maksic, Z. B., Eckert-Maksic, M., Eds.; Ellis Horwood: New York, 1991; p 103.

(76) Colquhoun, H. M.; Jones, G.; Maud, J. M.; Stoddart, J. F.; Williams, D. J. *J. Chem. Soc., Dalton Trans.* **1984**, 63.

(77) (a) Miertus, S.; Scrocco, E.; Tomasi, J. *J. Chem. Phys.* **1981**, *55*, 117. (b) Pascal-Ahuir, J. L.; Tomasi, J.; Bonaccorsi, R. *J. Comput. Chem.* **1987**, *8*, 778.

Table 11. Comparison of B–N Bond Lengths for $(H_3N-BH_3)_n$ (n = 1, 2, 4) and $(H_3N-BF_3)_n$ (n = 1, 2)

		H_3N-BH_3 **2** (C_{3v})	$(H_3N-BH_3)_2$ (C_{2h})	$(H_3N-BH_3)_4$ (C_{3v})	H_3N-BF_3 **5** (C_{3v})	$(H_3N-BF_3)_2$ (C_s)
X-ray:	B^1-N^1	1.564[a]			1.60[d]	
	B^1-N^1	1.56[b]				
	B^1-N^2	3.49[b]				
gas phase:	B^1-N^1	1.657[c]			1.59[e]	
HF	B^1-N^1	1.690	1.660	1.622	1.693	1.642
MP2	B^1-N^1	1.662	1.637	1.604	1.679	1.629
HF	B^2-N^2			1.669		1.638
MP2	B^2-N^2			1.645		1.628
HF	B^1-N^2		3.493	3.583		4.014
MP2	B^1-N^2		3.340	3.409		3.424
HF	B^2-N^1			3.581		3.937
MP2	B^2-N^1			3.411		3.337

[a] Reference 8a. [b] Reference 51. [c] Reference 9. [d] Reference 53. [e] Reference 24.

hypersurface. The theoretical and experimental bond lengths are listed in Table 11.

The donor–acceptor bond length of **2** is calculated at the MP2/6-31G(d) level to become significantly shorter in going from the monomer (1.662 Å) to the dimer (1.637 Å) and the tetramer (1.604 Å). It follows that the dipole–dipole interactions of the tetramer account already for 60% of the shortening of the N–B bond length between the gas phase and the solid state. Also the calculated interatomic N–B distances between the monomeric units in the tetramer (3.409 and 3.411 Å) are in reasonable agreement with the experimental average value for the solid state (3.49 Å).[51] It should be noted, however, that the optimized geometry of the tetramer of **2** does *not* really mimic the solid-state structure. The unit cell of **2** shows that each monomer is surrounded by eight H_3N-BH_3 molecules.[75] The present calculations indicate only that the dipole–dipole interactions of the dimer and the tetramer of **2** lead already to a significantly shorter donor–acceptor bond.

We also calculated the dimeric form of H_3N-BF_3 (**5**). Monomeric **5** has a calculated dipole moment of 6.14 D (MP2/TZ2P). The optimized dimer of **5** (C_s) is slightly different from the dimer of **2** (C_{2h}), because the former structure is additionally stabilized by hydrogen bonding between fluorine and hydrogen atoms (Figure 5). The monomeric moieties of **2** are not equivalent in the dimer. Table 11 shows that the dimer of **5** has clearly shorter B–N bonds (1.629 and 1.628 Å) than the monomer (1.679 Å). The short-range dipolar interactions of the donor–acceptor complexes are responsible for the significant shortening of the dative bonds.

