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Microwave Spectra and Structure of HCN–BF<sub>3</sub>: An Almost Weakly Bound Complex

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Rotational spectra of the complex HCN–BF<sub>3</sub> have been observed using pulsed-nozzle Fourier transform microwave spectroscopy. Spectra have been observed for the <sup>11</sup>B and <sup>10</sup>B species with both HC<sup>14</sup>N and HC<sup>15</sup>N, and the hyperfine structure has been analyzed. The complex has the expected C<sub>3v</sub> structure, with the nitrogen end of the HCN toward the boron, but the observed BN bond length of 2.473(29) Å is notably shorter than that in the related weakly bound systems N≡N–BF<sub>3</sub> and N≡C–C≡N–BF<sub>3</sub>. The out-of-plane distortion of the BF<sub>3</sub> cannot be determined accurately but is probably less than 3°. We compare the structure, force constants, quadrupole coupling constants, and binding energy of the complex with those of other species formed from BF<sub>3</sub> and a variety of nitrogen donors. Despite the rather short B–N bond length, the force constant for the intermolecular bond, as well as the boron and nitrogen nuclear quadrupole coupling constants, is comparable to those of a truly weakly bound system.

## Introduction

In a recent paper,<sup>1</sup> we reported the microwave spectrum and structure of the donor–acceptor complex CH<sub>3</sub>CN–BF<sub>3</sub>. This species was found to have a symmetric structure with the nitrogen end of the CH<sub>3</sub>CN toward the boron and the C<sub>3</sub> axes of the two monomers coincident. Though reminiscent of both stable, datively bonded species such as (CH<sub>3</sub>)<sub>3</sub>N–BF<sub>3</sub><sup>2</sup> and weakly bound van der Waals complexes such as N<sub>2</sub>–BF<sub>3</sub><sup>3</sup> or NCCN–BF<sub>3</sub>,<sup>4</sup> the structure was, in fact, quite unusual in that the B–N bond length and NBF angle were intermediate between those expected for true covalent or true van der Waals type interactions. Moreover, comparison with X-ray studies of the crystalline adduct<sup>5</sup> revealed that the structure of the gas-phase dimer was significantly different than that of the discrete molecular units found in the solid. In particular, the B–N bond length was 0.4 Å longer and the NBF angle 10° smaller in the gas-phase species, indicating an unusually large effect of the crystalline environment on the structure of a single molecule.

In interpreting these results, we considered a variety of gas-phase and crystalline complexes of BF<sub>3</sub> with nitrogen donors and examined the relationship between the B–N bond distance and the out-of-plane distortion of the BF<sub>3</sub>. Across the series of species considered, we found a 1.2-Å variation in B–N bond length, accompanied by a monotonic progression from a planar to tetrahedral configuration at the boron. Species with long B–N distances showed essentially a planar BF<sub>3</sub> subunit, indicative of true van der Waals type interactions, while those with short, covalent bond lengths displayed an approximately tetrahedral configuration at the boron. By analogy with well-known crystallographic work of Bürgi and Dunitz et al.,<sup>6</sup> we interpreted this correlated variation in bond length and bond angle as a representation of the response of a BF<sub>3</sub> molecule to the approach of a nitrogen donor as a new B–N bond forms. Such an interpretation parallels the widely used “structure correlation”

method, which has been applied extensively in crystalline systems to map “reaction paths” for simple chemical transformations.<sup>6</sup>

The observation of structure correlations has been ubiquitous in crystalline systems, and indeed it has not been uncommon to find that the distances between the same two atoms in a related series of compounds can span those characteristic of weak, nonbonded interactions to those normally associated with ordinary chemical bonds. An unusual and particularly encouraging feature of the acid–base complexes of BF<sub>3</sub>, however, is that the full range between van der Waals and covalent bond distances is represented by species in the gas phase. The implication of this is that if intermediate interaction distances can occur in isolated molecules, then correlations among related series of compounds need not be restricted to those involving structure. Indeed any property accessible via high-resolution spectroscopy could, in principle, be followed between the van der Waals and covalent limits. Though less information of this kind was available, we were able to discuss nuclear quadrupole coupling constants, as well as bending and stretching force constants with regard to the dative bond.<sup>1</sup>

We present the observation and analysis of the microwave spectrum of the complex HCN–BF<sub>3</sub>. While acetonitrile reacts with BF<sub>3</sub> to form a solid which is stable to about 50 °C, HCN and BF<sub>3</sub> form a crystalline material with a vapor pressure of about 5 × 10<sup>4</sup> Pa (400 Torr) at only 19 °C.<sup>7</sup> These data suggest that the HCN–BF<sub>3</sub> interaction may be stronger than that in an ordinary “van der Waals” complex but weaker than that between CH<sub>3</sub>CN and BF<sub>3</sub>. Thus, a gas-phase study of the HCN–BF<sub>3</sub> adduct might reveal a species with a B–N bond length shorter than a van der Waals bond but longer than that observed in the gas-phase acetonitrile complex. If such were the case, the determination of quadrupole coupling and centrifugal distortion constants could yield additional information about the electronic and mechanical properties of species with only partially developed bonds. As reported below, our observations confirm that the B–N bond length is in the expected “intermediate” range, though the quadrupole coupling and hyperfine data portray a complex which is decidedly van der Waals in nature. These observations are discussed, together with the results of a recent series of ab

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*initio* studies of BF<sub>3</sub> adducts<sup>8</sup> to provide additional information about the intermediate regime between van der Waals and covalent bonding.

## Experimental Section

Rotational spectra were recorded using the Balle-Flygare type pulsed-nozzled Fourier transform microwave spectrometer<sup>9</sup> which has been described previously.<sup>10</sup> Spectral searches were done while mixing 1 vol % gas mixtures of HCN and BF<sub>3</sub> in argon through separate inlets immediately prior to the expansion. All experiments were done at a nominal stagnation pressure of 120 kPa (1.2 atm) with continuous flow at both inlets. Time domain signals were averaged over 200–2000 pulses depending upon the transition strength, and Fourier transformed to obtain frequency domain spectra. In each case 512 data points were taken for each pulse providing a frequency resolution of 3.9063 kHz.

Initial searches were conducted using predictions based on a recent *ab initio* study by Jurgens-Lutovsky and Almlöf.<sup>8b</sup> Rotational spectra for the known species HCN-HF, (HCN)<sub>2</sub>, BF<sub>2</sub>OH, and Ar-BF<sub>3</sub>, as well as spectral transitions for an unidentified trimer species (whose signal increased with higher HCN flow and increased pressure) were observed during the course of the searches. Preliminary identification of the HC<sup>14</sup>N-<sup>11</sup>BF<sub>3</sub> spectra was based on the observation that elimination of either gas from the expansion mixture extinguished the signal. The spectra displayed complex hyperfine patterns due to quadrupole coupling of the <sup>14</sup>N and the <sup>11</sup>B nuclei, providing additional evidence of the complex's identity. Final, unambiguous identification was made by the prediction and subsequent observation of spectra of the <sup>10</sup>B species as well as those for both the <sup>10</sup>B and <sup>11</sup>B complexes with HC<sup>15</sup>N. <sup>10</sup>B spectra were readily observed in natural abundance, but observation of the <sup>15</sup>N complexes required the use of isotopically enriched samples.

