

# The Vibrational Spectra of the Boron Halides and Their Molecular Complexes. 3. *Ab Initio* Predictions of the Structures, Energetics, and Mulliken Atomic Charges of the Complexes of Boron Trifluoride with Some Linear Nitrogen Donors

L. M. Nxumalo<sup>†</sup>

Department of Chemistry, University of the Witwatersrand, Johannesburg, Wits 2050, South Africa

M. Andrzejak<sup>‡</sup> and T. A. Ford\*

Centre for Theoretical and Computational Chemistry, Department of Chemistry and Applied Chemistry, University of Natal, Durban, Private Bag X10, Dalbridge 4014, South Africa

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The structures of the 1:1 electron donor–acceptor complexes of boron trifluoride with a number of linear nitrogen bases (N<sub>2</sub>, N<sub>2</sub>O, HCN, FCN, C<sub>2</sub>N<sub>2</sub>, and HCCCN) have been optimized by means of a series of *ab initio* molecular orbital calculations, performed at the second order level of Møller–Plesset perturbation theory with the 6-31G\*\* split-valence polarized basis set. The interaction energies have been computed and corrected for basis set superposition error and for zero-point energy difference. The Mulliken atomic charges of each atom have also been determined, and the changes on going from monomer to complex have been noted. The structural results are discussed in terms of the perturbation of the monomer properties (BF bond length and distortion from planarity) and the establishment of new complex properties (B···N bond length and FBN bond angle) on complexation. The structural changes and shifts of electronic charge, and the interaction energies, are correlated with the strengths of the interactions, estimated by the experimentally determined proton affinities and the absolute electronegativities of the nitrogen donors.

## INTRODUCTION

Boron trifluoride is a classical Lewis acid and readily forms molecular complexes with electron donor molecules.<sup>1</sup> Among the classes of electron donors whose interactions with boron trifluoride have been most extensively studied are the nitrogen bases. Table 1 summarizes a number of publications reporting experimental studies of such complexes, the techniques employed varying from gas phase electron diffraction,<sup>2,3</sup> X-ray diffraction,<sup>4–11</sup> and microwave,<sup>12–17</sup> ESCA,<sup>18</sup> and UPS<sup>19–21</sup> spectroscopy to vibrational spectroscopy in the gas,<sup>22</sup> liquid,<sup>23,24</sup> and solid<sup>25,26</sup> states and in cryogenic matrices.<sup>27–30</sup> A similar summary of *ab initio* theoretical studies on this family of molecular adducts appears in Table 2.<sup>18–21,30–39</sup>

According to the conventional picture of orbital hybridization, nitrogen atoms bonded to other atoms may be found in the sp, sp<sup>2</sup>, or sp<sup>3</sup> hybrid states, e.g., in nitriles, imines, and amines, respectively. In those molecules in which the remaining atoms or groups are symmetrically substituted with respect to the nitrogen atom, the nitrogen lone pair is assumed to lie along the threefold axis in sp and sp<sup>3</sup> hybridized cases, e.g., CH<sub>3</sub>CN and (CH<sub>3</sub>)<sub>3</sub>N. In primary and secondary amines, e.g., CH<sub>3</sub>NH<sub>2</sub> and (CH<sub>3</sub>)<sub>2</sub>NH, the lone pair axis is expected to make an approximately tetrahedral angle with the CN and NH bonds and to lie in the symmetry plane, if one exists, as in these two examples. Thus, in complexes with boron trifluoride, whose monomer possesses a threefold

**Table 1.** Summary of Experimental Studies of Some Complexes of Boron Trifluoride with Nitrogen Bases

| technique                       | electron donor  | refs     |
|---------------------------------|---|----------|
| gas phase electron diffraction  | (CH <sub>3</sub> ) <sub>3</sub> N   | 2, 3     |
|                                 | HCN   | 11       |
| X-ray diffraction               | NH <sub>3</sub>   | 4, 7, 9  |
|                                 | CH <sub>3</sub> CN  | 6, 9, 10 |
| microwave spectroscopy          | CH <sub>3</sub> NH <sub>2</sub>   | 5, 9     |
|                                 | (CH <sub>3</sub> ) <sub>3</sub> N   | 8, 9     |
|                                 | N <sub>2</sub>  | 12       |
|                                 | NO  | 13       |
|                                 | HCN   | 14       |
|                                 | N <sub>2</sub> O, C <sub>2</sub> N <sub>2</sub>   | 15       |
|                                 | CH <sub>3</sub> CN  | 16       |
|                                 | (CH <sub>3</sub> ) <sub>3</sub> N   | 17       |
|                                 | NH <sub>3</sub> , CH <sub>3</sub> CN, C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> ,<br>C <sub>5</sub> H <sub>5</sub> N, 2,6-C <sub>5</sub> H <sub>3</sub> N(CH <sub>3</sub> ) <sub>2</sub>                  | 18       |
|                                 | NO, CH <sub>3</sub> CN  | 19, 20   |
| ESCA spectroscopy               | C <sub>5</sub> H <sub>5</sub> N   | 21       |
| infrared and Raman spectroscopy | gas phase   | 22       |
|                                 | liquid phase  | 23, 24   |
| solid phase                     | HCN, HCCCN  | 25       |
|                                 | CH <sub>3</sub> NH <sub>2</sub> , C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> ,<br>(CH <sub>3</sub> ) <sub>2</sub> NH, C <sub>4</sub> H <sub>9</sub> NH <sub>2</sub> ,<br>(CH <sub>3</sub> ) <sub>3</sub> N | 26       |
| matrix isolation                | CH <sub>3</sub> CN  | 27       |
|                                 | (CH <sub>3</sub> ) <sub>3</sub> N   | 28–30    |

symmetry axis, nitrogen compounds will interact with their nitrogen lone pairs aligned with the C<sub>3</sub> axis of BF<sub>3</sub>. If the nitrogen base itself is linear or possesses a threefold axis, e.g., HCN or NH<sub>3</sub>, then the threefold symmetry will be preserved in the resulting complex. The degeneracies of the normal modes of vibration of the boron trifluoride fragment in the complex will then be maintained; the symmetric BF<sub>3</sub> stretching and bending modes of a complex belonging to

\* Corresponding author: E-mail address: FORD@CHE.UND.AC.ZA.

<sup>†</sup> Present address: Department of Chemistry, Vista University, Soweto Campus, Private Bag X09, Bertsham 2013, South Africa.

<sup>‡</sup> On leave from Faculty of Chemistry, Jagiellonian University, Ingardena 5, Kraków, Poland.

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**Table 2.** Summary of Theoretical Studies of Some Complexes of Boron Trifluoride with Nitrogen Bases

| electron donor                                | theory   | basis set                    | refs   |
|---|----------|------------------------------|--------|
| N <sub>2</sub>                                | SCF      | 4-31G                        | 31     |
| NO  | SCF      | 3-21G                        | 19, 20 |
| NH <sub>3</sub>                               | SCF      | DZ                           | 32     |
|   | SCF      | DZ                           | 18     |
|   | SCF      | STO-3G, 4-31G                | 33     |
|   | SCF      | 3-21G                        | 34     |
|   | SCF      | 3-21G                        | 35     |
|   | SCF      | 6-31G**                      | 36     |
|   | MP2      | 6-31G**                      | 30     |
| C <sub>2</sub> N <sub>2</sub>                 | SCF, MP2 | van Duijneveldt <sup>a</sup> | 37     |
| CH <sub>3</sub> CN                            | SCF      | DZ                           | 18     |
|   | SCF      | 3-21G                        | 19, 20 |
|   | SCF, MP2 | van Duijneveldt <sup>a</sup> | 37     |
| C <sub>2</sub> H <sub>5</sub> NH <sub>2</sub> | SCF      | DZ                           | 18     |
| C <sub>5</sub> H <sub>5</sub> N               | SCF      | 3-21G                        | 21     |
|   | SCF      | 3-21G                        | 35     |
| (CH <sub>3</sub> ) <sub>3</sub> N             | SCF      | 3-21G                        | 35     |
|   | SCF      | 3-21G                        | 38     |
|   | SCF      | 6-31G**                      | 36     |
|   | SCF      | STO-3G, 3-21G                | 39     |
| 2-, 3-, and 4-picoline                        | SCF      | 3-21G                        | 35     |
| 2,3- and 3,5-lutidines                        | SCF      | 3-21G                        | 35     |

<sup>a</sup> Van Duijneveldt's [3s2p1d] (B, C, N), [3s3p1d] (F) and [2s1p] (H) basis sets (see ref 40).

the *C*<sub>3v</sub> point group will have *a*<sub>1</sub>, and the antisymmetric BF<sub>3</sub> stretching and bending counterparts will have *e* symmetry.

