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Large Effects of Medium on Geometries. An *ab Initio* Study

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A number of examples of remarkably large differences between the geometries of donor–acceptor complexes in the solid state and in the gas phase are coming to light.[1-4] Most recently, Burns and Leopold[4a] reported differences in $HCN-BF_3$ of 0.84 Å in the N–B separation and 14° in the NBF bond angle as determined by microwave spectroscopy and by X-ray diffraction. The N–B shortening (0.38 Å) and NBF angle widening (10°) also were large for the CH_3CN-BF_3 complex in going from the gas phase to the solid phase. We now report an *ab initio* (Gaussian 92)[5] self-consistent reaction field (SCRF)[6] investigation of medium effects which reproduce these experimental results (Table 1).

The first, closely related study of this type involved a combined theoretical/experimental investigation of H_3N-BH_3. Bühl et al.[1a] attributed the 0.093 Å change in N–B separation from the gas phase (1.657 Å) to the solid phase (1.564 Å) to the effect of the dipolar field on this very polar species (dipole moment, 5.22 D) in the crystal. This was modeled by partial optimization of the structure in a reaction field. The structures of other amine–borane complexes also are influenced by the medium, but to a lesser extent. The similar but more detailed examination of H_3N-BH_3 by Cremer et al.[1b] and the investigation of H_2O-SO_3 by Hofmann and Schleyer[1c] supported these conclusions. Likewise, Wong, Wiberg, and Frisch[3] found that the zwitterionic $^+H_3NSO_3^-$ form of sulfamic acid is strongly favored in a medium with a high dielectric constant and that the N–S separation is decreased by 0.1 Å.

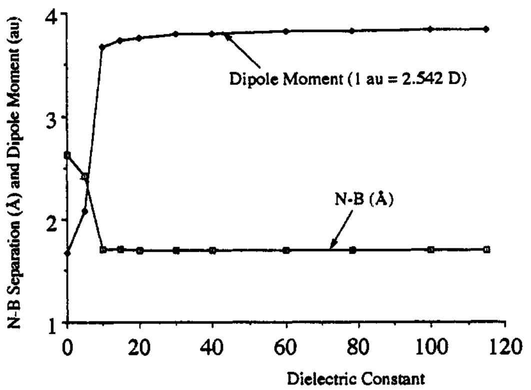

Figure 1. SCRF/6-31+G** N–B separation (Å) and dipole moment (au) of $HCN-BF_3$ complex as a function of the dielectric constant.

Jurgens and Almlöf's[2] 1991 MP2 computation on the CH_3CN-BF_3 complex gave $r(NB) = 2.17$ Å, i.e., much longer than the value (1.64 Å) in the solid state.[4b] Rather than being a shortcoming of the theory, this discrepancy was attributed to "crystal packing effects". In contrast, the MP2 and the gas-phase N–B distances for the weaker $NCCN-BF_3$ complex were nearly identical (2.60 and 2.64 Å, respectively).

Table 1 summarizes our results of geometries, dipole moments, and complexation as well as solvation energies for BF_3 complexes of HCN, CH_3CN, and NCCN as well as N_2, which has been included for comparison. Our RMP2/6-31G** N–B bond length (2.441 Å) and NBF bond angle (93.1°) agree well with the MW values of 2.473 Å and 91.5° for the $HCN-BF_3$ complex. In a model polar medium ($\epsilon = 78.54$, H_2O at 25 °C),[7] the computed SCRF/6-31+G** N–B separation is shortened dramatically to 1.695 Å, and the NBF angle is extended to 104.9°. Both are very close to the X-ray values (1.638 Å and 105.6°).[4a]

Similar agreement between the measured and calculated results are found for the $H_3CCN-BF_3$ complex as for $HCN-BF_3$. But the difference in N–B separation between the gas-phase and the RMP2/6-31G** value for $H_3CCN-BF_3$ (0.266 Å) is larger and of opposite sign than that for $HCN-BF_3$ (0.032 Å). Moreover, the N–B distances for both complexes are nearly the same in the solid state, but a difference of ca. 0.05 Å is found at SCRF/6-31+G**. Again, the RMP2/6-31G** N–B difference in both complexes of 0.164 Å is significantly shorter than the gas-phase value (0.462 Å) (Table 1).