## Results

Tables I–IV list the observed transition frequencies for the isotopic forms of HCN-BF<sub>3</sub> studied, and Figure 1 shows a portion of the  $J = 4 \leftarrow 3$  transition of the HC<sup>15</sup>N-<sup>11</sup>BF<sub>3</sub>. Spectral lines were typically between 40 and 60 kHz wide due to unresolved or partially resolved spin-spin hyperfine structure, which limited the accuracy of the measurements to typically 10–20 kHz. Transition frequencies were fit using the usual expression for a symmetric rotor with  $J$ - and  $K$ -dependent centrifugal distortion terms, viz.

$$\nu = 2(J'' + 1)[B - D_{JK}K^2] - 4D_J(J'' + 1)^3 + \Delta E_{\text{Quad}} \quad (1)$$

Here  $\Delta E_{\text{Quad}}$  is the difference in hyperfine energies for the lower and upper states, and was calculated using the usual first-order treatment<sup>11,12</sup> for one or two quadrupolar nuclei, as appropriate.

Spectroscopic constants determined from a least-squares analysis for each isotopic derivative appear in Table V, and residuals from the fit are also listed in Tables I–IV. Due to the relatively large spectral linewidths noted above and to severe congestion in some of the spectra (particularly those for the <sup>14</sup>N species), several sets of assignments for weaker components were found for each isotope which gave acceptable fits. The assignments in Tables I–IV and therefore the constants in Table V were selected since they reproduced the largest number of transitions to within the experimental uncertainties, and because the resulting quadrupole coupling and centrifugal distortion constants most closely exhibited the expected isotopic scaling.<sup>11,12</sup> Even with alternate sets of assignments of weaker components, the constants determined were very nearly the same as those given here. The rotational constants, for example, varied by only a few kilohertz

TABLE I: Observed Transitions of HC<sup>14</sup>N-<sup>11</sup>BF<sub>3</sub><sup>a,b</sup>

$J'$	$F_1'$	$F'$	$J''$	$F_1''$	$F''$	$K$	frequency <sup>c</sup>	obs - calc
3	4.5	4.5	2	3.5	3.5	2	12 291.413	-0.003
3	1.5	1.5	2	1.5	1.5	0	12 291.579	0.007
3	1.5	2.5	2	1.5	2.5	0	12 291.579	-0.003
3	2.5	2.5	2	2.5	1.5	0	12 291.579	-0.004
3	3.5	3.5	2	3.5	2.5	2	12 291.732	-0.014
3	4.5	4.5	2	3.5	4.5	1	12 291.910	-0.008
3	4.5	4.5	2	3.5	3.5	1	12 292.541	0.001
3	4.5	5.5	2	3.5	4.5	2	12 292.670	0.010
3	3.5	3.5	2	2.5	2.5	0	12 292.670	-0.002
3	2.5	3.5	2	2.5	2.5	1	12 292.747	0.005
3	4.5	3.5	2	3.5	2.5	1	12 292.747	-0.009
3	2.5	3.5	2	2.5	3.5	0	12 292.747	-0.005
3	2.5	1.5	2	2.5	1.5	1	12 292.835	-0.005
3	3.5	2.5	2	2.5	1.5	0	12 292.871	0.010
3	2.5	2.5	2	1.5	1.5	1	12 292.871	-0.002
3	4.5	4.5	2	3.5	3.5	0	12 292.917	0.003
3	4.5	5.5	2	3.5	4.5	1	12 292.917	0.009
3	4.5	3.5	2	3.5	3.5	1	12 292.917	-0.004
3	4.5	5.5	2	3.5	4.5	0	12 292.988	-0.003
3	2.5	3.5	2	1.5	2.5	0	12 293.085	0.004
3	4.5	3.5	2	3.5	2.5	0	12 293.085	-0.008
3	3.5	4.5	2	2.5	3.5	1	12 293.085	-0.003
3	1.5	2.5	2	0.5	1.5	0	12 293.154	-0.007
3	2.5	1.5	2	1.5	0.5	1	12 293.154	0.006
3	3.5	2.5	2	2.5	2.5	1	12 293.287	0.000
3	3.5	4.5	2	2.5	3.5	2	12 293.287	-0.008
3	3.5	3.5	2	3.5	4.5	1	12 293.370	0.005
3	3.5	4.5	2	3.5	4.5	1	12 293.408	0.002
3	3.5	3.5	2	2.5	2.5	2	12 293.594	0.007
3	3.5	2.5	2	2.5	1.5	2	12 293.911	-0.002
3	3.5	3.5	2	3.5	3.5	1	12 293.995	0.008
3	3.5	2.5	2	3.5	2.5	1	12 294.204	-0.003
4	2.5	2.5	3	2.5	1.5	0	16 387.971	0.003
4	4.5	4.5	3	4.5	3.5	3	16 387.971	0.006
4	2.5	2.5	3	2.5	2.5	0	16 388.874	0.006
4	2.5	3.5	3	2.5	3.5	0	16 388.874	-0.011
4	4.5	4.5	3	4.5	5.5	3	16 388.977	-0.003
4	3.5	3.5	3	3.5	2.5	0	16 389.037	0.007
4	5.5	6.5	3	4.5	5.5	3	16 389.162	0.006
4	2.5	2.5	3	1.5	1.5	2	16 389.162	0.006
4	3.5	2.5	3	2.5	3.5	3	16 389.379	-0.008
4	2.5	3.5	3	2.5	2.5	2	16 389.379	-0.005
4	2.5	3.5	3	2.5	2.5	0	16 389.450	0.013
4	3.5	3.5	3	3.5	3.5	0	16 389.538	-0.007
4	3.5	3.5	3	3.5	4.5	1	16 389.538	-0.013
4	4.5	3.5	3	3.5	3.5	3	16 389.538	-0.017
4	2.5	2.5	3	1.5	2.5	1	16 389.655	0.005
4	3.5	2.5	3	3.5	3.5	3	16 389.655	0.003
4	3.5	3.5	3	2.5	2.5	2	16 389.734	0.001
4	5.5	6.5	3	4.5	5.5	2	16 389.782	-0.007
4	3.5	4.5	3	3.5	3.5	3	16 389.782	0.006
4	3.5	4.5	3	3.5	4.5	3	16 389.850	0.005
4	3.5	2.5	3	3.5	2.5	0	16 389.938	0.006
4	4.5	4.5	3	4.5	3.5	2	16 389.999	0.008
4	5.5	5.5	3	4.5	4.5	1	16 389.999	0.000
4	2.5	3.5	3	2.5	3.5	3	16 389.999	-0.008
4	3.5	4.5	3	3.5	3.5	0	16 390.082	-0.009
4	3.5	3.5	3	2.5	2.5	1	16 390.161	-0.004
4	5.5	6.5	3	4.5	5.5	1	16 390.161	-0.008
4	3.5	4.5	3	2.5	3.5	1	16 390.225	0.010
4	2.5	3.5	3	3.5	3.5	3	16 390.279	0.006
4	2.5	2.5	3	1.5	1.5	0	16 390.294	-0.001
4	5.5	6.5	3	4.5	5.5	0	16 390.294	-0.002
4	3.5	2.5	3	3.5	2.5	3	16 390.294	-0.001
4	3.5	2.5	3	2.5	1.5	0	16 390.314	0.004
4	3.5	3.5	3	2.5	2.5	0	16 390.314	0.005
4	4.5	5.5	3	3.5	4.5	0	16 390.314	0.005

<sup>a</sup> All values in megahertz. <sup>b</sup>  $F_1 = I_B + J$ ;  $F = F_1 + I_N$ . <sup>c</sup> Individual measurement uncertainties differ due to variable linewidths and spectral congestion but are typically 10–20 kHz. See text for discussion.

among fits using alternate sets of assignments, while the quadrupole coupling constants varied by at most a few percent. Thus, any ambiguities introduced by spectral line widths and congestion are minimal and produce a negligible effect on the structural analysis of the complex discussed below.