We have been undertaking a systematic study of the molecular complexes of boron trifluoride with a variety of electron donors, including CO,<sup>29,41</sup> SO<sub>2</sub>,<sup>29</sup> NH<sub>3</sub>,<sup>29,30</sup> and (CH<sub>3</sub>)<sub>2</sub>O,<sup>29</sup> and of the BF<sub>3</sub> dimer,<sup>42–44</sup> both experimentally, by matrix isolation infrared spectroscopy<sup>29,41,43</sup> and theoretically, by means of *ab initio* molecular orbital studies.<sup>30,41,42,44</sup> To this list we now wish to add the complexes of BF<sub>3</sub> with the linear nitrogen donors nitrogen, nitrous oxide, hydrogen cyanide, cyanogen fluoride, cyanogen, and cyanoacetylene. The bonded nitrogen atom in each of these six donors is sp hybridized, thus interaction of the donor with BF<sub>3</sub> at the boron atom will lead to the formation of an axial complex, in which the threefold symmetry of the BF<sub>3</sub> subunit is preserved. The forms of the normal modes of the BF<sub>3</sub> fragment should therefore experience very little variation from one complex to another, and the perturbations of the infrared spectra, computed as we have described previously,<sup>30,41,42,44</sup> are expected to be sensitive probes of the nature and strength of the molecular interaction in each complex. This paper describes the determination of the equilibrium structures and interaction energies of the six complexes and an analysis of the atomic charge reorganizations which take place on complexation. This set of computations is a precursor to the prediction of the infrared spectra, to be reported later, and we anticipate that these predicted spectra will serve as useful aids in the interpretation of the matrix isolation spectra of the molecular complexes.

Of the complexes discussed in this paper, Garcia-Leigh and Murrell have reported a study, at the restricted Hartree–Fock (RHF) level, using the 4-31G basis set, of some properties of BF<sub>3</sub>·N<sub>2</sub>.<sup>31</sup> They predicted an axial structure, with a B···N distance of 252.3 pm and an FBN angle of 91.6° but determined the interaction energy to be positive (0.649 kJ mol<sup>–1</sup>). However, they recognized the importance of the contribution of the distortion energy associated with the perturbation of the planarity of the BF<sub>3</sub> fragment;

**Table 3.** Optimized Bond Lengths of the Monomers

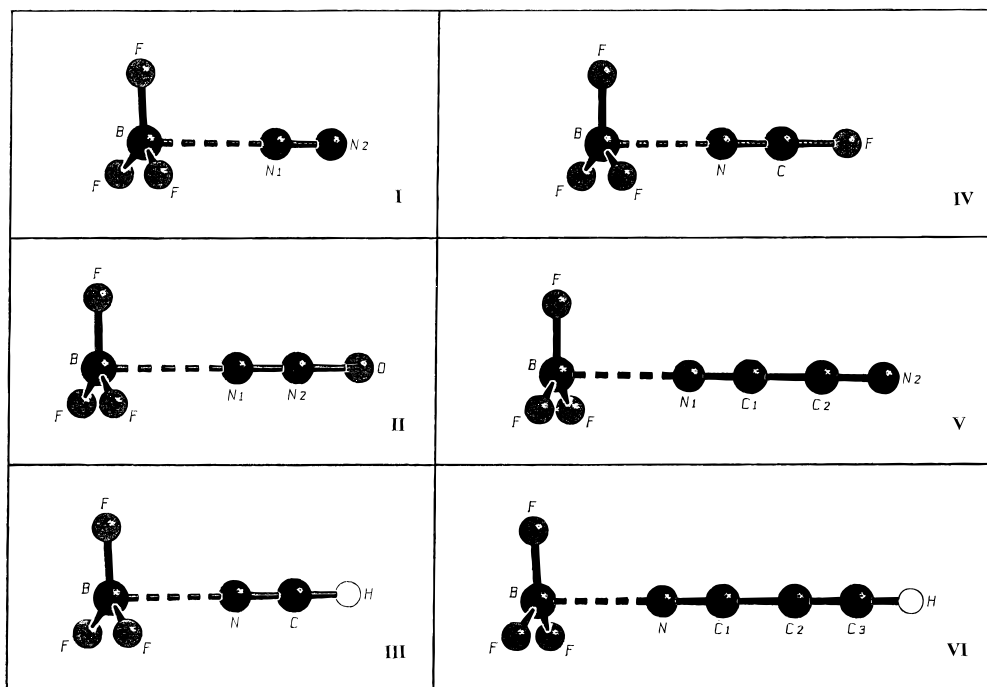
| molecule                                   | bond <sup>a</sup>           | bond length/pm |       |                         |
|--|-----------------------------|----------------|-------|-------------------------|
|  |                             | calcd          | exptl | difference <sup>b</sup> |
| BF <sub>3</sub> <sup>c</sup>               | <i>r</i> (BF)               | 132.4          | 130.7 | 1.7                     |
| N <sub>2</sub> <sup>d</sup>                | <i>r</i> (N1N2)             | 113.1          | 109.8 | 3.3                     |
| N <sub>2</sub> O <sup>c</sup>              | <i>r</i> (N1N2)             | 117.2          | 112.8 | 4.4                     |
|  | <i>r</i> (N <sub>2</sub> O) | 119.3          | 118.4 | 0.9                     |
| HCN <sup>c</sup>                           | <i>r</i> (CH)               | 106.4          | 106.5 | –0.1                    |
|  | <i>r</i> (CN)               | 117.7          | 115.3 | 2.4                     |
| FCN <sup>c</sup>                           | <i>r</i> (CF)               | 128.3          | 126.2 | 2.1                     |
|  | <i>r</i> (CN)               | 118.2          | 115.9 | 2.3                     |
| C <sub>2</sub> N <sub>2</sub> <sup>c</sup> | <i>r</i> (C1N1)             | 118.7          | 115.4 | 3.3                     |
|  | <i>r</i> (C1C2)             | 138.3          | 138.9 | –0.6                    |
| HC <sub>3</sub> N <sup>c</sup>             | <i>r</i> (C3H)              | 106.4          | 105.7 | 0.7                     |
|  | <i>r</i> (C2C3)             | 122.4          | 120.3 | 2.1                     |
|  | <i>r</i> (C1C2)             | 137.7          | 138.2 | –0.5                    |
|  | <i>r</i> (C1N)              | 118.8          | 115.7 | 3.1                     |

<sup>a</sup> See Figure 1 for numbering of atoms. <sup>b</sup> Calculated – experimental bond length. <sup>c</sup> Reference 50. <sup>d</sup> Reference 51.

correcting for this contribution they assessed the interaction energy of the distorted fragments to be –5.130 kJ mol<sup>–1</sup>. These authors also acknowledged the necessity of including an estimation of dispersion energy in such weakly-bound systems but did not incorporate such a correction in their calculations.<sup>31</sup> They computed the total charge transfer from N<sub>2</sub> to BF<sub>3</sub> to be 0.0114 *e*. Jurgens and Almlöf considered the BF<sub>3</sub>·NCCN complex at the second order Møller–Plesset (MP2)<sup>45</sup> level and obtained an optimized geometry with a B···N bond length of 260 pm and an FBN angle of 93°, although they fixed the CC and CN bond lengths at their monomer values.<sup>37</sup> Their binding energy at the equilibrium geometry was found to be 30.24 kJ mol<sup>–1</sup>, which reduced to 14.92 kJ mol<sup>–1</sup> after correcting for basis set superposition error (BSSE).<sup>46</sup>

