J. Am. Chem. Soc. **1995**, *117*, 12549-12556

12549

Microwave and ab Initio Investigation of HF—BF$_3$

J. A. Phillips, M. Canagaratna, H. Goodfriend, A. Grushow,† J. Almlöf,* and K. R. Leopold*

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received August 16, 1995®

Abstract: The complex HF—BF$_3$ has been examined by *ab initio* methods and the rotational spectra of four isotopic species have been observed via pulsed-nozzle Fourier transform microwave spectroscopy. The experimental structure places the fluorine of the HF near the C$_3$ axis of the BF$_3$, with an intermolecular B—F separation of 2.544(2) Å. The proton is off axis, but rapid vibrational averaging produces a complex which is effectively a symmetric top in the ground vibrational state. The average B- -F—H angle determined from the moments of inertia is 104.1(1)°. These results are in excellent agreement with the *ab initio* calculations, which give a binding energy of 3—4 kcal/mol for the complex and a 2° out-of-plane distortion of the BF$_3$ moiety. Taken together, the results indicate a complex which is essentially weakly bound in nature, though interestingly, the intermolecular B—F distance is slightly shorter than the sum of reasonable van der Waals radii. The complex resembles an incipient donor—acceptor adduct of the kind frequently observed or invoked in solution-phase Friedel—Crafts reactions, and its relationship to such chemistry is discussed. The experiments were performed on a newly constructed instrument featuring direct software-driven control of the pulse timing sequence without the need for home-built digital electronics. The essential characteristics of the apparatus are described.

Introduction

Friedel—Crafts reactions comprise a wide variety of synthetically useful processes, of which the BF$_3$-catalyzed alkylation of aromatics is a well-known example.[1] When the source of the alkyl group is the corresponding alkyl fluoride, these reactions often proceed via the formation of donor—acceptor type intermediates, viz.,

$$[R-F^{\delta+}- -^{\delta-}BF_3]$$
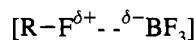
and several such complexes have even been isolated at low temperatures.[2] Although their structures were not determined, conductivity measurements of molten samples were able to provide some insight into the nature of the bonding. In particular, complexes with larger alkyl groups are apt to ionize to form carbocation tetrafluoroborates, whereas the methyl and ethyl fluoride complexes are best described as stable but unionized donor—acceptor complexes. In either case, subsequent reaction with aromatics gave rise to the same products as those obtained *in situ*. Thus, even in the non-ionic intermediates, the alkyl group appears to be an effective electrophile, suggesting a significant perturbation of the carbon—fluorine bond, and in turn, a significantly developed B- -F dative bond.

Though HF is undoubtedly less basic than the alkyl fluorides, there are intriguing aspects to its interaction with BF$_3$ as well. Solutions of BF$_3$ in liquid HF comprise a widely exploited, cost-effective superacid medium.[3,4] Its use is frequently mentioned

in the patent literature,[3] and industrial applications include the production of liquid hydrocarbons from coal[5] and the preparation of carbon fibers.[6] Also, HF/BF$_3$ is frequently used as a Friedel—Crafts catalyst in reactions which require a proton source (co-catalyst) to proceed. The solvation of BF$_3$ in HF is described by[3]

$$BF_3 + 2HF \rightleftharpoons BF_4^- + H_2F^+ \tag{1}$$
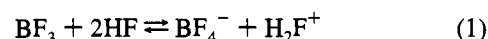
Though salts of the tetrafluoroborate (BF$_4^-$) ion are quite common, no stable tetrafluoroboric acid ("HBF$_4$") exists in the absence of a suitable proton acceptor.[1,3,7] Early studies of HF/BF$_3$ solutions, however, noted subtle indications of HF—BF$_3$ complex formation, though they were largely ignored at the time.[8,9] Interestingly, while the action of Group V pentafluorides in liquid HF has been extensively investigated, corresponding studies detailing the behavior of BF$_3$ in HF solutions are relatively rare.[10]

In light of the importance of these systems, Silla and co-workers have conducted a series of theoretical studies on HF—BF$_3$ and related alkyl fluoride complexes.[11—14] Several of these studies report minimum energy structures and indeed suggest that formation of HF—BF$_3$ plays a vital energetic role in the

* Authors to whom correspondence should be addressed.