TABLE II: Observed Transitions of  $\text{HC}^{14}\text{N}-^{10}\text{BF}_3^{a,b}$ 

$J'$	$F_1'$	$F'$	$J''$	$F_1''$	$F''$	$K$	frequency <sup>c</sup>	obs - calc
3	3	4	2	4	5	0	12 233.260	0.002
3	3	3	2	4	3	0	12 333.471	-0.002
3	2	3	2	3	4	1	12 333.471	0.010
3	1	1	2	2	1	1	12 334.298	-0.002
3	5	4	2	4	3	1	12 334.298	-0.013
3	3	3	2	3	2	1	12 334.379	0.008
3	2	2	2	2	2	1	12 334.379	-0.001
3	6	5	2	5	4	1	12 334.379	-0.008
3	3	3	2	2	2	2	12 334.379	0.006
3	4	3	2	4	3	0	12 334.379	0.007
3	2	2	2	2	2	0	12 334.379	-0.004
3	5	5	2	4	4	1	12 334.447	-0.001
3	1	1	2	1	0	1	12 334.478	0.002
3	4	4	2	4	3	0	12 334.478	0.003
3	4	5	2	4	4	0	12 334.478	-0.006
3	3	4	2	2	3	1	12 334.551	0.004
3	2	1	2	2	2	1	12 334.551	0.008
3	6	5	2	5	5	1	12 334.636	0.002
3	6	7	2	5	6	0	12 334.636	0.010
3	1	2	2	1	2	0	12 334.636	-0.004
3	4	5	2	4	4	1	12 334.679	-0.012
3	4	3	2	4	3	1	12 334.718	0.004
3	5	6	2	4	5	1	12 334.718	0.003
3	3	3	2	2	2	1	12 334.718	-0.005
3	6	5	2	5	4	0	12 334.718	0.017
3	4	4	2	4	3	1	12 334.788	-0.003
3	4	4	2	3	3	2	12 334.788	0.004
3	1	1	2	1	0	0	12 334.788	0.005
3	3	2	2	3	3	1	12 334.788	-0.010
4	1	1	3	0	1	3	16 443.140	0.001
4	7	6	3	6	6	3	16 443.140	-0.014
4	3	4	3	2	3	3	16 443.717	0.013
4	4	5	3	3	4	3	16 444.098	0.007
4	4	5	3	4	4	1	16 444.292	0.005
4	2	1	3	2	2	3	16 444.487	-0.006
4	3	3	3	2	2	3	16 444.487	-0.006
4	1	1	3	1	1	0	16 444.487	-0.008
4	7	7	3	6	7	0	16 444.487	-0.008
4	6	5	3	5	4	3	16 445.234	-0.001
4	2	2	3	2	1	1	16 445.234	-0.002
4	4	4	3	5	5	3	16 445.234	0.005
4	2	2	3	3	3	3	16 445.234	0.006
4	3	3	3	2	2	2	16 445.302	-0.007
4	6	6	3	5	6	1	16 445.467	0.000
4	6	6	3	5	6	0	16 445.467	0.000
4	7	7	3	6	6	1	16 445.524	0.012
4	3	4	3	3	4	1	16 445.524	0.011
4	4	3	3	4	4	1	16 445.524	0.007
4	7	6	3	6	5	1	16 445.621	-0.012
4	2	3	3	2	3	0	16 445.621	-0.002
4	6	5	3	6	5	2	16 445.621	-0.008
4	7	8	3	6	7	1	16 445.684	-0.003
4	3	4	3	3	4	0	16 445.684	0.004
4	5	5	3	4	4	0	16 445.684	-0.007
4	4	5	3	5	4	3	16 445.684	-0.003
4	1	1	3	0	1	0	16 445.684	-0.005
4	5	5	3	4	4	1	16 445.715	0.001
4	4	5	3	3	4	1	16 445.715	-0.010

<sup>a</sup> All values in megahertz. <sup>b</sup>  $F_1 = I_B + J$ ;  $F = F_1 + I_N$ . <sup>c</sup> Individual measurement uncertainties differ due to variable linewidths and spectral congestion but are typically 10–20 kHz. See text for discussion.

### Structural Analysis

The spectroscopic constants in Table V can be used to obtain information about the vibrationally averaged geometry of the complex once a number of simplifying assumptions have been made. In doing so, two preliminary observations are particularly pertinent. First, an approximate calculation of the B–N bond length from the observed rotational constants indicates a value of about 2.5 Å. This is in good agreement with the results of an *ab initio* study,<sup>8b</sup> which has predicted both a bond length of 2.56 Å and an angular distortion of the  $\text{BF}_3$  of only 3° upon complexation. Since the van der Waals and covalent bond distances expected for a boron–nitrogen interaction are 2.9 and

TABLE III: Observed Transitions of  $\text{HC}^{15}\text{N}-^{11}\text{BF}_3^a$ 

$J'$	$F'$	$J''$	$F''$	$K$	frequency <sup>c</sup>	obs - calc
3	1.5	2	0.5	2	12 167.220	0.013
3	4.5	2	3.5	2	12 167.695	0.000
3	1.5	2	1.5	1	12 167.764	-0.006
3	4.5	2	3.5	1	12 168.107	0.000
3	4.5	2	3.5	0	12 168.245	0.001
3	3.5	2	2.5	0	12 168.245	0.001
3	3.5	2	2.5	1	12 168.274 <sup>b</sup>	-0.003
3	2.5	2	1.5	1	12 168.274 <sup>b</sup>	-0.003
3	3.5	2	2.5	2	12 168.360	-0.018
3	2.5	2	1.5	0	12 168.425	0.012
3	1.5	2	0.5	0	12 168.425	0.012
3	3.5	2	3.5	1	12 168.620 <sup>d</sup>	0.001
3	3.5	2	3.5	0	12 168.928 <sup>d</sup>	0.001
4	5.5	3	4.5	3	16 222.660	-0.003
4	3.5	3	2.5	3	16 222.976	0.013
4	4.5	3	3.5	3	16 223.269	-0.008
4	4.5	3	3.5	2	16 223.681	0.003
4	5.5	3	4.5	1	16 223.846	-0.004
4	4.5	3	3.5	1	16 223.902	-0.016
4	4.5	3	3.5	0	16 223.992	-0.006
4	5.5	3	4.5	0	16 223.992	-0.006
4	2.5	3	1.5	0	16 224.077	-0.001
4	3.5	3	2.5	0	16 224.077	-0.001
4	4.5	3	4.5	1	16 224.434	0.004
4	4.5	3	4.5	0	16 224.698	0.017

<sup>a</sup> All values in megahertz. <sup>b</sup> On shoulder of the transition at 12 168.245 MHz. <sup>c</sup> Individual measurement uncertainties differ due to variable linewidths and spectral congestion but are typically 10–20 kHz. See text for discussion. <sup>d</sup> Center frequency of a broad doublet.

1.6 Å, respectively,<sup>1</sup> the 2.5-Å value together with the small calculated angular distortion of the  $\text{BF}_3$  is indicative of a complex which lies between these two limits but is significantly closer to being weakly bound.