Janda *et al.* reported the experimental structure of BF<sub>3</sub>·N<sub>2</sub> by molecular beam electric resonance (MBER) microwave spectroscopy and derived a B···N separation of 287.5 pm and an FBN angle of 90.5°. <sup>12</sup> These authors drew attention to the unexpectedly large dipole moment of the complex (0.35 D) and pointed out that such a large value could not be explained by the assumption of a quadrupole induced dipole. <sup>12</sup> Using a similar technique, Leopold *et al.* deduced that while BF<sub>3</sub>·NCCN is a symmetric top, BF<sub>3</sub>·NNO is not. <sup>15</sup> They measured the B···N bond length of BF<sub>3</sub>·NCCN to be 264.7 pm and estimated the FBN angle to lie between 90 and 100°. Although their conclusion regarding the structure of the BF<sub>3</sub>·NNO adduct was based on limited data, the spectra of this complex and that of BF<sub>3</sub>·NCCN were sufficiently different that their assignment of the structure as an asymmetric top is unambiguous. Although Leopold *et al.* did not speculate on the mode of bonding, an O-bonded BF<sub>3</sub>·ONN structure is indicated. <sup>15</sup> Reeve *et al.* used the pulsed-nozzle microwave method to characterize the BF<sub>3</sub>·NCH species and obtained a bond length of 247.3 pm, with an out-of-plane distortion of the BF<sub>3</sub> fragment of less than 3°. <sup>14</sup> The substantial differences in the structures of BF<sub>3</sub>·NCH in the gas phase and in the solid state were pointed out by Burns and Leopold on the basis of a crystallographic study, which established a contraction of 83.5 pm in the B···N bond length and of 14° in the FBN angle on crystallization. <sup>11</sup>

The vibrational spectra of the BF<sub>3</sub>·N<sub>2</sub>,<sup>27</sup> BF<sub>3</sub>·NCH, and BF<sub>3</sub>·NCCCH<sup>22</sup> complexes have been studied, in an argon matrix<sup>27</sup> and in the gas phase.<sup>22</sup> Gebicki and Liang observed



**Figure 1.** Optimized structures and numbering of the atoms of the 1:1 molecular complexes of boron trifluoride with (I) nitrogen, (II) nitrous oxide, (III) hydrogen cyanide, (IV) cyanogen fluoride, (V) cyanogen, and (VI) cyanoacetylene.

small red shifts of 3.9 ( $^{10}\text{B}$ ) and 6.5  $\text{cm}^{-1}$  ( $^{11}\text{B}$ ) in the antisymmetric  $\text{BF}_3$  stretching and 23.2 ( $^{10}\text{B}$ ) and 21.0  $\text{cm}^{-1}$  ( $^{11}\text{B}$ ) in the out-of-plane  $\text{BF}_3$  bending modes of the  $\text{BF}_3\cdot\text{N}_2$  adduct on complexation, indicative of very weak bonding.<sup>27</sup> In contrast, the corresponding  $\text{BF}_3$  modes in the substantially more strongly bonded  $\text{BF}_3\cdot\text{NH}_3$  complex suffer shifts of  $-225.8$  ( $^{10}\text{B}$ ) and  $-224.3$  ( $^{11}\text{B}$ ) and 17.6  $\text{cm}^{-1}$  ( $^{10}\text{B}$  and  $^{11}\text{B}$ ) in argon.<sup>30</sup> The  $\text{BF}_3\cdot\text{NCH}$  and  $\text{BF}_3\cdot\text{NCCCH}$  complexes were the subjects of an infrared study, in the CH stretching region, by Kerstel *et al.*, using a molecular beam optothermal spectrometer at sub-Doppler resolution.<sup>22</sup> Red shifts of 0.1455 ( $^{10}\text{B}$ ), 0.1447 ( $^{11}\text{B}$ ), 2.701 ( $^{10}\text{B}$ ), and 2.691  $\text{cm}^{-1}$  ( $^{11}\text{B}$ ) were measured for the two complexes, respectively. The significantly smaller complex–monomer wavenumber shifts in  $\text{BF}_3\cdot\text{NCH}$  compared with those in  $\text{BF}_3\cdot\text{NCCCH}$  were attributed to a long range anharmonic vibrational interaction.

The computed structural, energetic, and electronic properties of the six complexes examined in this work will now be discussed in the light of the theoretical and experimental data referred to above.

#### COMPUTATIONAL DETAILS

The computations were carried out using the GAUSSIAN-92 computer program,<sup>47</sup> at the MP2 level of theory<sup>45</sup> and with the 6-31G\*\* split-valence polarized basis set.<sup>48</sup> The structures of the monomer units were optimized, maintaining linearity in the cases of the bases and fixing the FBF angle of  $\text{BF}_3$  at  $120^\circ$ . The complex structures were fully optimized, under the constraint of  $C_{3v}$  symmetry, routinely with the VERYTIGHT convergence criterion.<sup>47</sup> (The complexes with  $\text{N}_2$ , HCN,  $\text{C}_2\text{N}_2$ , and HCCCN resisted successful optimization at this level, the structures oscillating along the  $\text{B}\cdots\text{N}$  axes on successive iterations. In these cases the optimizations were performed at the TIGHT level.) All molecular orbitals were included in the post-self-consistent-field (SCF) steps. The binding energies were computed and corrected for

BSSE<sup>46</sup> by the Boys–Bernardi full counterpoise method.<sup>49</sup> In the cases of the complexes with  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , HCN, and FCN the interaction energies were also corrected for zero-point energy differences. A Mulliken population analysis was carried out, in order to determine the extents (and directions) of the charge shifts on complexation. The calculations were performed using a Hewlett-Packard HP 720 computer.

#### RESULTS

**Structures.** The optimized bond lengths of the monomers are presented in Table 3, with the corresponding experimental gas-phase values for comparison. Agreement is generally good but is consistently worse for the multiple bond lengths, as observed earlier.<sup>52</sup> The structures of the six complexes, plotted using the SCHAKAL-92 program,<sup>53</sup> are illustrated in Figure 1, and the values of the optimized parameters are collected in Table 4. Our  $\text{B}\cdots\text{N}$  bond length of  $\text{BF}_3\cdot\text{N}_2$  lies below the experimental value of Janda *et al.*<sup>12</sup> and above the theoretical value of Garcia-Leigh and Murrell.<sup>31</sup> Our FBN bond angle, too, is intermediate in value between the experimental and theoretical literature values.<sup>12,31</sup> Agreement between the computed intermonomer distance and FBN angle of  $\text{BF}_3\cdot\text{NCH}$  and the gas-phase values of Reeve *et al.* is remarkably good.<sup>14</sup> In the case of  $\text{BF}_3\cdot\text{NCCN}$  our  $\text{B}\cdots\text{N}$  distance compares slightly less favorably with the experimental bond length of Leopold *et al.*<sup>15</sup> than does the computed value of Jurgens and Almlöf,<sup>37</sup> but our FBN angle is in closer agreement. Table 4 also shows the differences between the monomer and complex bond length values; the BF bonds typically lengthen on complexation, while the bond associated with the bonded nitrogen atom (usually  $\text{C}\equiv\text{N}$ ) almost invariably shortens. In some instances ( $\text{N}_2\text{O}$  and FCN) the adjacent bond in the base also shortens. These bond length changes are fairly minor, however, testifying to the weakness of the interactions. Since the  $\text{B}\cdots\text{N}$  interactions are apparently similar in nature in all six complexes, it may be expected that the  $\text{B}\cdots\text{N}$  bond length and the distortion of

**Table 4.** Optimized Geometrical Parameters of the Complexes and Complex–Monomer Differences

| complex   | parameter <sup>a</sup> | calcd | difference <sup>b</sup> |
|---|------------------------|-------|-------------------------|
| BF <sub>3</sub> ·N <sub>2</sub> <sup>c</sup>    | <i>r</i> (BF)/pm       | 132.5 | 0.1                     |
|   | <i>r</i> (N1N2)/pm     | 113.0 | 0.0                     |
|   | <i>r</i> (B···N1)/pm   | 272.5 |                         |
|   | FBN1/deg               | 90.8  |                         |
| BF <sub>3</sub> ·N <sub>2</sub> O <sup>d</sup>  | <i>r</i> (BF)/pm       | 132.5 | 0.1                     |
|   | <i>r</i> (N1N2)/pm     | 117.0 | −0.2                    |
|   | <i>r</i> (N2O)/pm      | 119.1 | −0.2                    |
|   | <i>r</i> (B···N1)/pm   | 266.9 |                         |
|   | FBN1/deg               | 91.0  |                         |
| BF <sub>3</sub> ·NCH <sup>c</sup>               | <i>r</i> (BF)/pm       | 132.9 | 0.5                     |
|   | <i>r</i> (CH)/pm       | 106.6 | 0.2                     |
|   | <i>r</i> (CN)/pm       | 117.4 | −0.3                    |
|   | <i>r</i> (B···N)/pm    | 244.3 |                         |
|   | FBN/deg                | 93.1  |                         |
| BF <sub>3</sub> ·NCF <sup>d</sup>               | <i>r</i> (BF)/pm       | 132.8 | 0.4                     |
|   | <i>r</i> (CF)/pm       | 127.8 | −0.5                    |
|   | <i>r</i> (CN)/pm       | 117.8 | −0.4                    |
|   | <i>r</i> (B···N)/pm    | 249.6 |                         |
|   | FBN/deg                | 92.6  |                         |
| BF <sub>3</sub> ·NCCN <sup>c</sup>              | <i>r</i> (BF)/pm       | 132.6 | 0.2                     |
|   | <i>r</i> (C1N1)/pm     | 118.4 | −0.3                    |
|   | <i>r</i> (C1C2)/pm     | 138.3 | 0.0                     |
|   | <i>r</i> (C2N2)/pm     | 118.7 | 0.0                     |
|   | <i>r</i> (B···N1)/pm   | 256.9 |                         |
| BF <sub>3</sub> ·NC <sub>3</sub> H <sup>c</sup> | FBN1/deg               | 91.9  |                         |
|   | <i>r</i> (BF)/pm       | 132.9 | 0.5                     |
|   | <i>r</i> (C3H)/pm      | 106.5 | 0.1                     |
|   | <i>r</i> (C2C3)/pm     | 122.4 | 0.0                     |
|   | <i>r</i> (C1C2)/pm     | 137.5 | 0.2                     |
|   | <i>r</i> (C1N)/pm      | 118.4 | −0.4                    |
|   | <i>r</i> (B···N)/pm    | 244.0 |                         |
|   | FBN/deg                | 93.1  |                         |