† Present Address: Department of Chemistry, University of Nevada, Reno, Nevada 89557.

® Abstract published in *Advance ACS Abstracts*, December 1, 1995.

(1) (a) Olah, G. A. *Friedel—Crafts and Related Reactions*; John Wiley and Sons; New York, 1963. (b) Olah, G. A. *Friedel—Crafts Chemistry*; John Wiley and Sons; New York, 1973.

(2) Olah, G.; Kuhn, S.; Olah, J.; *J. Chem. Soc.* **1957**, 2174.

(3) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*; John Wiley and Sons; New York, 1985.

(4) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Science* **1979**, *206*, 13.

(5) Olah, G. A.; Bruce, M. R.; Edelson, E. H.; Husain, A. *Fuel* **1984**, *63*, 1130.

(6) Korai, Y.; Nakamura, M.; Mochida, I. *Carbon* **1991**, *29*, 561.

(7) Sharp, D. W. A. In *Advances in Fluorine Chemistry*; Stacey, M., Tatlow, J. C., Sharpe, A. G., Eds.; Academic Press: New York, 1960; Vol. 1.

(8) McCaulay, D. A.; Shoemaker, B. H.; Lien, A. P. *Ind. Eng. Chem.* **1950**, *42*, 2103.

(9) Hughes, E. C.; Darling, S. M. *Ind. Eng. Chem.* **1951**, *43*, 746.

(10) O'Donnel, T. A. *Superacids and Acidic Melts as Inorganic Chemical Reaction Media*; VCH Publishers: New York, 1993.

(11) Silla, E.; Scrocco, E.; Tomasi, J. *Theor. Chim. Acta Berlin* **1975**, *40*, 343.

(12) Alagona, G.; Scrocco, E.; Silla, E.; Tomasi, J. *Theor. Chim. Acta Berlin* **1977**, *45*, 127.

(13) Bertrán, J.; Mora, F.; Silla, E. *J. Chem. Soc., Perkin Trans. 2* **1982**, 647.

(14) Arnau, A.; Bertrán, J.; Silla, E. *J. Chem. Soc., Perkin Trans. 2* **1989**, 509.

superacidity of HF/BF$_3$ solutions. In the most recent report,[14] *ab initio* calculations on the HF—BF$_3$ complex, predicted an intermolecular B- -F bond distance of 1.84 Å and an out-of-plane distortion of the BF$_3$ moiety of 6°.[15] The optimum B- -F—H angle was 113.3°, and the calculated binding energy of the complex (relative to the separated monomers) was 18.5 kcal/mol. Interestingly, the effect of complex formation on the strength of the H—F bond was also examined, and a 90.7 kcal/mol lowering of the heterolytic HF bond dissociation energy was reported. Thus, it was suggested that complex formation was an essential step in the mechanism of eq 1.

There are some interesting (if not startling) aspects of the above structure. The intermolecular B- -F distance, for example, is 0.4 Å longer than the 1.43 Å single bond distance in BF$_4^-$,[7,16] yet nearly an angstrom shorter than the sum of any reasonable van der Waals radii for boron and fluorine. Moreover, the distortion of the BF$_3$ moiety is clearly substantial, though the geometry at the boron is not tetrahedral. These results, therefore, suggest a partially formed boron—fluorine bond between the moieties, even in the gas phase, and indeed the calculated binding energy is approximately 50% of that of a typical fully-formed dative bond. Thus, it would appear that the system is reminiscent of complexes between BF$_3$ and nitrile donors which have been previously investigated in our laboratory, in which the B—N bond lengths and out-of-plane distortion of the BF$_3$ lie between the van der Waals and chemically bound limits.[17-19] Quantitatively, however, this picture is at odds with chemical intuition in that the calculated binding energy of the HF adduct is substantially larger than that previously determined for either HCN—BF$_3$[20] or CH$_3$CN—BF$_3$.[21] Moreover, the calculated out-of-plane distortion of the BF$_3$ subunit is greater than that in the HCN complex,[18] and comparable to that observed in the CH$_3$-CN adduct.[17] Such results are somewhat surprising since nitriles are almost certainly more basic than fluorides, and should form the more strongly bound complexes.