In order to better understand the medium effect, we explored the SCRF/6-31+G** calculated N–B separation and the dipole moment of $HCN-BF_3$ as a function of the dielectric constant (ϵ). As shown in Figure 1, the N–B separation is 2.63 Å in a nonpolar medium ($\epsilon = 0$) with a dipole moment of 4.27 D. In a simulated $\epsilon = 15$ medium, the N–B separation is shortened dramatically to 1.707 Å, and the dipole moment increases to 9.48 D. From $\epsilon = 20$–115, neither the N–B separation nor the dipole moment changes further to a significant extent. Thus, the medium effect is ascribed to the dipolar crystal field. The calculated dipole moments for $HCN-BF_3$ are 4.13 D at RMP2/6-31G** and 9.72 D at SCRF/6-31+G** ($\epsilon = 78.54$). The dipole moment for $H_3CCN-BF_3$ are 5.63 D (RMP2/6-31G**) and 12.14 D (SCRF/6-31+G**, $\epsilon = 78.54$). Thus, very large dipole moments may be expected in the solid state for both the $HCN-BF_3$ and the $H_3CCN-BF_3$ complexes.

Based on the bonding energy and dipole moment, Oh et al.[4c] ascribed the increased stability and structure difference in the $SO_2N(CH_3)_3$ complex in the solid state to the strong dipole–induced dipole interaction which stabilizes the complex more than the free donor and acceptor molecules. The computed complexation energy for $HCN-BF_3$ is −5.6 kcal/mol [RMP2/

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[1] (a) Bühl, M.; Steinke, T.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1991,** *30,* 1160. (b) Cremer, D.; Olsson, L.; Reichel, F.; Kraka, E. *Isr. J. Chem.* **1993,** *33,* 369. (c) Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994,** *116,* 4947.

[2] Jurgens, R.; Almlöf, J. *Chem. Phys. Lett.* **1991,** *176,* 263.

[3] (a) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *J. Am. Chem. Soc.* **1991,** *113,* 4776. (b) Wong, M. W.; Wiberg, K. B.; Frisch, M. J. *Ibid.* **1992,** *114,* 523 and references cited therein.

[4] (a) Burns, W. A.; Leopold, K. R. *J. Am. Chem. Soc.* **1993,** *115,* 11622. (b) Dvorak, M. A.; Ford, R. S.; Suenram, R. D.; Lovas, F. J.; Leopold, K. R. *Ibid.* **1992,** *114,* 108 and the references cited, e.g., Janda, K. C.; Bernstein, L. S.; Steed, J. M.; Novick, S. E.; Klemperer, W. *Ibid.* **1978,** *100,* 8074. (c) The N–S separation in the $SO_2N(CH_3)_3$ complex shortens from 2.26 Å in the gas phase to 2.05 Å in the crystal: Oh, J. J.; LaBarge, M. S.; Matos, J.; Kampf, J. W.; Hillig, W. W., II; Kuczkowski, R. L. *Ibid.* **1991,** *113,* 4732.

[5] (a) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986. (b) Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. K.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. L.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Revision B; Gaussian, Inc.: Pittsburgh PA, 1992. (c) Foresman, J. B.; Frisch, Æ. *Exploring Chemistry with Electronic Structure Methode. A Guide to Using Gaussian*; Gaussin, Inc.: Pittsburgh, PA, 1993.

[6] The self-consistent reaction field (SCRF) method implemented in the Gaussian 92 program is based on the Onsager reaction field theory of the electrostatic solute–solvent interaction. In this reaction field model, the solute is placed in a spherical cavity immersed in a continuous medium with a dielectric constant ϵ. The dipole of the solute will induce a dipole in the medium, which in turn will interact with the molecular dipole to lead to stabilization. For the SCRF method and the SCRF MO formalism as well as its useful applications, see refs 3a,b and 5c cited here. A referee has expressed justifiable misgivings concerning the sensitivity of spherical cavity models especially for the NCCN and N_2 donors which have no permanent dipole moments. We have explored this matter further with a number of complexes using other continuum models; the results (which do not change the basic conclusions) will be reported in the full paper.

[7] Lide, D. R. *CRC Handbook of Chemistry and Physics*, 74th ed.; CRC Press, Inc.: Boca Raton, FL, 1993–1994.