<sup>a</sup> See Figure 1 for numbering of atoms. <sup>b</sup> Difference = complex – monomer parameter. <sup>c</sup> TIGHT optimization criterion. <sup>d</sup> VERYTIGHT optimization criterion.

the BF<sub>3</sub> fragment from planarity constitute good indicators of the interaction energy, with the shorter bond lengths and the larger FBN bond angles being associated with the stronger interactions. On this basis the nitrogen donors yield the following predicted order of binding energies: N<sub>2</sub> < N<sub>2</sub>O < C<sub>2</sub>N<sub>2</sub> < FCN < HCN < HCCCN.

**Mulliken Atomic Charges.** The atomic charges of the monomers and of the complexes, as defined by Mulliken,<sup>54</sup> are listed in Table 5. The table also shows the amount of charge lost or gained by each atom on complexation, and the net charge associated with each fragment. Positive values in the last column of Table 5 identify the electron donor in each case. This table immediately indicates the totally unexpected observation that in the complexes of BF<sub>3</sub> with N<sub>2</sub> and N<sub>2</sub>O both N<sub>2</sub> and N<sub>2</sub>O appear to be the electron acceptor in each case. However, in the light of the fact that the amount of charge transferred in BF<sub>3</sub>·N<sub>2</sub> and BF<sub>3</sub>·N<sub>2</sub>O is minimal, we should probably conclude that the results in these two cases are so close to the limit of sensitivity for this particular property that they should not be taken too literally. Of the remaining four complexes, the order of increasing amount of charge transferred mirrors that of the structural perturbation almost exactly (C<sub>2</sub>N<sub>2</sub> < FCN < HCCCN < HCN).

**Interaction Energies.** Table 6 shows the interaction energies for the six complexes, both before and after correction for BSSE.<sup>49</sup> In the cases of the complexes with N<sub>2</sub>, N<sub>2</sub>O, HCN, and FCN, for which vibrational analyses have been completed at the MP2 level, the interaction energies

**Table 5.** Mulliken Atomic Charges of the Monomers and of the Complexes

| complex                            | atom <sup>a</sup> | charge/e       |                |                                |                              |
|------------------------------------|-------------------|----------------|----------------|--------------------------------|------------------------------|
|                                    |                   | complex charge | monomer charge | charge difference <sup>b</sup> | fragment charge <sup>c</sup> |
| BF <sub>3</sub> ·N <sub>2</sub>    | B                 | 1.0259         | 0.9852         | 0.0407                         |                              |
|                                    | F                 | −0.3419        | −0.3284        | −0.0135                        |                              |
|                                    | N1                | −0.0043        | 0.0            | −0.0043                        | 0.0002                       |
|                                    | N2                | 0.0039         | 0.0            | 0.0039                         | −0.0004                      |
| BF <sub>3</sub> ·N <sub>2</sub> O  | B                 | 1.0373         | 0.9852         | 0.0521                         |                              |
|                                    | F                 | −0.3444        | −0.3284        | −0.0160                        |                              |
|                                    | N1                | −0.0325        | −0.0645        | 0.0320                         | 0.0041                       |
|                                    | N2                | 0.5778         | 0.6017         | −0.0239                        |                              |
|                                    | O                 | −0.5493        | −0.5372        | −0.0121                        | −0.0040                      |
| BF <sub>3</sub> ·NCH               | B                 | 1.0467         | 0.9852         | 0.0615                         |                              |
|                                    | F                 | −0.3544        | −0.3284        | −0.0260                        |                              |
|                                    | N                 | −0.4217        | −0.3863        | −0.0354                        | −0.0165                      |
|                                    | C                 | 0.1406         | 0.1124         | 0.0282                         |                              |
| BF <sub>3</sub> ·NCF               | H                 | 0.2975         | 0.2740         | 0.0235                         | 0.0163                       |
|                                    | B                 | 1.0441         | 0.9852         | 0.0589                         |                              |
|                                    | F                 | −0.3518        | −0.3284        | −0.0234                        |                              |
|                                    | N                 | −0.4023        | −0.3757        | −0.0266                        | −0.0113                      |
|                                    | C                 | 0.6259         | 0.6024         | 0.0235                         |                              |
| BF <sub>3</sub> ·NCCN              | F                 | −0.2123        | −0.2267        | 0.0144                         | 0.0113                       |
|                                    | B                 | 1.0374         | 0.9852         | 0.0522                         |                              |
|                                    | F                 | −0.3478        | −0.3284        | −0.0194                        |                              |
|                                    | N1                | −0.4534        | −0.3920        | −0.0614                        | −0.0060                      |
|                                    | C1                | 0.4332         | 0.3920         | 0.0412                         |                              |
| BF <sub>3</sub> ·NC <sub>3</sub> H | C2                | 0.4051         | 0.3920         | 0.0131                         |                              |
|                                    | N2                | −0.3788        | −0.3920        | 0.0132                         | 0.0061                       |
|                                    | B                 | 1.0482         | 0.9852         | 0.0630                         |                              |
|                                    | F                 | −0.3544        | −0.3284        | −0.0260                        | −0.0150                      |
|                                    | N                 | −0.5439        | −0.4608        | −0.0831                        |                              |
|                                    | C1                | 0.2824         | 0.2209         | 0.0615                         |                              |
|                                    | C2                | 0.2568         | 0.2514         | 0.0054                         |                              |
|                                    | C3                | −0.2996        | −0.3220        | 0.0224                         |                              |
|                                    | H                 | 0.3193         | 0.3106         | 0.0087                         | 0.0149                       |

<sup>a</sup> See Figure 1 for numbering of atoms. <sup>b</sup> Difference = complex – monomer atomic charge. <sup>c</sup> Minor discrepancies between net fragment charges are due to rounding off errors.

have also been corrected for zero-point energy difference. The sequence of increasing binding energies, corrected for BSSE only, is N<sub>2</sub> < N<sub>2</sub>O < C<sub>2</sub>N<sub>2</sub> < FCN < HCN < HCCCN, perfectly consistent with the order of increasing structural perturbation. The vibrational analysis of the BF<sub>3</sub>·N<sub>2</sub>O complex suggests a fundamental difference between its mode of bonding and those of the complexes with N<sub>2</sub>, HCN, and FCN; one of the eigenvalues of BF<sub>3</sub>·N<sub>2</sub>O was found to be negative, indicating that the axial B···N bonded complex is actually a transition state. Inspection of the form of the normal mode associated with the imaginary wave-number, aided by the use of Dillen's vibrational mode animation program VIBRAM,<sup>55</sup> showed it to be the degenerate libration of the N<sub>2</sub>O fragment. Execution of this mode would convert the axial N-bonded structure into the nonaxial O-bonded species, which was found to have a full set of positive eigenvalues at the RHF level,<sup>56</sup> and which is therefore a true minimum on the potential energy surface.