The second observation is that the nuclear quadrupole coupling constants determined for the boron and nitrogen in the complex, are very similar to those observed for these nuclei in other systems which are truly weakly bound. For example, the value of 2.813-(16) MHz for the boron in  $\text{HC}^{14}\text{N}-^{11}\text{BF}_3$  is quite close to the value of 2.70(5) MHz reported for  $\text{Ar}-^{11}\text{BF}_3$ ,<sup>3</sup> and the -4.080-(13) MHz for  $^{14}\text{N}$  is nearly identical to the -4.075(14) MHz value previously determined for the T-shaped, nitrogen bound isomer of  $\text{HCN}-\text{CO}_2$ .<sup>13</sup>

Since the number of isotopic derivatives studied is insufficient to locate all atoms in the complex, preliminary assumptions regarding the monomer structures should be made. In the case of complexes which are clearly weakly bound, it is commonplace to assume that the binding partners are unperturbed from their free-molecule structures. For  $\text{HCN}-\text{BF}_3$ , however, which has an intermediate B–N bond length and a calculated 3° distortion of the  $\text{BF}_3$ , such an assumption needs to be made with some caution. Indeed, in light of the *ab initio* prediction, we will not assume a priori that the  $\text{BF}_3$  retains its planarity in the complex.

For monomer bond lengths, however, the usual approximations are readily made. Small changes in the H–C and C≡N distances are expected on the basis of chemical intuition, since no appreciable change in bond order takes place, even when the donor–acceptor bond formation proceeds to completion. This is supported by the results of a recent low-temperature crystallographic study of the solid  $\text{HCN}-\text{BF}_3$  adduct<sup>14a</sup> in which the C≡N bond was determined to be only 0.033 Å shorter in the crystal than that in the free monomer.<sup>14b</sup> For the B–F bond, where some change in bond order does occur, the change is still small, with the solid-state bond distance only 0.051 Å longer than that in free  $\text{BF}_3$ . It is significant to note, however, that in the solid state, the B–N bond length and the NBF angle are 1.64 Å and 106°, respectively, indicating that the  $\text{HCN}-\text{BF}_3$  interaction is essentially covalent. Thus, the molecule is quite different in the solid state and in the gas phase, and the crystallographic bond distances therefore define upper limits to the changes expected for the moieties in the gas-

TABLE IV: Observed Transitions of HC<sup>15</sup>N-<sup>10</sup>BF<sub>3</sub><sup>a</sup>

<i>J'</i>	<i>F'</i>	<i>J''</i>	<i>F''</i>	<i>K</i>	frequency <sup>b</sup>	obs - calc
3	2	2	1	2	12 209.105	-0.008
3	1	2	1	2	12 209.105	-0.008
3	0	2	1	2	12 209.105	-0.008
3	6	2	5	2	12 209.681	0.000
3	5	2	5	2	12 209.681	0.000
3	4	2	5	2	12 209.681	0.000
3	3	2	2	2	12 209.845	0.002
3	2	2	2	2	12 209.845	0.002
3	1	2	2	2	12 209.845	0.002
3	6	2	5	1	12 210.224	-0.001
3	2	2	2	1	12 210.224	-0.005
3	3	2	3	0	12 210.224	0.007
3	3	2	3	1	12 210.286	-0.010
3	5	2	4	0	12 210.347	0.009
3	2	2	2	0	12 210.347	-0.010
3	5	2	4	1	12 210.432	0.004
3	4	2	4	1	12 210.500	0.001
3	4	2	3	1	12 210.570	-0.010
3	4	2	3	0	12 210.600	0.005
3	1	2	1	0	12 210.600	0.005
3	2	2	1	1	12 210.600	0.005
3	5	2	4	2	12 210.691	-0.005
3	5	2	5	1	12 210.954	0.019
3	5	2	5	0	12 211.354	0.001
4	7	3	6	3	16 278.703	0.008
4	3	3	2	3	16 278.703	0.008
4	4	3	3	3	16 279.215	-0.006
4	1	3	0	2	16 279.339	-0.006
4	1	3	1	2	16 279.339	-0.006
4	6	3	5	2	16 279.910	0.005
4	6	3	6	2	16 279.910	0.005
4	7	3	6	1	16 280.060	0.007
4	6	3	5	1	16 280.120	0.008
4	6	3	5	0	16 280.177	-0.003
4	7	3	6	0	16 280.235	0.012
4	5	3	4	0	16 280.280	-0.005
4	4	3	3	1	16 280.280	-0.010
4	6	3	6	1	16 280.831	0.009
4	6	3	6	0	16 281.119	-0.008

<sup>a</sup> All values in megahertz. <sup>b</sup> Individual measurement uncertainties differ due to variable linewidths and spectral congestion but are typically 10–20 kHz. See text for discussion.

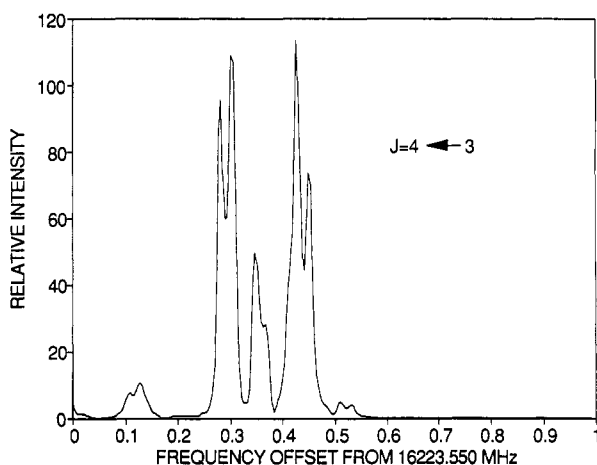


Figure 1. Portion of the  $J = 4 \leftarrow 3$  transition of HC<sup>15</sup>N-<sup>11</sup>BF<sub>3</sub>. Each hyperfine component is split into a pair of Doppler components with a splitting of about 23 kHz.

phase adduct relative to those of the free monomers. Hence, the structural calculations described below can safely use the moments of inertia for the isotopes of HCN obtained from gas-phase data.<sup>15</sup> Similarly, the B–F bond length can reasonably be constrained to its free monomer values of 1.3102 Å.<sup>16</sup> Fortunately, as discussed below, the moment of inertia of the adduct depends only weakly on these bond lengths, and therefore any errors resulting from their use are negligible.

Since the complex, at least in some respects, appears weakly

TABLE V: Spectroscopic Constants for the Isotopic Derivatives of HCN-BF<sub>3</sub><sup>a</sup>

	HC <sup>15</sup> N <sup>10</sup> BF <sub>3</sub>	HC <sup>15</sup> N <sup>11</sup> BF <sub>3</sub>
<i>B</i>	2035.1376(18)	2028.1023(26)
<i>D<sub>JK</sub></i>	0.016 12(18)	0.016 10(20)
<i>D<sub>J</sub></i>	0.003 261(66)	0.003 122(98)
<i>eqQ(B)</i>	5.683(46)	2.731(36)

	HC <sup>14</sup> N <sup>10</sup> BF <sub>3</sub>	HC <sup>14</sup> N <sup>11</sup> BF <sub>3</sub>
<i>B</i>	2055.831 14(84)	2048.885 36(96)
<i>D<sub>JK</sub></i>	0.016 364(82)	0.016 964(82)
<i>D<sub>J</sub></i>	0.003 149(34)	0.003 112(40)
<i>eqQ(B)</i>	5.761(36)	2.813(16)
<i>eqQ(N)</i>	-4.057(16)	-4.080(13)

<sup>a</sup> All values in megahertz. Uncertainties are two standard errors in the fit.