In this paper, we present an experimental determination of the structure of HF—BF$_3$ by pulsed nozzle Fourier transform microwave spectroscopy, as well as a re-investigation of the complex by *ab initio* theory. The inclusion of electron correlation and the use of large basis sets substantially change the calculated structure and binding energy of the complex relative to previous reports, and the microwave structure determination is in excellent agreement with the new theoretical results. The complex appears to be much more weakly bound than earlier calculations have indicated, and the results provide a baseline for possible future studies of the analogous alkyl fluoride complexes. The complex is compared with related adducts of BF$_3$ and implications to widely known solution-phase synthetic chemistry are discussed.

Experimental Section

Rotational spectra were recorded on a newly constructed, Balle-Flygare type pulsed nozzle Fourier transform microwave spectrometer. This technique is well established, and has previously been described in detail.[22] Our system is designed to operate in the 2 to 18 GHz range, utilizing a Fabry-Perot cavity composed of two circular mirrors each with an 84 cm radius of curvature and each machined to a 40 μin. finish. The cavity is evacuated by a 20 000 L/s diffusion pump, which allows for high gas throughput and enhances ultimate sensitivity. This feature of the apparatus has aided in recent studies on dimers formed between reactive species,[23] in which one component flows continuously into the vacuum system.

The Fabry-Perot cavity is operated in reflectance mode, and complete coverage of the desired frequency range is accomplished with a single coaxial coupling source. The use of a double-stub tuner (Maury Microwave, No. 1719C) that operates throughout the desired frequency range eliminated the necessity of a waveguide coupling system for high-frequency operation. Because the microwave energy is coupled into and out of the cavity via a single antenna (located in the stationary mirror), the pulsed valve can be placed behind the mirror opposite the coupling. This allows for the injection of the component gases along the cavity axis, which can enhance sensitivity and resolution. Gasses can also be injected via the top of the cavity, perpendicular to its axis. While this is less efficient from a performance standpoint, the top of the vacuum chamber is fitted with an air lock which permits the removal and subsequent repair of the nozzle without a shutdown of the vacuum system. This feature has also facilitated recent studies of reactive species,[23] in which the nozzle source can be prone to clogging.

The interface of the instrument was done in a manner similar to that of Chuang *et al.*[24] though recent advances in computer technology have greatly simplified the procedure. Specifically, two digital counter-timer boards (Data Translation No. DT2819) are used to control all the pulse timing sequences, thus eliminating the need for home-built digital electronics. The boards each contain five digital counter-timers, and together they supply sufficient TTL voltage to all the necessary components, including the microwave switches and the pulsed valve driver (General Valve Corporation, Iota One). In addition, they provide a trigger and a 1.25 MHz timing clock for the signal digitizer (Markenrich Corporation, WAAGII). The instrument samples up to 1024 points per free induction decay (FID) signal, and can collect up to 15 FID's per gas pulse. The maximum nozzle rate is limited by the ability of the computer to store the data, but rates approaching 20 Hz are not unreasonable with a sufficiently small sample size. Typically, 10 to 15 FID's of 256 or 512 points are collected at a nozzle rate of 5 to 10 Hz. The signal is detected in quadrature, and thus the absolute molecular frequencies are measured, rather than their offset from the cavity frequency. Once collected, the signal is automatically zero-filled to 1024 points, resulting in a per-point frequency resolution of 1.22 kHz. The software allows for subsequent change of the zero-fill, and the exclusion of any of the previously collected FID sections which lack appreciable signal, thus allowing the user to further maximize the quality of a given spectrum.