**Table 6.** Calculated Interaction Energies of the Complexes

| complex                            | energy/kJ mol <sup>-1</sup> |                   |                   |                        |                        |
|------------------------------------|-----------------------------|-------------------|-------------------|------------------------|------------------------|
|                                    | uncorrected                 | BSSE <sup>a</sup> | $\Delta E_o^b$    | corrected <sup>c</sup> | corrected <sup>d</sup> |
| BF <sub>3</sub> ·N <sub>2</sub>    | -11.58                      | 7.23              | 2.08              | -4.35                  | -2.27                  |
| BF <sub>3</sub> ·N <sub>2</sub> O  | -14.45                      | 7.94              | 1.45 <sup>e</sup> | -6.51                  | -5.06                  |
| BF <sub>3</sub> ·NCH               | -25.98                      | 7.59              | 2.86              | -18.39                 | -15.53                 |
| BF <sub>3</sub> ·NCF               | -23.63                      | 7.75              | 2.37              | -15.88                 | -13.51                 |
| BF <sub>3</sub> ·NCCN              | -19.30                      | 7.93              |                   | -11.37                 |                        |
| BF <sub>3</sub> ·NC <sub>3</sub> H | -25.98                      | 7.57              |                   | -18.41                 |                        |

<sup>a</sup> Basis set superposition error. <sup>b</sup> Zero-point energy difference. <sup>c</sup> Corrected for BSSE only. <sup>d</sup> Corrected for BSSE and  $\Delta E_o$ . <sup>e</sup> Complex has one negative eigenvalue.

**Table 7.** Dipole Moments of the Monomers and the Complexes and Dipole Moment Enhancements on Complexation

| base                          | dipole moment/D <sup>a</sup> |         |                          |
|-------------------------------|------------------------------|---------|--------------------------|
|                               | monomer                      | complex | enhancement <sup>b</sup> |
| N <sub>2</sub>                | 0.0000                       | 0.4559  | 0.4559                   |
| N <sub>2</sub> O              | -0.5024                      | 0.1500  | 0.6524                   |
| C <sub>2</sub> N <sub>2</sub> | 0.0000                       | 1.0644  | 1.0644                   |
| FCN                           | 2.2445                       | 3.3984  | 1.1539                   |
| HCN                           | 3.2445                       | 4.5560  | 1.3115                   |
| HCCCN                         | 4.2388                       | 5.8675  | 1.6287                   |

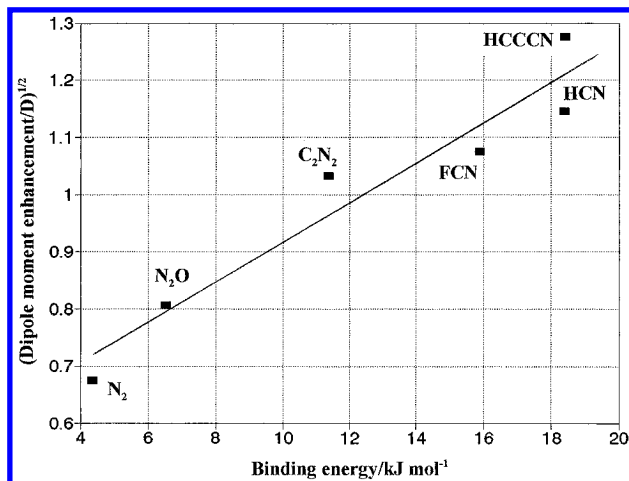
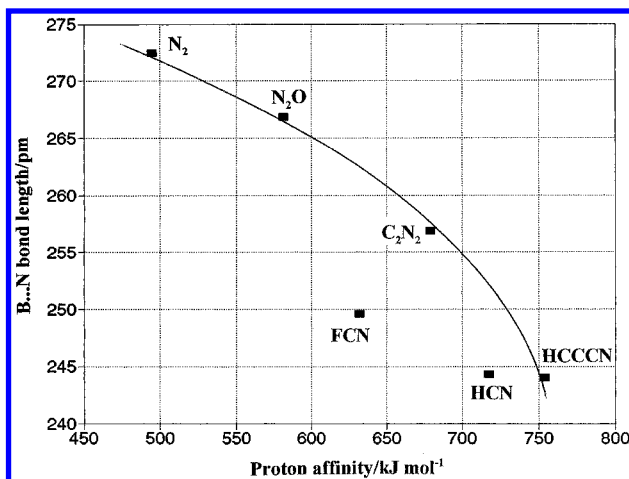
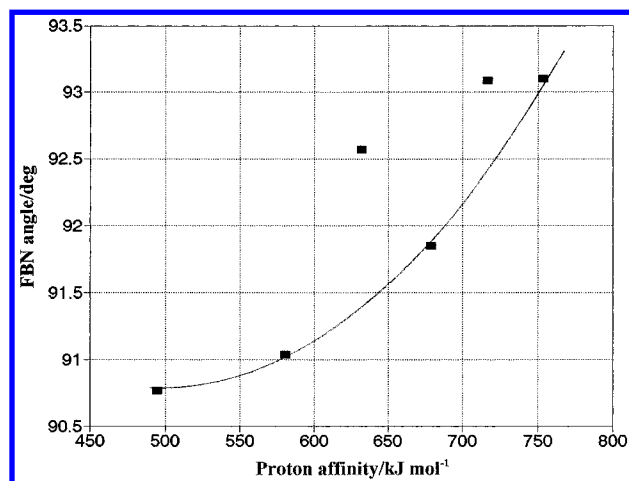
<sup>a</sup> 1D  $\equiv 3.336 \times 10^{-30}$  Cm. <sup>b</sup> In the sense B  $\leftarrow$  N.

In the N<sub>2</sub>O monomer the O atom is much more highly negatively charged than the terminal N (see Table 5), which suggests that the mode of bonding in the BF<sub>3</sub>·N<sub>2</sub>O complex would be expected to involve the O, rather than the terminal N atom. If that is the case the coordination around the O atom is predicted to be trigonal, rather than linear, which is consistent with the observation by Leopold *et al.* that the complex in the gas phase is an asymmetric top.<sup>15</sup>

**Dipole Moment Enhancements.** A further property of the complexes under consideration here, which may be conveniently computed by the GAUSSIAN-92 program,<sup>47</sup> is the enhancement of the dipole moment of the base resulting from complexation with BF<sub>3</sub>. The dipole moments of the base monomers and of the complexes and the dipole moment enhancements are shown in Table 7. Again the complexes are found to be ranked in an order consistent with that for the other properties discussed above. Ratajczak and Orville-Thomas have correlated the square root of the charge transfer dipole moment enhancement of a number of hydrogen bonded complexes with the hydrogen bond enthalpy.<sup>57-61</sup> A plot of the square root of the enhancement against the corrected binding energy (which is related to the enthalpy of interaction) of the complexes studied here is presented in Figure 2. While the plot reveals some scatter, a sensible correlation is certainly observed.

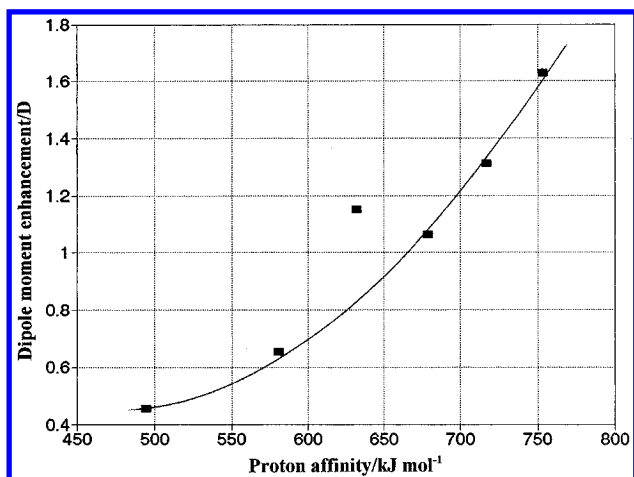
## DISCUSSION

In this study we have computed a range of structural properties of the complexes, including the bond length changes of the BF and NX bonds (X = N or C), the B···N intermonomer separation and the FBN angle, a pair of electronic parameters (the Mulliken atomic charge shifts and the dipole moment enhancements), and the binding energies. All of these theoretically determined quantities should be dependent on those properties of the base molecules which govern their electron donating capacity, such as the gas phase basicity and proton affinity and the absolute electronegativity