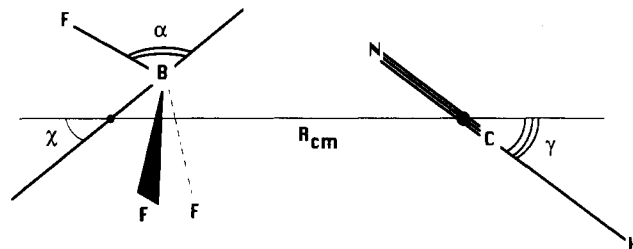


Figure 2. Definition of coordinates used to describe the structure of HCN-BF<sub>3</sub>.

bound, we adopt the usual approach in which two interacting monomers undergo large amplitude vibrations about the equilibrium geometry of the complex. Thus, the coordinates needed to describe the system are illustrated in Figure 2.  $R_{cm}$  is the distance between the centers of mass of the monomers, and the zero-point angular excursions of the BF<sub>3</sub> and HCN away from the presumed  $C_{3v}$  equilibrium geometry are described by the angles  $\chi$  and  $\gamma$ , respectively. The angle  $\alpha$ , which describes the out-of-plane distortion of the BF<sub>3</sub> is seen to equal the NBF angle at  $\gamma = \chi = 0$ . In terms of these coordinates, the vibrationally averaged moment of inertia of the complex may be written<sup>17</sup>

$$\langle I_{bb} \rangle = M_s \langle R_{cm}^2 \rangle + \left( \frac{1}{2} \right) I_{bb}(\text{BF}_3) [1 + \langle \cos^2 \chi \rangle] + \left( \frac{1}{2} \right) I_{cc}(\text{BF}_3) \langle \sin^2 \chi \rangle + \left( \frac{1}{2} \right) I_{bb}(\text{HCN}) [1 + \langle \cos^2 \gamma \rangle] \quad (2)$$

where  $M_s$  is the pseudodiatom reduced mass and is given by  $m(\text{BF}_3)m(\text{HCN})/m(\text{HCNBF}_3)$ .  $I_{gg}$  refers to the moment of inertia of the indicated species about its  $g$ -inertial axis, and  $\langle I_{bb} \rangle$  is obtained directly from the observed rotational constant of the complex, viz.,  $\langle I_{bb} \rangle = h^2/8\pi^2 B$ . The dependence of  $\langle I_{bb} \rangle$  on  $\alpha$  is contained in the inertial moments of the pyramidally distorted BF<sub>3</sub>, which are given by

$$I_{bb}(\text{BF}_3) = \left( \frac{3}{2} \right) m_F r^2 \sin^2 \beta + [3m_B m_F / (m_B + 3m_F)] r^2 \cos^2 \beta \quad (3)$$

$$I_{cc}(\text{BF}_3) = 3m_F r^2 \sin^2 \beta \quad (4)$$

where  $\beta = 180^\circ - \alpha$  and  $r$  is the B–F bond length.

The implementation of eq 2 to determine  $R_{cm}$  requires that values of  $\langle \cos^2 \gamma \rangle$  and  $\langle \cos^2 \chi \rangle$  be known. In the usual treatment of weakly bound systems, these expectation values are obtained from the measured nuclear quadrupole coupling constants, assuming that their reduction from the free monomer values are purely projective, viz.

$$eqQ_{\text{complex}} = eqQ_{\text{monomer}} \langle (3 \cos^2 \phi - 1)/2 \rangle \quad (5)$$

where  $\phi$  is either  $\chi$  or  $\gamma$ , depending on the nucleus chosen. With hyperfine structure due to both boron and nitrogen fully analyzed, the application of eq 5 is straightforward. The validity of

determining  $\langle \cos^2 \chi \rangle$  and  $\langle \cos^2 \gamma \rangle$  in this way, however, requires some special discussion, especially for the  $\text{BF}_3$ , which is assumed to be distortable upon complexation and therefore potentially subject to significant electronic as well as projective contributions to  $eqQ$ .

For both subunits, this issue is best handled by comparison of the measured  $eqQ$  values listed in Table V with known values in truly weakly bound systems. For the  $\text{BF}_3$ , for example, we noted above that the value of  $eqQ(^{11}\text{B})$  in  $\text{HCN-BF}_3$  is essentially identical to that obtained in the complex  $\text{Ar-BF}_3$ .<sup>3</sup> Since the latter is truly weakly bound,  $eqQ(\text{B})$  can be reasonably assumed to be free of electronic contributions and may therefore be taken as a good indicator of  $\text{BF}_3$ 's angular excursions in that system. Moreover, since it is common to observe similar bending amplitudes for the same species in different complexes,<sup>13</sup> the near equality of  $eqQ(\text{B})$  in  $\text{Ar-BF}_3$  and  $\text{HCN-BF}_3$  suggests that a reasonable approximation to  $\langle \cos^2 \chi \rangle$  in the latter will also be obtained by direct use of the measured coupling constant in eq 5. We note, of course, that the data do not necessarily demand the same value of  $\langle \cos^2 \chi \rangle$  for the two systems but that substantially different vibrational averaging would imply a fortuitous cancellation of electronic and vibrational effects. In any case,  $\langle I_{bb} \rangle$  depends only weakly on  $\langle \cos^2 \chi \rangle$  and therefore any reasonable approximation is sufficient to determine the more important structural parameters of the adduct. Thus, we use the recently determined value of  $eqQ(\text{B}) = 3.002(13) \text{ MHz}$ <sup>18</sup> for free  $^{11}\text{BF}_3$ , together with  $eqQ_{\text{complex}}$  in Table V to obtain  $\langle \cos^2 \chi \rangle$  directly from eq 5. For  $^{10}\text{BF}_3$  the quadrupole coupling constant has not been measured but is readily obtained from the known value of the ratio of the  $^{10}\text{B}/^{11}\text{B}$  nuclear quadrupole moments ( $2.084 \pm 0.002$ ).<sup>12</sup> Values of  $\cos^{-1}(\langle \cos^2 \chi \rangle^{1/2})$  obtained for the four isotopic derivatives studied are scattered between  $11.82^\circ$  and  $14.31^\circ$ , with an average value of  $13.1^\circ$ . We note that the scatter is likely due to the combined effect of measurement errors, model errors, and correlation between fitted parameters than to true variations in the average vibrational amplitudes for the different isotopic species. This follows, even for species of different boron isotope, from the extremely weak dependence of  $I_{bb}(\text{BF}_3)$  on boron mass, to be described in more detail below. Thus, for the purposes of the structural calculations, the average value of  $\cos^{-1}(\langle \cos^2 \chi \rangle^{1/2}) = 13.1^\circ$  obtained from the four isotopic derivatives studied is the most realistic choice to use. This choice also turns out to produce a somewhat more consistent set of B-N bond lengths for the four isotopic species studied than does use of the individually determined values of  $\langle \cos^2 \chi \rangle$ , lending further support to this approach.