In the current study, optimum signals were obtained by pulsing a mixture of 0.5% HF and 1% BF$_3$ in an argon carrier through a 0.8-mm orifice at a stagnation pressure of 600 Torr. Spectral searches corresponding to intermolecular B- -F bond lengths in the ranges 1.8—2.0 and 2.6—2.8 Å failed to produce any transitions attributable to the complex. However, following the *ab initio* calculations described below, spectra were rapidly located. Signals due to the $J = 1 \rightarrow 0$ transition of HF—^{10}BF$_3$ were initially identified on the basis of the ^{10}B quadrupole pattern. The corresponding HF—^{11}BF$_3$ transitions were promptly located and displayed a characteristic ^{11}B hyperfine pattern. The $J = 2 \leftarrow 1$ transitions were then observed at approximately twice the frequency of the $J = 1 \leftarrow 0$ for both isotopomers. Elimination of either component gas from the pulsed mixture was not entirely possible, as the handling system was well passivated with both HF and BF$_3$ after several weeks of searching. Spectra of the HF complex, however, did essentially vanish upon passivation of the system with deuterium, and absolute confirmation of the spectral carriers was obtained by the ability to predict and observe new transitions of the deuterated isotopomer.

(15) In the calculated structure, the HF leans toward one of the fluorines of the BF$_3$ creating two distinct F—B- -F angles whose reported values are 92.7° and 99.6°. The 6° out-of-plane distortion is calculated from this structure as $\alpha - 90°$, where α is the angle between the approximate C$_3$ axis of the BF$_3$ and the B—F bonds in the BF$_3$.

(16) (a) Hoard, J. L.; Blair, V. *J. Am. Chem. Soc.* **1935**, *57*, 1985. (b) Pendred, D.; Richards, R. *Trans. Faraday Soc.* **1955**, 51, 468.

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

(18) Reeve, S. W.; Burns, W. A.; Lovas, F. J.; Suenram, R. D.; Leopold, K. R. *J. Phys. Chem.* **1993**, *97*, 10630.

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

(20) Hankinson, D.; Almlöf, J.; Leopold, K. R. Submitted.

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

(22) Balle, T. J.; Flygare, W. H. *Rev. Sci. Instrum.* **1981**, 52, 33.

(23) (a) Phillips, J. A.; Canagaratna, M.; Goodfriend, H.; Leopold, K. R. *J. Phys. Chem.* **1995**, *99*, 501. (b) Canagaratna, M.; Goodfriend, H.; Phillips, J. A.; Leopold, K. R. Manuscript in preparation.

(24) Chuang, C.; Hawley, C. J.; Emilsson, T.; Gutowsky, H. S. *Rev. Sci. Instrum.* **1990**, *61*, 1629.

No additional transitions attributable to excited internal rotor states were observed for either the HF or DF species.

Computational Methods and Results

The geometry of HF−BF₃ was fully optimized at the Hartree−Fock, MP2, and MP4(SDTQ) levels using several basis sets, the largest containing multiple polarization functions on all atoms—d95v++(2df,2p) in standard nomenclature. The potential surface is extremely flat in the degrees of freedom describing the relative orientation of the two monomer units. The only minimum found on the potential surface is a weakly bound complex, with a B- -F distance of 2.45 Å at the MP4/d95v++(2df,2p) level of theory. While the treatment of correlation effects is crucial to obtain an even qualitatively correct structure, these effects appear to be well accounted for with second-order perturbation theory. The MP2 and MP4 structures differ by less than 0.02 Å in the B- -F distance, and show negligible differences in all other geometry parameters. The somewhat smaller 6-311++G** basis gives a B- -F distance of 2.42 Å. The basis set would thus appear to be essentially converged with a basis set of this quality—however, a pointwise calculation of basis set superposition (BSSE) effects with the counterpoise method increases the B- -F distance by as much as 0.10 Å. At the present level of theory the counterpoise method almost certainly overestimates the BSSE, and the calculation thus places the best theoretical estimate of the B- -F distance in the range 2.45−2.55 Å. All calculations were done with the program systems Supermolecule[25a] and Gaussian94[25b] on a Cray C90 at the Minnesota Supercomputer Center.

