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Unusually Large Gas–Solid Structure Differences: A Crystallographic Study of HCN–BF$_3$

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It is well-known that molecules in the gas phase retain very nearly the same structure when assembled in a molecular crystal. Although small gas–solid structure differences are common, their magnitudes are typically hundredths of an angstrom or less for lengths and tenths of a degree for angles,[1] reflecting the relatively minor perturbation that a crystalline environment imposes on any particular molecule. In this communication, however, we describe a crystallographic study of the donor–acceptor complex HCN–BF$_3$, whose gas-phase structure we have previously determined by microwave spectroscopy in a supersonic jet.[2] We find this axially symmetric adduct to be most unusual in that the B–N bond length and NBF angle change by 0.84 Å and 14°, respectively, upon crystallization. While we have previously reported a similar effect in the related complex CH$_3$CN–BF$_3$,[3] the results described here are, to the best of our knowledge, unprecedented in magnitude.

Previous work on solid HCN–BF$_3$ appears to be limited to two vapor pressure measurements and the report that the gaseous adduct is fully dissociated at room temperature.[4] In our work, a 1:1 gas mixture of HCN and BF$_3$ at 432 Torr was prepared in a glass vessel at room temperature and cooled to 0 °C to obtain crystals. Precooled hydrocarbon vacuum pump oil was injected into the vessel to protect the crystals from air and moisture, and X-ray analysis was performed at -101 ± 3 °C.[5] Bond lengths and bond angles are given in Table I, and a stereoscopic projection is shown in Figure 1.

Table II compares the B–N bond lengths and NBF angles for HCN–BF$_3$ and CH$_3$CN–BF$_3$ in the gas and crystal phases. The most striking feature of these data is the 0.835(31) Å contraction of the B–N bond and the 14.1(18)° widening of the NBF angle of the HCN adduct upon crystallization. Also of interest are the relative B–N bond lengths for CH$_3$CN–BF$_3$ and HCN–BF$_3$, which differ by 0.462(36) Å in the gas phase but are virtually identical in the crystal. In ref 3 we argued that a true van der Waals complex of this type should have a B–N distance of about 2.9 Å and a planar configuration at the boron, while a covalently bound species should have a 1.6-Å B–N bond length and a tetrahedral geometry at the boron. Thus, the data in Table II show that both species appear intermediate between van der Waals and covalent bonding in the gas phase, but both become essentially covalent in the solid. Note that since HCN–BF$_3$ forms a *molecular* crystal, the situation here is qualitatively distinct from that of gas-phase ion pairs or metal dimers, for which bond length changes are also observed upon crystallization, but for which the solid is not a collection of identifiable dimeric units.

Table I. Intramolecular Distances and Angles for HCN–BF$_3$(c)

bond distance (Å)		bond angle (deg)	
B–F(1)	1.362(2)	F(1)–B–F(2)	113.5(1)
B–F(2)	1.352(2)	F(1)–B–F(3)	112.5(1)
B–F(3)	1.369(2)	F(1)–B–N	105.5(1)
B–N	1.638(2)	F(2)–B–F(3)	113.1(1)
N–C	1.122(2)	F(2)–B–N	105.9(1)
C–H	0.96(2)	F(3)–B–N	105.4(1)
		B–N–C	178.4(1)

Table II. Comparison of B–N Bond Lengths and NBF Angles for HCN–BF$_3$ and CH$_3$CN–BF$_3$ in the Gas Phase and the Solid State

	HCN–BF$_3$		CH$_3$CN–BF$_3$	
	R(B–N) (Å)	α(NBF) (deg)	R(B–N) (Å)	α(NBF) (deg)
gas	2.473(29)[a]	91.5(15)[a]	2.011(7)[b]	95.6(6)[b]
solid	1.638(2)[c]	105.6(3)[c,d]	1.630(4)[e]	105.6(6)[e]
gas–solid difference	0.835(31)	14.1(18)	0.381(11)	10(1)

[a] Reference 2. [b] Reference 3. [c] This work. [d] Average of three values. See Table I. [e] Reference 6.

Although the compounds in Table II show large gas–solid structural changes, it seems unlikely that the crystals simply consist of a second, short bond length "isomer" which was unobserved in the gas phase. For CH$_3$CN–BF$_3$, extensive microwave searches revealed only one form, though a more stable isomer, if it existed, would almost certainly have been produced during the collisional phase of the supersonic expansion. More importantly, however, we have noted previously[3] that, within a series of BF$_3$ complexes with nitrogen donors, one observes a continuum ranging from van der Waals to covalent structures. Moreover, the B–N distances and NBF angles are well correlated, and following classic work of Bürgi and Dunitz et al.,[7] we argued that *because* such a correlation is observed, each complex in the series may be interpreted as a snapshot along the reaction path for adduct formation. This idea has been explored extensively in crystals[7] and is simpler and more reasonable than assuming each member of the series to be trapped in one of many local minima. Indeed, *ab initio* calculations show no evidence for multiple minima along the R(B–N) coordinate for either adduct.[8,9]