For the  $\text{HCN}$  moiety, similar arguments regarding  $\langle \cos^2 \gamma \rangle$  are readily applied. Using the free monomer value of  $eqQ(\text{N}) = -4.70789(8) \text{ MHz}$  in  $\text{HC}^{14}\text{N}$ ,<sup>19</sup> application of eq 5 gives values of  $\cos^{-1}(\langle \cos^2 \gamma \rangle^{1/2}) = 17.36^\circ$  and  $17.69^\circ$  for the  $^{11}\text{B}/^{14}\text{N}$  and  $^{10}\text{B}/^{14}\text{N}$  species, respectively. These are very similar to the values obtained in other nitrogen bonded  $\text{HCN}$  complexes,<sup>13</sup> suggesting that the reduction of  $eqQ$  from that in free  $\text{HCN}$  is also largely projective in this case. For the  $^{14}\text{N}$  species, therefore, we also estimate  $\langle \cos^2 \gamma \rangle$  by direct use of eq 5. For the  $^{15}\text{N}$  species, for which no nitrogen hyperfine structure is available,  $\cos^{-1}(\langle \cos^2 \gamma \rangle^{1/2})$  is readily scaled with the inverse fourth root of the  $\text{HCN}$  rotational constant. Finally, we emphasize again that the angular terms in eq 2 are small compared with  $M_s \langle R_{\text{cm}} \rangle^2$ , and their precise choice has little effect on our final conclusions regarding structure.

With angular expectation values chosen and with monomer geometries appropriately constrained, only two structural parameters,  $R_{\text{cm}}$  and  $\alpha$ , remain to be determined from the data. Our initial approach to this problem followed that used previously for similar systems<sup>1,3,4</sup> in which a locus of points ( $R_{\text{cm}}, \alpha$ ) which reproduce the observed rotational constant is constructed for each isotopic species studied. Substitution at the boron is a minimum requirement for determining  $\alpha$  with the available data, and

therefore unique solutions for the molecular geometry were expected to occur at the intersection of loci for species which at least differ in their boron isotope.

Our initial attempts to analyze the data by this procedure, however, did not yield a satisfactory structure. Although the bond lengths obtained were reasonable and consistent among the isotopic species studied, the values of  $\alpha$  obtained were consistently between  $88$  and  $90^\circ$ , implying that the fluorines bend toward the  $\text{HCN}$  upon complexation rather than away. This result is entirely unphysical and was immediately rejected, though we note that the B-N bond lengths themselves were quite close to that eventually obtained in subsequent analysis described below. Since this procedure has been used previously for  $\text{CH}_3\text{CN-BF}_3$ , however, with apparently successful results, we first briefly clarify the difference between these two systems.

The origin of the problem may be realized by closer inspection of eqs 3 and 4, from which we can show that the determination of  $\alpha$  is expected to be particularly tenuous in this complex. As noted above, the only terms in  $\langle I_{bb} \rangle$  which depend on  $\alpha$  occur in  $I_{bb}(\text{BF}_3)$  and  $I_{cc}(\text{BF}_3)$ . Moreover, eqs 4 and 5 show that of the contributions to the  $\text{BF}_3$  inertial moments, only the second term in  $I_{bb}(\text{BF}_3)$  depends on the mass of the boron. Thus, it is through this term that isotopic substitution at the boron effectively extracts  $\beta$  from the observed moment of inertia of the complex. The dependence on  $\cos^2 \beta$ , however, dictates that when the  $\text{BF}_3$  is undistorted ( $\beta = 90^\circ$ ) the resulting contribution to  $\langle I_{bb} \rangle$  in eq 2, viz.

$$(\frac{1}{2})[3m_{\text{B}}m_{\text{F}}/(m_{\text{B}} + 3m_{\text{F}})]r^2 \cos^2 \beta [1 + \langle \cos^2 \chi \rangle] \quad (6)$$

will vanish for either boron isotope and that only as  $\beta$  deviates from  $90^\circ$  will boron substitution become sensitive to this angle.<sup>20</sup>

A few numbers further illustrate the situation. For  $^{10}\text{BF}_3\text{-HC}^{15}\text{N}$ , for example, a  $1^\circ$  distortion of the  $\text{BF}_3$  introduces a  $0.00434 \text{ u } \text{\AA}^2$  contribution to  $\langle I_{bb} \rangle$  via expression 6 and hence a  $36\text{-kHz}$  contribution to  $B$ . For the  $^{11}\text{B}$  species, the contribution to the moment of inertia increases to  $0.00470 \text{ u } \text{\AA}^2$  and correspondingly accounts for  $38 \text{ kHz}$  in the rotational constant of that species. Although the  $M_s \langle R_{\text{cm}}^2 \rangle$  term in eq 2 accounts for most of the dependence of the rotational constant on boron mass, it does not contain the angle  $\beta$ , and consequently, it is the small difference between the contributions from expression 6 which must be analyzed to determine this angle. Clearly, the  $2\text{-kHz}$  difference indicated above is too small in comparison with the standard errors in the rotational constants to be interpreted meaningfully. Moreover, contributions of this magnitude are potentially masked by model errors (e.g., vibrational averaging effects) which are not reflected in the estimated uncertainties in the effective rotational constants reported. Thus, if  $\beta$  is near  $90^\circ$ , the analysis originally described does little more than analyze statistical and/or model errors, and the unphysical values of  $\beta$  obtained are readily explained. It is worth noting, however, at  $\beta = 84^\circ$ , which is the angle determined previously for  $\text{CH}_3\text{CN-BF}_3$ ,  $\cos^2 \beta$  is larger by about a factor of 10, so that the  $2\text{-kHz}$  difference which would need to be analyzed for the case of  $1^\circ$  distortion, is increased to  $20 \text{ kHz}$ . This is well outside the statistical errors in the rotational constants and likely accounts for our success in determining the NBF angle in that case.

From the above discussion, it is clear that if the  $\text{BF}_3$  were only minimally distorted in the adduct, the contribution of  $\beta$ -dependent terms to the rotational constant of the complex can be small enough to preclude a reasonable determination of the NBF angle. Such a scenario is consistent with our inability to obtain a chemically reasonable value of this angle by the analysis originally attempted. Note that a small angular distortion of the  $\text{BF}_3$  is also consistent with the observed value of  $eqQ(\text{B})$ , whose value was almost identical with that in  $\text{Ar-BF}_3$ , in which the molecular subunit is presumed to be truly unperturbed. Moreover, it is perhaps significant that the *ab initio* calculations for the  $\text{HCN-}$

**TABLE VI:** Calculated Values of the B–N Bond Length at Limiting Values of  $\alpha^{a,b}$ 

$\alpha$ , deg	$^{10}\text{B}-^{14}\text{N}$	$^{11}\text{B}-^{14}\text{N}$	$^{10}\text{B}-^{15}\text{N}$	$^{11}\text{B}-^{15}\text{N}$	av	$\sigma^c$
90.0	2.5014	2.5019	2.5010	2.5014	2.5014	0.0003
93.0	2.4440	2.4452	2.4435	2.4447	2.4443	0.0007

Preferred Structure:  $R(\text{BN}) = 2.473 \pm 0.029 \text{ \AA}$   
 $\alpha = 91.5 \pm 1.5^\circ$

<sup>a</sup> All bond lengths in angstroms. <sup>b</sup> Structures derived using  $\langle \cos^2 \chi \rangle = \cos^2(13.40^\circ)$  for all species,  $\langle \cos^2 \gamma \rangle = \cos^2(17.53^\circ)$  for  $^{14}\text{N}$  species, and  $\langle \cos^2 \gamma \rangle = \cos^2(17.40^\circ)$  for the  $^{15}\text{N}$  derivatives. <sup>c</sup> Standard deviation among isotopic pairs. <sup>d</sup> This method of quoting  $\alpha$  is intended as a compact means of expressing its probable range (90–93°) but does not imply that 91.5° is the statistically most likely value. See text for discussion.