In light of the weak interaction and the poorly defined equilibrium structure, the potential surface was systematically searched for other possible minima. In particular, the existence of a short bond length (tetrafluoroboric acid type) structure as suggested in previous theoretical work[14] was thoroughly investigated, as was an FH--FBF₂ hydrogen-bonded structure. While the B- -FH distance was found to vary dramatically depending on the level of theory, a nonlinear geometry with the hydrogen atom eclipsed relative to one of the fluorine atoms of BF₃ was the only minimum found on the potential surface with all but the smallest basis sets. However, the torsional barrier for the FH unit is only 100 cm⁻¹, and the internal rotation of the HF about an axis perpendicular to the intermolecular bond is also quite facile.

The binding energy is at 3.9 kcal/mol, calculated at the MP4 level with the optimized MP2 geometries. The value is reduced to 3.4 kcal/mol after correction for basis set superposition error (BSSE). Consistent with the small binding energy, the calculation indicates that the BF₃ and HF units are only weakly disturbed by the interaction. The out-of-plane distortion angle of the BF₃ is less than 2°, the B−F distance eclipsed relative to HF is elongated by 0.007 Å relative to free BF₃, and the other two B−F bonds are unchanged. The HF distance is elongated by 0.003 Å. The equilibrium structure is shown in Figure 1a.

(25) (a) Feyereisen, M. W.; Almlöf, J, SUPERMOLECULE: a program for electronic structure calculations (University of Minnesota). (b) Gaussian 94, Revision B.3, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1995.

(26) Janda, K. C.; Bernstein, L. S.; Steed, J. M.; Novick, S. E.; Klemperer, W. *J. Am. Chem. Soc.* **1978**, *100*, 8074.
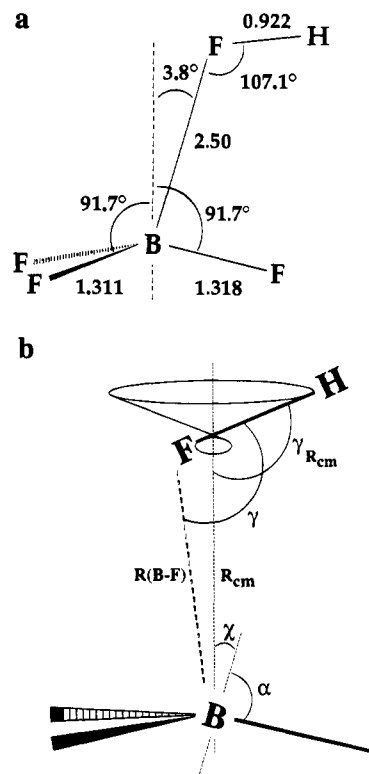
Figure 1. (a) The equilibrium structure of HF—BF₃ determined from *ab initio* calculations. (b) Convenient coordinates for determining the vibrationally averaged structure of the complex from measured moments of inertia.

The dipole moment of the complex is 2.093 D and it lies along an axis rotated 57° from the intermolecular B- -F bond (clockwise in Figure 1a). The dipole moment of HF is calculated to be 1.963 D, and the induced moment of the complex, $\mu_{ind} = \mu_{complex} - \mu_{HF}$, has a magnitude of 0.58 D. μ_{ind} lies 12.2° off the B- -F axis, and its component parallel to the B- -F bond is 0.57 D. This is perhaps somewhat large, but it can be partially accounted for on the basis of the BF₃ polarity generated by its deformation out of plane. Jurgens and Almlöf[21] have calculated a dipole moment of 1.016 D for an 8° pyramidally distorted BF₃, giving an effective B−F bond moment of about 2.43 D. Thus the calculated 1.8° deformation of the BF₃ accounts for approximately 0.23 D along its axis (which is very nearly coincident with the B- -F axis).