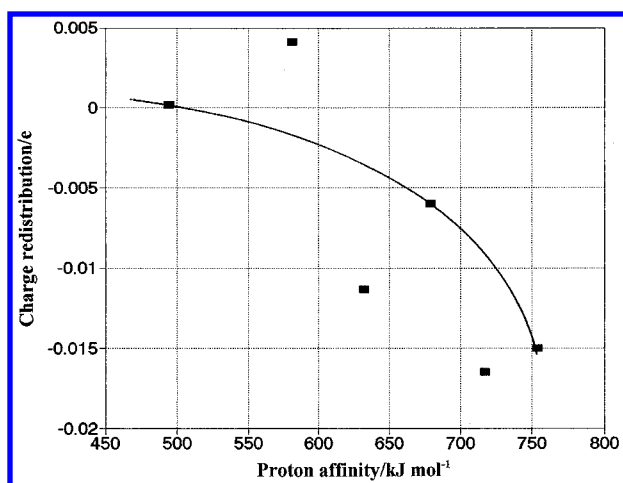
**Figure 2.** Plot of the square root of the dipole moment enhancement versus the corrected binding energy of the complex.**Figure 3.** Plot of the B···N bond length versus the proton affinity of the base.**Figure 4.** Plot of the FBN angle versus the proton affinity of the base. See Figure 3 for identification of individual points.

and hardness. Values of the proton affinities of all six bases considered here are available in the literature,<sup>62</sup> while the absolute electronegativities and hardnesses of N<sub>2</sub>, N<sub>2</sub>O, C<sub>2</sub>N<sub>2</sub>, and HCN have been reported by Pearson.<sup>63,64</sup>

Figures 3 and 4 show plots of the B···N bond length and the FBN bond angle as functions of the proton affinity of the base. The expected trend, of contraction of the B···N bond length and increasing distortion from planarity at the boron atom with increasing proton affinity, and hence



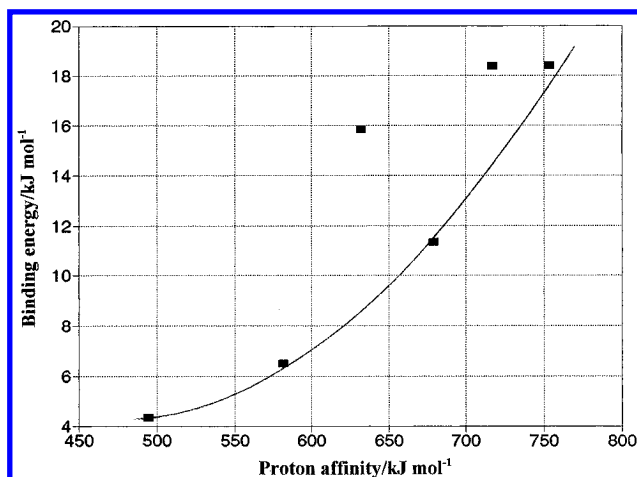
**Figure 5.** Plot of the dipole moment enhancement *versus* the proton affinity of the base. See Figure 3 for identification of individual points.



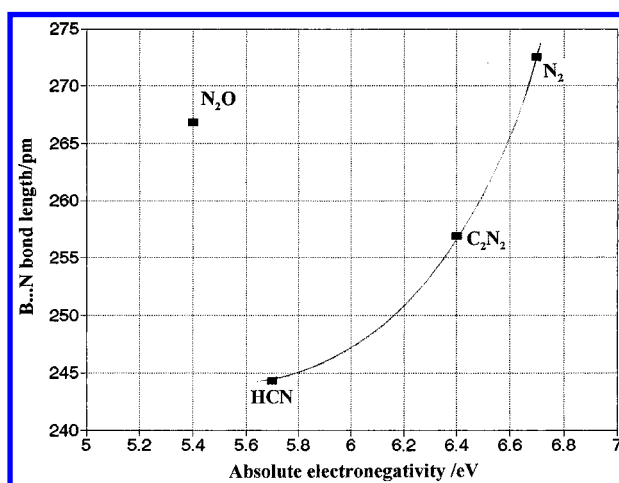
**Figure 6.** Plot of the charge redistribution *versus* the proton affinity of the base. See Figure 3 for identification of individual points.

strength of interaction, is indeed observed. The correlations follow smooth curves; however, the points for FCN and, to a lesser extent, for HCN are anomalous. The plots of the NX bond contraction ( $X = N$  for  $N_2$  and  $N_2O$  and  $C$  for the other four bases) and of the BF bond lengthening against the proton affinity are qualitatively identical to Figures 3 and 4, respectively, and are therefore not shown here; the anomalous behavior of the complexes with HCN and FCN is observed in these cases also.

When the dipole moment enhancement is plotted against the proton affinity, however (see Figure 5), the datum for the  $BF_3 \cdot NCH$  complex now conforms closely with the curve fitting the points for  $N_2$ ,  $N_2O$ ,  $C_2N_2$ , and  $HCCCN$ , although the complex with FCN is still unique. Figure 6 shows a plot of the amount of charge shift occurring on complexation, again as a function of the proton affinity of the electron donor. In this case, in addition to the expected deviation from the trend for the HCN and FCN data, the point representing the  $BF_3 \cdot N_2O$  complex also lies off the correlation curve. The explanation for this behavior is clearly to be found in the fact that the  $BF_3 \cdot N_2O$  complex is bonded through the O, rather than the terminal N atom, as indicated above. Finally, Figure 7 shows the correlation between the corrected binding energy and the proton affinity. Once again, the HCN and FCN complexes fail to conform with the trend followed by the other adducts. Our results are consistent in



**Figure 7.** Plot of the corrected binding energy *versus* the proton affinity of the base. See Figure 3 for identification of individual points.

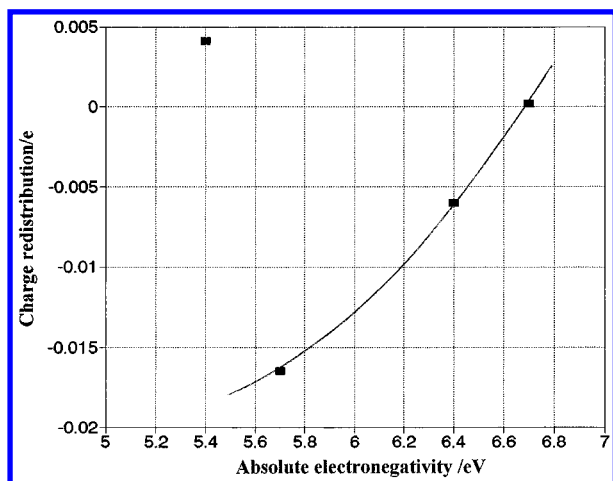


**Figure 8.** Plot of the B...N bond length *versus* the absolute electronegativity of the base.

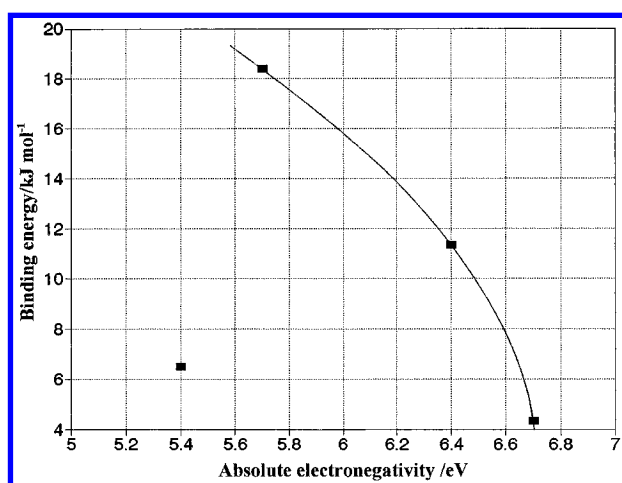
suggesting that the literature proton affinity of FCN may be underestimated by as much as  $100 \text{ kJ mol}^{-1}$ ; it is possible that the measured value<sup>62</sup> is that for protonation at the fluorine site.

The second experimental parameter with which we have chosen to correlate our computed properties is the absolute electronegativity.<sup>63,64</sup> Values of this quantity are available only for  $N_2$ ,  $N_2O$ , HCN, and  $C_2N_2$ . Therefore it is not possible to confirm whether it is our calculated data or the experimental behavior of FCN which is responsible for the departure of the  $BF_3 \cdot NCF$  results from conformity. In the case of the dependence of our calculated geometrical, electronic, and energetic properties on the absolute electronegativity of the electron donor, we find that the more strongly interacting complexes correlate with low values of this parameter. Figures 8–10 exemplify the ways in which the absolute electronegativity governs the complex properties (B...N bond length, charge redistribution and binding energy). It is clear from these figures that  $N_2O$  is an anomalous member of this series. The deviation of the  $BF_3 \cdot N_2O$  data points from the smooth curves is clearly a function of the fact that the electronegativity is controlled predominantly by the oxygen “end” of the molecule, and this property is therefore not an appropriate parameter with which to correlate the behavior of the N-bonded isomer of





**Figure 9.** Plot of the charge redistribution *versus* the absolute electronegativity of the base. See Figure 8 for identification of individual points.