BF<sub>3</sub> adduct predict an out-of-plane distortion of only 3° and that the analogous calculation for CH<sub>3</sub>CN–BF<sub>3</sub> gave a value that was about 2° higher than that determined by experiment.<sup>1</sup>

With the observed moments of inertia of the complex insensitive to  $\alpha$ , we are left only to determine the B–N bond length. Nonetheless, since eq 2 contains terms which depend on this angle (but vary very little across its range of plausible values), some choice of  $\alpha$  is necessary. We can bracket the possible values by setting a lower limit of 90° in accord with chemical intuition, and an upper limit of 93° from the *ab initio* calculation, which slightly overestimated the corresponding angle in CH<sub>3</sub>CN–BF<sub>3</sub>, as noted above. Also, it is satisfying to see that at 93°, the difference in the contributions to the observed rotational constant arising from expression 6 is about 10 kHz, which is a reasonable threshold above statistical errors. Thus, Table VI lists values of  $R(\text{BN})$  calculated for each isotope at  $\alpha = 90.0^\circ$  and  $93.0^\circ$ , using the values of  $\langle \cos^2 \gamma \rangle$  and  $\langle \cos^2 \chi \rangle$  determined above. Note that in contrast with the NBF angle, the B–N bond distance is well determined through the pseudodiatomic reduced mass term in eq 2, and its accuracy is reflected in the relative consistency between isotopic determinations.

To assess the uncertainty in the calculated B–N bond distance, we first note that assumptions regarding monomer bond lengths and angular expectation values made above introduce minor changes relative to those resulting from uncertainty in  $\alpha$ . For example, as  $\alpha$  is varied from 90° to 93°, the calculated value of  $R(\text{BN})$  decreases by 0.057 Å. In contrast, it is readily shown that changes in  $R(\text{BN})$  resulting from changes in the choice of effective values of  $\chi$  and  $\gamma$  are only 0.002 Å/deg and 0.0005 Å/deg, respectively. Thus, since progress toward chemical bonding can only attenuate the angular amplitudes, any reasonable choice of these angles will give essentially the same result. If the calculation of  $R(\text{BN})$  is repeated with either the C≡N or B–F bond lengths changed to the values observed in the crystalline adduct,<sup>14</sup> the B–N bond length obtained decreases by 0.034 Å. Thus, in principle, uncertainties in the monomer bond lengths could contribute an uncertainty in  $R(\text{BN})$  comparable to that due to  $\alpha$ . However, as noted above, it seems unlikely that the crystal phase distances are realistic approximations to those in the gas-phase complex. We therefore choose as our most reasonable value for the B–N bond length the value obtained at  $\alpha = 91.5^\circ$ , with errors which encompass values obtained at 90° and 93°. This approach is reflected in the “preferred structure” given in Table VI.

Finally, the stretching force constant for the weak bond may be estimated from the observed centrifugal distortion constant of the complex using the expression<sup>21</sup>

$$k_s = (4\pi)^4 (M_s R_{\text{cm}})^2 B^4 / 2hD_J \quad (7)$$

The value obtained for the  $^{11}\text{B}/^{14}\text{N}$  species is 10.3 N/m, with values obtained for the other isotopic derivatives in agreement to within 4%. In the next section, comparisons will be made with a number of other related systems, but we note here that the magnitudes are consistent with our assumption that, apart from

**TABLE VII:** Comparison of Physical Properties of Selected BF<sub>3</sub> Complexes

donor	$R(\text{BN})$ (Å)	$\alpha$ (deg)	$k_s$ (N/m)	$eqQ(^{11}\text{B})$ (MHz)	$eqQ(^{14}\text{N})$ (MHz)	$\Delta E$ (kJ/mol)
Ar		90 <sup>a</sup>	2.9 <sup>a</sup>	2.70(5) <sup>a</sup>		
N <sub>2</sub>	2.88 <sup>a</sup>	90.5 <sup>a</sup>				
NCCN	2.64 <sup>b</sup>	93 <sup>c</sup>				15 <sup>d</sup>
HCN	2.47 <sup>e</sup>	90–93 <sup>e</sup>	10.3 <sup>e</sup>	2.813(16) <sup>e</sup>	–4.08 <sup>e</sup>	22 <sup>f</sup>
CH <sub>3</sub> CN	2.01 <sup>g</sup>	95.6 <sup>g</sup>	9.4 <sup>g</sup>	2.377(9) <sup>g</sup>	–3.93 <sup>g</sup>	24 <sup>d</sup>
NH <sub>3</sub>	1.59 <sup>h</sup>	<i>i</i>	414 <sup>h</sup>	1.21 <sup>h,j</sup>	–2.301 <sup>h,j</sup>	75 <sup>d</sup>

<sup>a</sup> Reference 3. <sup>b</sup> Reference 4. <sup>c</sup> Low-resolution microwave data of ref 4 consistent with an NBF angle spanning 90–100°. Table quotes the *ab initio* value from ref 8a. <sup>d</sup> Reference 8a. <sup>e</sup> This work. <sup>f</sup> Reference 8b. <sup>g</sup> Reference 1. <sup>h</sup> Reference 22. <sup>i</sup> A tetrahedral geometry at the boron was consistent with experimental data, but the precise angle was not determined. <sup>j</sup> “A” internal rotor state value.

the B–N bond length, the complex is more like a van der Waals complex than a covalently bonded donor–acceptor adduct.

## Discussion

It is of interest to consider the above results in the broader context of the donor–acceptor bonding of BF<sub>3</sub> with nitrogen donors. As described in the Introduction, the wide variation in bond lengths and bond angles among such systems offers an opportunity to examine the changes which take place as a van der Waals bond is transformed into a chemical bond. This view stems from the hypothesis widely used in crystalline systems<sup>6</sup> and extended to the gas phase in our previous work<sup>1</sup> in which structures of *individual* members of a related series of compounds are regarded as snapshots along a *generalized* reaction path for some simple chemical transformation. In the BF<sub>3</sub> complexes, for example, the transformation was the formation of a new B–N bond, and the correlated variation in the B–N bond length and N–B–F angle was interpreted as a portrayal of the response of the initially planar BF<sub>3</sub> to the approach of an arbitrary nitrogen donor. The information available for systems in the gas phase, however, is not only limited to structure, and thus it is natural to explore the transition between the van der Waals and covalent limits from the perspective of each of the variety of physical properties which are accessible from gas-phase spectra. In addition, *ab initio* calculations are directly comparable to experiment, and the energetics across a series can be followed.

Table VII lists the structures, stretching force constants, quadrupole coupling constants, and calculated binding energies for a number of BF<sub>3</sub> species with nitrogen donors. The complex Ar–BF<sub>3</sub> is included in the table as a reference point. The species are listed in order of decreasing bond length (which correlates with an increased angular distortion of the BF<sub>3</sub>), and the table spans the full range from van der Waals complexes to stable, covalently bonded molecules. N<sub>2</sub>–BF<sub>3</sub>, with a 2.88-Å bond length and no distortion of the planarity of BF<sub>3</sub> represents the truly weakly bound limit, while NH<sub>3</sub>–BF<sub>3</sub> has a covalent boron–nitrogen bond length and an approximate tetrahedral geometry at the boron.