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Table 1. Comparison of B–N Bond Lengths (in Angstroms) and NBF Bond Angles (in Degrees) for Complexes of HCN, H_3CCN, NCCN, and N_2 with BF_3 in the Gas Phase and Solid State[a] as Well as the Computed Values (Given in Parentheses) and the Calculated Complexation (E_{comp}) and Solvation Energies (E_{solv}, kcal/mol) with Dipole Moments (μ, D)

	gas phase (RMP2/6-31G**)			X-ray (SCRF/6-31+G**, $\epsilon = 78.54$)		
complex	N–B	∠NBF	E_{comp},[d] μ [D][f]	N–B	∠NBF	E_{solv},[g] μ [D][h]
$HCN–BF_3$[b]	2.473 (2.441)	91.5 (93.1)	–5.6,[e] 4.13	1.638 (1.695)	105.6 (104.9)	–7.6, 9.72
$H_3CCN–BF_3$[b,c]	2.011 (2.277)	95.6 (94.8)	–7.0, 5.63	1.630 (1.646)	105.6 (106.2)	–13.9, 12.14
$NCCN–BF_3$[c]	2.647 (2.570)	90 (91.8)	–4.2, 0.98	*a* (2.772)	*a* (91.5)	–0.1, 0.99
$N_2–BF_3$[c]	2.875 (2.725)	90.5 (90.8)	–2.3, 0.43	*a* (3.052)	*a* (90.5)	0.0, 0.32

[a] No X-ray values are reported. [b] Reference 4a. [c] Reference 4b. [d] E_{comp}(RMP2/6-31G**) + ZPE(RHF/6-31G**). [e] At RMP2/6-31G** + ZPE(RMP2/6-31G**). [f] At RMP2/6-31G**. [g] $E_{solv} = E(\epsilon = 78.54) - E(\epsilon = 0.0)$. [h] At SCRF/6-31+G** ($\epsilon = 78.54$).

6-31G** + ZPE(RMP2/6-31G**)]. In $HCN–BF_3$, the calculated solvation energy is –7.6 kcal/mol when $\epsilon = 0$ is increased to 20. From $\epsilon = 30–115$, the solvation energy is nearly constant (7.2–7.8 kcal/mol). This behavior is in agreement with the change in the $HCN–BF_3$ dipole moment as well as the N–B separation as a function of dielectric constant (see Figure 1). Thus, the dipole moment and stability as well as the N–B separation in $HCN–BF_3$ are greater and shorter, respectively, in a dipolar than in a nonpolar medium.

For comparison, we also have optimized the donor–acceptor complexes of NCCN and N_2 with BF_3. As given in Table 1, the RMP2/6-31G** N–B separations in $NCCN–BF_3$ (2.570 Å; cf. Almlöf's 2.60 Å[2]) and $N_2–BF_3$ (2.725 Å) agree well with the gas-phase values of 2.647 and 2.875 Å (no X-ray values for these two complexes have been reported).[4b] In a polar medium (ϵ = 78.54), the SCRF/6-31+G** N–B separations for both complexes (2.772 and 3.051 Å) are nearly the same as at RHF/6-31+G** 2.804 and 3.060 Å). Thus, no shortening effect on geometries is found here. We attribute this to the lack of a dipole moment in the donor molecules. While N_2 and NCCN are nonpolar, the dipole moments of HCN and H_3CCN are 3.12 and 3.98 D at the RMP2(fu)/6-31+G* level (the measured values are 2.98 and 3.89 D).[7] The computed complexation energies for HCN and H_3CCN with BF_3 (–5.6 and –7.0 kcal/mol) are, as expected, larger that those for NCCN and N_2 with BF_3 (–4.2 and –2.3 kcal/mol). Also no solvation effects on the complexation energies are found for the complexes of NCCN and N_2 with BF_3 (E_{solv} = –0.1 and 0.0 kcal/mol). This contrasts with the solvation energies for complexes of HCN and H_3CCN with BF_3, which are very large, e.g., –7.6 and –13.9 kcal/mol.

In conclusion, the large differences in geometries of the donor–acceptor complexes $HCN–BF_3$ and $H_3CCN–BF_3$ determined experimentally in the solid state and in the gas phase are medium effects and are mainly due to the crystal dipolar field interaction. This was one of the mechanisms suggested in ref 4a. Such medium effects seem to be found only for complexes in which the donor molecule has a permanent dipole moment. Donors without permanent dipoles (NCCN and N_2) may have no or only small medium effects on geometries.

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