Summary

The theoretically predicted geometries and bond energies of the donor–acceptor complexes **1–18** at the MP2/TZ2P level of theory are generally in very good agreement with accurate experimental gas-phase values. BH_3 binds strongly to CO, NH_3, and NMe_3 with calculated dissociation energies at 298 K of 25.1 kcal/mol ($OC-BH_3$), 30.7 kcal/mol (H_3N-BH_3), and 41.1 kcal/mol (Me_3N-BH_3). The B–H bond lengths of the complexes are slightly longer than in free BH_3. BF_3 is calculated to be a weaker Lewis acid than BH_3. The calculated bond strengths of H_3N-BF_3 and Me_3N-BF_3 are 22.0 and 32.9 kcal/mol, respectively. $OC-BF_3$ is theoretically predicted to be a weakly bound van der Waals complex ($D_0(298)$ = 4.7 kcal/mol) with a very long donor–acceptor bond (r_{BN} = 2.824 Å), which is in agreement with experiment. The calculated bond strengths of the BF_3 complexes with Me_2O (17.3 kcal/mol), HCN (7.2 kcal/mol), MeCN (9.1 kcal/mol), benzaldehyde (13.0 kcal/mol), and 2-methylacrolein (12.8 kcal/mol) are intermediate between those of the CO and the amine complexes. The calculations show that the B–F bond length is a very sensitive probe for the strength of the donor–acceptor interactions. It becomes significantly longer in the strongly bound donor–acceptor complexes.

The BCl_3 complexes have clearly longer B–Cl interatomic distances by up to 0.1 Å than free BCl_3. The calculated bond strengths of the BCl_3 complexes with NH_3 (29.7 kcal/mol) and Me_3N (40.5 kcal/mol) are higher than those of the respective BF_3 complexes. However, the weakly bound molecules $OC-BCl_3$ (4.0 kcal/mol) and $MeCN-BCl_3$ (6.4 kcal/mol) are predicted to be *more weakly* bound than the BF_3 analogues. The comparison of $OC-BH_3$ ($D_0(298)$ = 25.1 kcal/mol) with $OC-BCl_3$ ($D_0(298)$ = 4.0 kcal/mol) shows that the substitution of hydrogen by chlorine at boron in donor–acceptor complexes may have a dramatic effect upon the bond strength. The most strongly bound donor–acceptor complex investigated in our study is $Me_3N-AlCl_3$. The calculated bond strength of 49.3 kcal/mol agrees very well with the experimental value of 47.5 ± 2.0 kcal/mol.[66] The calculated bond lengths of the Lewis acids $AlCl_3$ and SO_2 in the donor–acceptor complexes $Me_3N-AlCl_3$, $EtCClO-AlCl_3$ ($D_0(298)$ = 24.8 kcal/mol), and Me_3N-SO_2 ($D_0(298)$ = 15.5 kcal/mol) are also longer than in the isolated molecules.

The analysis of the electronic structure using the NBO partitioning scheme indicates that there is no correlation between the charge transfer from the donor to the acceptor and the calculated strength of the donor–acceptor bond. The topological analysis of the electronic structure reveals that the strongly bound complexes of BH_3, BF_3, and BCl_3 have significantly covalent contributions to the donor–acceptor bonds. Electrostatic interactions are responsible for the binding of the weakly bound van der Waals complexes of the boron Lewis acids. However, electrostatic interactions alone may also lead to very strongly bound complexes. The topological analysis of the binding interactions in the $AlCl_3$ and SO_2 complexes shows very little covalent contributions. The donor–acceptor bonds in these structures are nearly exclusively caused by electrostatic interactions. Thus, while the most strongly bound boron complex Me_3N-BH_3 ($D_0(298)$ = 41.1 kcal/mol) has significant covalent contributions, the most strongly bound complex $Me_3N-AlCl_3$ ($D_0(298)$ = 49.3 kcal/mol) is mainly bound by electrostatic interactions.

The bond shortening of the donor–acceptor bonds between the gas phase and the solid state is calculated to be mainly due to short-range dipole–dipole interactions. The calculated bond length of the B–N bond of H_3N-BH_3 decreases from the monomer (r_{BN} = 1.662 Å) to the dimer (r_{BN} = 1.637 Å) and the tetramer (r_{BN} = 1.604 Å). Also the dimer of H_3N-BF_3 has a clearly shorter B–N bond in the dimer (r_{BN} = 1.629 Å) than in the monomer (r_{BN} = 1.679 Å).

Acknowledgment. We thank Dr. J.-F. Gal and Prof. H. Mayr for helpful suggestions and one anonymous referee for useful comments. This study was supported by the Deutsche Forschungsgemeinschaft (SFB 260 and Leibniz program) and the Fonds der Chemischen Industrie. We thank the HLRZ Jülich and the TH Darmstadt for additional computer time at the CRAY Y-MP 864 and the Fujitsu S400/40 supercomputers. Excellent service by the computer center HRZ Marburg is gratefully acknowledged.