First, with regard to the structure of HCN–BF<sub>3</sub>, we note that our plot of  $R(\text{BN})$  vs  $\alpha(\text{NBF})$  in ref 1 included our preliminary results and that the final structure presented here is very similar to that in our earlier report. Also, it is seen from Table VII that the bond length in HCN–BF<sub>3</sub> of 2.47 Å is significantly shorter than the 2.78-Å distance found in the van der Waals complex N<sub>2</sub>–BF<sub>3</sub> but still considerably longer than the 2.01 Å bond length in CH<sub>3</sub>CN–BF<sub>3</sub>. Note that it would be unreasonable to regard the 0.46-Å lengthening of the B–N bond in the HCN complex relative to that in the CH<sub>3</sub>CN complex as arising simply from a variation in the van der Waals radius of nitrogen between the two donors. This may be seen by considering that the N–F distances in HCN–HF<sup>24</sup> and CH<sub>3</sub>CN–HF<sup>25</sup> are 2.796 and 2.759 Å, respectively, and thus differ by only 0.037 Å. Rather, the



shortening of the B–N bond upon replacement of the proton in HCN by a methyl group might be considered at least superficially consistent with chemical intuition: Since the methyl group is more “electron releasing” than a hydrogen,<sup>26</sup> methyl substitution renders the nitrile a better electron-pair donor and decreases the B–N interaction distance. Correspondingly, of course, the BF<sub>3</sub> is distorted further toward a tetrahedral geometry.

While such an electronic effect produces clearly discernible structural consequences, its influence on other properties of these systems is somewhat more variably pronounced. With regard to the stretching force constants, for example, it is seen that the value obtained for HCN–BF<sub>3</sub> is quite similar to that determined for the CH<sub>3</sub>CN adduct. This is somewhat remarkable, in that going from HCN–BF<sub>3</sub> to CH<sub>3</sub>CN–BF<sub>3</sub>, the dative bond length decreases by 0.46 Å, or 40% of the total spread represented in the table, yet the stretching force constant barely changes at all! Moreover, while both the HCN–BF<sub>3</sub> and CH<sub>3</sub>CN–BF<sub>3</sub> force constants are about 3–4 times larger than that for the argon complex, they are about a factor of 40 smaller than the 414 N/m value observed in the covalently bonded species NH<sub>3</sub>–BF<sub>3</sub>.<sup>22</sup> Indeed, the latter value is more typical of force constants for single bonds between second-row elements,<sup>27</sup> illustrating that although there is a noticeable shortening of the B–N bond in these complexes relative to, say, the van der Waals complex N<sub>2</sub>–BF<sub>3</sub>, the stretching force constant has made little progress toward its limiting covalent value. It is noteworthy that (HF)<sub>2</sub> (a relatively strongly hydrogen-bonded species) has an effective intermolecular stretching force constant of about 14 N/m,<sup>28</sup> demonstrating that the values obtained for both HCN–BF<sub>3</sub> and CH<sub>3</sub>CN–BF<sub>3</sub> are well within the range expected for true weakly bound systems. The observation of boron and nitrogen quadrupole coupling constants, which are similar to those in weakly bound systems, is indicative of bending force constants which are also comparable to those of weakly bound complexes.

A similar picture is revealed upon examination of the binding energies across the series, as recently calculated by Jurgens-Lutovsky and Almlöf. It may be seen from Table VII that the complex NCCN–BF<sub>3</sub>, in which the B–N bond length is fairly long and the BF<sub>3</sub> nearly planar, has a calculated binding energy relative to the free monomers of about 15 kJ/mol. In contrast, the covalent complex NH<sub>3</sub>–BF<sub>3</sub> has a binding energy of 75 kJ/mol, and taken together, these values effectively set the energy scale which encompasses the van der Waals and covalent limits for the boron–nitrogen dative bond. It is readily seen that the 22 and 24 kJ/mol binding energies of the HCN and CH<sub>3</sub>CN adducts lie between these limits but that they are significantly closer to the van der Waals side. Also, it is somewhat remarkable that despite the large difference in bond lengths observed for these two adducts, the binding energies are nearly the same. The relative ordering, of course, is consistent with the reduced donor ability of HCN and the longer bond length in the complex.

While the differences in donor abilities of HCN and CH<sub>3</sub>CN appear to have little discernible effect on the stretching force constants or binding energies for the corresponding adducts, a somewhat different result is seen upon examination of the boron nuclear quadrupole coupling constants. In the previous section, we compared  $eqQ(^{11}\text{B})$  in both Ar–BF<sub>3</sub> and HCN–BF<sub>3</sub> and concluded that the projective contribution to  $eqQ$  dominated over what was presumed to be a negligible electronic contribution. In contrast, examination of the boron nuclear quadrupole coupling constant in the CH<sub>3</sub>CN–BF<sub>3</sub> adduct shows that the value of  $eqQ(^{11}\text{B})$  has shifted toward the 1.21(2) MHz value seen in NH<sub>3</sub>–BF<sub>3</sub>.<sup>22</sup> Note that if the change were simply due to vibrational averaging one should expect  $eqQ(\text{B})$  to increase in the CH<sub>3</sub>CN complex, since the higher binding energy and shorter bond would presumably be consistent with reduced vibrational amplitudes. Thus, it is more likely that the reduction of  $eqQ$  in CH<sub>3</sub>CN–BF<sub>3</sub> is of genuinely electronic origin, and this is consistent with the

significant (6°) angular distortion determined in that case. While the CH<sub>3</sub>CN adduct is structurally intermediate between the van der Waals and covalent limits, the quadrupole coupling constant remains much closer to that of a weakly bound complex. Note finally that the vibrational amplitudes of the nitrile moiety in HCN– and CH<sub>3</sub>CN–BF<sub>3</sub> also appear very similar as judged from the nearly identical values of  $eqQ(^{14}\text{N})$  observed.

In summary, the above discussion clearly shows that HCN–BF<sub>3</sub> and CH<sub>3</sub>CN–BF<sub>3</sub> lie, both structurally and energetically, between the limits of van der Waals and covalent bonding. From a structural standpoint, the former is more like a weakly bound complex. The two systems differ substantially in their boron–nitrogen bond lengths and angular distortions of the BF<sub>3</sub> but appear very similar in their weak bond force constants and binding energies. The quadrupole coupling constants of the boron are measurably different, but both are closer to that expected for a van der Waals complex. Thus, it is clear that significant changes in the boron nitrogen distance can give rise to only small changes in other physical properties of these systems.

Although these results may at first seem counterintuitive, there is no reason to expect different physical properties across the series to evolve at the same rate. These Lewis acid–base complexes are different from ordinary weakly bound systems in that a new bond can form between the subunits. Thus, the moieties have the opportunity to realize shorter-than-normal intermolecular distances. It is certainly possible that at these unusually short distances, electrostatic interactions can be strong enough to induce a small angular distortion of the BF<sub>3</sub>, while electron pair sharing, which is the essence of a chemical bond, is not yet significant. The details of the transformation of a purely physical interaction into an essentially chemical one are presently unclear, but, in light of the above comments, properties such as force constants and energetics need not vary linearly with distance between the van der Waals and covalent limits. Further electronic structure calculations will be quite interesting in this respect and are currently in progress.<sup>29</sup>

## Conclusion

The structure of the complex HCN–BF<sub>3</sub> has been determined by microwave spectroscopy to be that of a symmetric top with the nitrogen end of the HCN toward the boron. The B–N bond length is 2.473(29) Å, which is considerably shorter than that expected for a true van der Waals interaction between these moieties. Centrifugal distortion and hyperfine data, however, indicate stretching and bending force constants for the intermolecular bond to have values typical of weakly bound systems. The out-of-plane distortion of the BF<sub>3</sub> is too small to measure but probably lies between 0° and 3°. These results indicate that for BF<sub>3</sub> adducts with nitrogen donors, a substantial shortening of the B–N van der Waals distance is possible before other properties of the adduct show measurable progress toward covalent bonding.

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