**Figure 10.** Plot of the corrected binding energy *versus* the absolute electronegativity of the base. See Figure 8 for identification of individual points.

$\text{BF}_3 \cdot \text{N}_2\text{O}$  which we initially assumed to be the preferred structure.

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#### REFERENCES AND NOTES

- Greenwood, N. N.; Martin, R. L. Boron Trifluoride Coordination Compounds. *Quart. Rev.* **1954**, 8, 1–39.
- Shibata, S.; Iijima, K. Molecular Structures of Donor-Acceptor Complexes of Boron Trifluoride with Trimethylamine and Dimethyl Ether. *Chem. Lett.* **1977**, 29–32.
- Iijima, K.; Shibata, S. Molecular Structure and Internal Rotation of Trimethylamine-Boron Trifluoride. A Combination of Electron Diffraction and Spectroscopic Data. *Bull. Chem. Soc. Jpn.* **1979**, 52, 711–715.
- Laubengayer, A. W.; Condikey, G. F. Donor-Acceptor Bonding. IV. Ammonia-Boron Trifluoride. *J. Am. Chem. Soc.* **1948**, 70, 2274–2276.
- Geller, S.; Hoard, J. L. Structures of Molecular Addition Compounds. I. Monomethylamine-Boron Trifluoride,  $\text{H}_3\text{CH}_2\text{N} \cdot \text{BF}_3$ . *Acta Crystallogr.* **1950**, 3, 121–129.
- Hoard, J. L.; Owen, T. B.; Buzzell, A.; Salmon, O. N. Structures of Molecular Addition Compounds. II. Methyl Cyanide-Boron Trifluoride,  $\text{H}_3\text{CCN} \cdot \text{BF}_3$ . *Acta Crystallogr.* **1950**, 3, 130–137.
- Hoard, J. L.; Geller, S.; Cashin, W. M. Structures of Molecular Addition Compounds. III. Ammonia-Boron Trifluoride. *Acta Crystallogr.* **1951**, 4, 396–398.
- Geller, S.; Hoard, J. L. Structures of Molecular Addition Compounds. IV. Trimethylamine-Boron Trifluoride. *Acta Crystallogr.* **1951**, 4, 399–405.
- Hoard, J. L.; Geller, S.; Owen, T. B. Structures of Molecular Addition Compounds. V. Comparison of Four Related Structures. *Acta Crystallogr.* **1951**, 4, 405–407.
- Swanson, B.; Shriver, D. F.; Ibers, J. A. Nature of the Donor-Acceptor Bond in Acetonitrile-Boron Trihalides. The Structures of the Boron Trifluoride and Boron Trichloride Complexes of Acetonitrile. *Inorg. Chem.* **1969**, 8, 2182–2189.
- Burns, W. A.; Leopold, K. R. Unusually Large Gas-Solid Structure Differences: A Crystallographic Study of  $\text{HCN} \cdot \text{BF}_3$ . *J. Am. Chem. Soc.* **1993**, 115, 11622–11623.
- Janda, K. C.; Bernstein, L. S.; Steed, J. M.; Novick, S. E.; Klemperer, W. Synthesis, Microwave Spectrum and Structure of  $\text{ArBF}_3$ ,  $\text{BF}_3\text{CO}$  and  $\text{N}_2\text{BF}_3$ . *J. Am. Chem. Soc.* **1978**, 100, 8074–8079.
- Novick, S. E.; Davies, P. B.; Dyke, T. R.; Klemperer, W. Polarity of van der Waals Molecules. *J. Am. Chem. Soc.* **1973**, 95, 8547–8550.
- Reeve, S. W.; Burns, W. A.; Lovas, F. J.; Suenram, R. D.; Leopold, K. R. Microwave Spectra and Structure of  $\text{HCN} \cdot \text{BF}_3$ : An Almost Weakly Bound Complex. *J. Phys. Chem.* **1993**, 97, 10630–10637.
- Leopold, K. R.; Fraser, G. T.; Klemperer, W. Rotational Spectroscopy of Molecular Complexes of  $\text{BF}_3$  with  $\text{NCCN}$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$ . *J. Am. Chem. Soc.* **1984**, 106, 897–899.
- Dvorak, M. A.; Ford, R. S.; Suenram, R. D.; Lovas, F. J.; Leopold, K. R. van der Waals *vs* Covalent Bonding: Microwave Characterization of a Structurally Intermediate Case. *J. Am. Chem. Soc.* **1992**, 114, 108–115.
- Cassoux, P.; Kuczkowski, R. L.; Serafini, A. Microwave Spectrum and Structure of Trimethylamine-Boron Trifluoride.  $\text{Me}_3\text{N} \cdot \text{BX}_3$  Adduct Stability and the Reorganization Energies of  $\text{BF}_3$  and  $\text{BH}_3$ . *Inorg. Chem.* **1977**, 16, 3005–3008.
- Barber, M.; Connor, J. A.; Guest, M. F.; Hillier, I. H.; Schwarz, M.; Stacey, M. Bonding in Some Donor-Acceptor Complexes Involving Boron Trifluoride. *J. Chem. Soc., Faraday Trans. II* **1973**, 69, 551–558.
- Pradeep, T.; Sreekanth, C. S.; Rao, C. N. R. An Ultraviolet Photoelectron Spectroscopic Study of  $\text{BF}_3$ -Donor Complexes. *J. Chem. Phys.* **1989**, 90, 4704–4708.
- Pradeep, T.; Rao, C. N. R. Electronic Structures of Electron Donor-Acceptor Complexes: Results from Ultraviolet Photoelectron Spectroscopy and Molecular Orbital Calculations. *J. Mol. Structure (Theochem)* **1989**, 200, 339–352.
- Hillier, I. H.; Vincent, M. A.; Connor, J. A.; Guest, M. F.; MacDowell, A. A.; von Niessen, W. *Ab Initio* Molecular Orbital and Photoelectron Spectroscopic Study of the Pyridine-Boron Trifluoride Electron Donor-Acceptor Complex. *J. Chem. Soc., Faraday Trans. II* **1988**, 84, 409–415.
- Kerstel, E. R. T.; Pate, B. H.; Mentel, T. F.; Yang, X.; Scoles, G. Sub-Doppler Infrared Spectroscopy of  $\text{HCCN} \cdot \text{BF}_3$  ( $\nu_1$ ) and  $\text{HCN} \cdot \text{BF}_3$  ( $\nu_1$  and  $2\nu_1$ ). *J. Chem. Phys.* **1994**, 101, 2762–2771.
- Delaule, J.; Taillandier, E.; Taillandier, M. Spectres d'Absorption Infrarouge de Complexes par Transfert de Charge. IV: Amines Trifluorure de Bore. *Compt. Rend., Ser. B* **1967**, 265, 849–852.
- Delaule, J.; Taillandier, E.; Taillandier, M. Spectres d'Absorption Infrarouge de Complexes par Transfert de Charge: Amine-Trifluorure de Bore. *Compt. Rend., Ser. B* **1967**, 265, 921–924.
- Swanson, B.; Shriver, D. F. Vibrational Spectra, Vibrational Analysis and Bonding in Acetonitrile-Boron Trifluoride. *Inorg. Chem.* **1970**, 9, 1406–1416.
- Amster, R. L.; Taylor, R. C. Spectroscopic Studies of Lewis Acid-Base Complexes - I. Vibrational Spectra and Assignments for Trimethylamine Complexes of Boron Halides. *Spectrochim. Acta* **1964**, 20, 1487–1502.
- Gebicki, J.; Liang, J. IR Evidence for the Formation of Weakly Bound Complexes  $\text{BF}_3\text{-CO}$  and  $\text{BF}_3\text{-N}_2$ . *J. Mol. Struct.* **1984**, 117, 283–286.
- Hunt, R. L.; Ault, B. S. Matrix Isolation Spectroscopic Study of the Boron Trihalide-Ammonia Complexes. *Spectroscopy* **1982**, 1, 31–44.
- Nxumalo, L. M.; Ford, T. A. Matrix Isolation Infrared Spectroscopic Studies of Some Boron Trifluoride Complexes. In 9th International Conference on Fourier Transform Spectroscopy; Bertie, J. E., Wieser, H., Eds.; Proc. SPIE **1993**, 2089, 200–201.
- Nxumalo, L. M.; Andrzejak, M.; Ford, T. A. The Structure of the Boron Trifluoride-Ammonia Complex: A Fourier Transform Matrix