It is, of course, of interest to comment on possible origins of this very dramatic effect. For HCN–BF$_3$, calculations indicate a rapid rise in dipole moment as the B–N distance shortens,[9] and thus one can readily envision a cooperative effect in which bond shortening is favored by the proximity of other dipoles. Interestingly, a similar explanation has recently been given and semiquantitatively verified by Oh et al.,[10] who observed a 0.21-Å contraction of the N–S bond in (CH$_3$)$_3$N–SO$_2$ upon crystallization.

If such a cooperative mechanism pertains, it would be interesting to know whether some small number of nearest neighbors can account for most of the effect, or whether the summation of interactions over a substantial range need be considered. In this regard, we note from Figure 1 that alongside each HCN–BF$_3$ unit is an antiparallel partner 3.8 Å away. Aside from the direct electrostatic effect of this pairing, such a configuration would act to reduce the contribution from dipolar interactions at long range. Also, it can be seen that, for each HCN–BF$_3$ molecule, one of the fluorines lies 2.05 Å from the hydrogen of another in a near-

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(1) See, for example: Hargittai, M.; Hargittai, I. *Phys. Chem. Miner.* **1987**, *14*, 413 and references therein.

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

(4) Pohland, V. E.; Harlos, W. *Z. Anorg. Allg. Chem.* **1932**, *207*, 242.

(5) X-ray analysis for HCN–BF$_3$: orthorhombic, space group Pbca (No. 61), $a = 9.064(3)$ Å, $b = 8.658(3)$ Å, $c = 8.733(5)$ Å, $V = 685.3(8)$ Å^3, $Z = 8$, and $d_{\text{calc}} = 1.838$ g/cm^3. A total of 783 unique reflections ($I > 2.00\sigma(I)$) were collected on an Enraf–Nonius CAD-4 diffractometer and refined by direct methods to give $R = 0.037$, $R_w = 0.040$, and $S = 1.40$. Additional details are given in the supplementary material.

(6) (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*, 2183.

(7) Bürgi, H. G.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153 and references therein.

(8) Jurgens-Lutovsky, R.; Almlöf, J. *Chem. Phys. Lett.* **1991**, *176*, 263.

(9) Jurgens-Lutovsky, R.; Almlöf, J. Private communication.

(10) Oh, J. J.; LaBarge, M. S.; Matos, J.; Kampf, J. W.; Hillig, K. W., II; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 4732.

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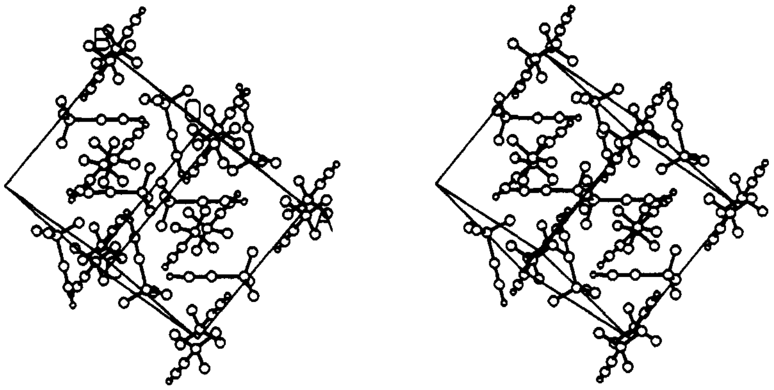

Figure 1. A stereoscopic projection of HCN–BF_3(c).

linear configuration, suggesting the formation of a hydrogen bond which might also provide stabilization of local origin.

Finally, the potential generality of this type of effect, regardless of mechanism, deserves some comment. For BF_3, electron deficiency at the boron leaves open the *possibility* of forming a new bond. The extent to which this actually occurs can be tuned by the basicity of the donor and gives rise to the propensity for intermediate type bonding in the gas phase. With this propensity for variable bonding built in, the system is particularly susceptible to external or environmentally induced perturbations which can similarly tune the degree of bond formation. Thus, it seems likely that there is a fundamental connection between intermediate type bonding and large gas–solid structure differences. Adducts containing elements with expandable octets should have similar possibilities to form new bonds and should therefore commonly display both phenomena. The data in Table II represent a particularly simple, clean test case which we hope will stimulate theoretical efforts to quantitatively account for these large gas–solid structure differences.

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Supplementary Material Available: Tables listing positional and thermal parameters and details of the structure solution for HCN–BF_3 (11 pages); listing of observed and calculated structure factors for HCN–BF_3 (6 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.