- Isolation Infrared Spectroscopic and *Ab Initio* Study. *Vibr. Spectrosc.* Submitted for publication.
- (31) Garcia-Leigh, A.; Murrell, J. N. On the Stability of  $\text{BH}_3$  and  $\text{BF}_3$  Adducts with  $\text{BF}$ ,  $\text{CO}$  and  $\text{N}_2$ . *Croat. Chem. Acta* **1984**, 57, 879–886.
- (32) Archibald, R. M.; Armstrong, D. R.; Perkins, P. G. *Ab Initio* Study of the Electronic Structures and Heats of Formation of Some Adducts of Boron Trifluoride. *J. Chem. Soc., Faraday Trans. II* **1973**, 69, 1793–1800.
- (33) Andres, J.; Arnau, A.; Bertran, J.; Silla, E. Relative Strength of  $\text{BF}_3$  and  $\text{BCl}_3$  as Lewis Acids. *J. Mol. Struct. (Theochem)* **1985**, 120, 315–320.
- (34) Hirota, F.; Miyata, K.; Shibata, S. *Ab Initio* Study on the Charge-Transfer Complexes of Boron Trihalide with Ammonia, Trimethylamine, Phosphine and Trimethylphosphine. *J. Mol. Structure (Theochem)* **1989**, 201, 99–111.
- (35) Sreekanth, C. S.; Mok, C. Y.; Huang, H. H. A UV Photoelectron Spectroscopic Study of Addition Compounds of Boron Trifluoride with Methyl-substituted Pyridines. *J. Electron Spectrosc. Relat. Phenom.* **1991**, 56, 105–116.
- (36) Sana, M.; Leroy, G.; Wilante, C. Enthalpies of Formation and Bond Energies in Lithium, Beryllium and Boron Derivatives. 2. Dative, Single and Triple Bonds. *Organometallics* **1992**, 11, 781–787.
- (37) Jurgens, R.; Almlöf, J. Two Very Different B...N Bond Distances: Electronic Structure Calculations on  $\text{BF}_3\cdots\text{NCCN}$  and  $\text{BF}_3\cdots\text{NCCH}_3$ . *Chem. Phys. Lett.* **1991**, 176, 263–265.
- (38) Greenberg, A.; Plant, C.; Venzani, C. A. *Ab Initio* Molecular Orbital Study of 1-Methylsilatrane and Model Compounds. *J. Mol. Struct. (Theochem)* **1991**, 234, 291–301.
- (39) Sreekanth, C. S.; Mok, C. Y.; Huang, H. H.; Tan, K. L. A Photoelectron Spectroscopic Study of the Electron Donor-Acceptor Complexes of Trimethylamine with Boron Trihalides  $\text{BX}_3$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}$ ). *J. Electron Spectrosc. Relat. Phenom.* **1992**, 58, 129–140.
- (40) van Duijneveldt, F. B. IBM Research Report RJ 945, 1971.
- (41) Nxumalo, L. M.; Ford, T. A. The Boron Trifluoride-Carbon Monoxide Complex. A Matrix Isolation Infrared Spectroscopic and *Ab Initio* Molecular Orbital Theoretical Study. *S. Afr. J. Chem.* In press.
- (42) Nxumalo, L. M.; Ford, T. A. The Vibrational Spectra of the Boron Halides and Their Molecular Complexes. Part 2. *Ab Initio* Predictions of the Structure and Vibrational Spectra of the Boron Trifluoride Dimer. *J. Mol. Struct.* **1993**, 300, 325–338.
- (43) Nxumalo, L. M.; Ford, T. A. Infrared Spectrum of the Boron Trifluoride Dimer. *Vibr. Spectrosc.* **1994**, 6, 333–343.
- (44) Nxumalo, L. M.; Ford, T. A. On the Energetics of the Dimerization of Boron Trifluoride. *J. Mol. Struct. (Theochem)* In press.
- (45) Møller, C.; Plesset, M. S. Note on an Approximation Treatment for Many-Electron Systems. *Phys. Rev.* **1934**, 46, 618–622.
- (46) Liu, B.; McLean, A. D. Accurate Calculation of the Attractive Interaction of Two Ground State Helium Atoms. *J. Chem. Phys.* **1973**, 59, 4557–4558.
- (47) GAUSSIAN-92, Rev. C.4; 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, R. 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.
- (48) Francel, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XXIII. A Polarization-type Basis Set for Second-row Elements. *J. Chem. Phys.* **1982**, 77, 3654–3665.
- (49) Boys, S. F.; Bernardi, F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, 19, 553–566.
- (50) Harmony, M. D.; Laurie, V. W.; Kuczkowski, R. L.; Schwendeman, R. H.; Ramsay, D. A.; Lovas, F. J.; Lafferty, W. J.; Maki, A. G. Molecular Structures of Gas-Phase Polyatomic Molecules Determined by Spectroscopic Methods. *J. Phys. Chem. Ref. Data* **1979**, 8, 619–721.
- (51) Herzberg, G. Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, 2nd ed.; van Nostrand: Princeton, 1950; p 553.
- (52) Tshela, T. M.; Ford, T. A. *Ab Initio* Molecular Orbital Calculations of the Infrared Spectra of Interacting Water Molecules. Part 5. Structures, Energetics and Mulliken Charges of the Complexes of Water with Hydrogen Cyanide, Acetylene and Cyanogen. *Bull. Polish Acad. Sci., Chem.* **1994**, 42, 397–412.
- (53) SCHAKAL-92. Keller, E. Kristallographisches Institut der Universität: Freiburg, Germany, 1992.
- (54) Mulliken, R. S. Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I. *J. Chem. Phys.* **1955**, 23, 1833–1840.
- (55) VIBRAM. Dillen, J. L. M. University of Pretoria: South Africa, 1991.
- (56) Nxumalo, L. M. PhD Thesis, University of the Witwatersrand: Johannesburg, 1993.
- (57) Ratajczak, H.; Orville-Thomas, W. J. On the Nature of Electron Donor-Acceptor Interactions. 1. Charge-Transfer Theory and the Relation between the Energy and the Enhancement of Dipole Moments of Amine-Iodine Complexes. *J. Mol. Struct.* **1972**, 14, 149–154.
- (58) Ratajczak, H.; Orville-Thomas, W. J. On the Nature of Electron Donor-Acceptor Interactions. 2. Mulliken's Charge-Transfer Theory and the Problem of the Increase in Intensity of the Infrared Band Associated with Iodine-Base Complexes. *J. Mol. Struct.* **1972**, 14, 155–163.
- (59) Ratajczak, H.; Mielke, Z.; Orville-Thomas, W. J. On the Nature of Electron Donor-Acceptor Interactions. 3. On the Problem of Dipole Moments of Amine-Iodine Electron Donor-Acceptor Complexes. *J. Mol. Struct.* **1972**, 14, 165–170.
- (60) Ratajczak, H.; Orville-Thomas, W. J. Charge-Transfer Properties of Hydrogen Bonds. III. Charge-Transfer Theory and the Relation between the Energy and the Enhancement of Dipole Moment of Hydrogen Bonded Complexes. *J. Chem. Phys.* **1973**, 58, 911–919.
- (61) Ratajczak, H.; Orville-Thomas, W. J. Charge-Transfer Theory and Vibrational Properties of the Hydrogen Bond. *J. Mol. Struct.* **1973**, 19, 237–245.
- (62) Lias, S. G.; Liebman, J. F.; Levin, R. D. Evaluated Gas Phase Basicities and Proton Affinities of Molecules; Heats of Formation of Protonated Molecules. *J. Phys. Chem. Ref. Data* **1984**, 13, 695–808.
- (63) Pearson, R. G. Absolute Electronegativity and Hardness. *Inorg. Chem.* **1988**, 27, 734–740.
- (64) Pearson, R. G. Absolute Electronegativity and Hardness: Applications to Organic Chemistry. *J. Org. Chem.* **1989**, 54, 1423–1430.

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