The intermolecular stretching force constant was also calculated. At the highest level of theory, but without correction for BSSE, a value of 0.129 mdyn/Å was obtained. With the BSSE correction, the value is reduced to 0.118 mdyn/Å. If the radial potential is fitted to the form $V(r-r_e) = a_0(r-r_e)^2 + a_1(r-r_e)^3$, the anharmonic zero-point extension of the B- -F bond is readily estimated in the pseudo-diatomic approximation[27] to be 0.0097 Å.

Rotational Spectrum and Analysis

Tables 1−4 list the observed transition frequencies of four isotopomers of HF−BF₃, and a sample spectrum is displayed in Figure 2. Several of the F″ ← F′ transitions observed in this study appeared as dense multiplets which could not be assigned as either HF spin−spin or deuterium quadrupole hyperfine structure. Moreover, a reexamination of the $J = 1$ ← 0 transitions in Ar--BF₃[26] revealed nearly identical splittings

(27) (a) Townes, C. H.; Schawlow, A. L. *Microwave Spectroscopy*; Dover: New York, 1975. (b) Gordy, W.; Cook, R. L. *Microwave Molecular Spectra*; John Wiley and Sons: New York, 1984.

Table 1. Observed Transitions of HF−^{10}BF$_3$[a]

J''	F''	J'	F'	K	freq[b]	obs − calc
0	3	1	2	0	6669.080	−0.001
0	3	1	4	0	6669.484	0.002
0	3	1	3	0	6670.626	−0.001
1	4	2	5	1	13338.718	0.000
1	3	2	3	0	13338.857	−0.001
1	2	2	1	0	13338.971	−0.001
1	3	2	4	0	13339.022	−0.001
1	4	2	5	0	13339.144	0.000
1	4	2	3	1	13339.144	−0.003
1	4	2	4	1	13339.231	0.002
1	3	2	2	1	13339.373	0.001
1	2	2	2	0	13339.716	0.005
1	3	2	3	1	13339.716	−0.006
1	3	2	4	1	13339.807	0.005
1	4	2	4	0	13340.165	−0.002
1	2	2	3	0	13340.405	0.001

[a] All values in MHz. [b] Measurement uncertainties are typically 4−6 kHz. See text for discussion.

Table 2. Observed Transitions of HF−^{11}BF$_3$[a]

J''	F''	J'	F'	K	freq[b]	obs − calc
0	1.5	1	0.5	0	6653.936	0.001
0	1.5	1	2.5	0	6654.491	0.001
0	1.5	1	1.5	0	6655.178	−0.007
1	1.5	2	0.5	0	13307.740	0.000
1	0.5	2	0.5	1	13308.099	−0.003
1	1.5	2	1.5	0	13308.434	0.000
1	0.5	2	1.5	1	13308.453	0.007
1	2.5	2	3.5	1	13308.622	−0.003
1	2.5	2	1.5	1	13308.726	0.002
1	1.5	2	0.5	1	13308.726	0.002
1	2.5	2	3.5	0	13308.926	−0.004
1	1.5	2	2.5	0	13308.926	−0.004
1	1.5	2	1.5	1	13309.073	0.002
1	1.5	2	2.5	1	13309.319	0.000
1	2.5	2	2.5	0	13309.622	−0.002
1	0.5	2	1.5	0	13309.686	0.002

[a] All values in MHz. [b] Measurement uncertainties are typically 4−6 kHz. See text for discussion.

Table 3. Observed Transitions of DF−^{10}BF$_3$[a]

J''	F''	J'	F'	K	freq[b]	obs − calc
0	3	1	2	0	6448.597	0.002
0	3	1	4	0	6448.996	0.000
0	3	1	3	0	6450.137	−0.004
1	2	2	1	1	12896.815	−0.002
1	2	2	2	1	12897.193	0.008
1	4	2	5	1	12897.303	−0.001
1	2	2	3	1	12897.536	0.003
1	4	2	3	1	12897.730	−0.004
1	4	2	4	1	12897.816	−0.001
1	3	2	3	0	12897.894	0.000
1	3	2	2	1	12897.959	0.001
1	2	2	1	0	12898.013	0.005
1	3	2	4	0	12898.053	−0.005
1	4	2	5	0	12898.180	0.000
1	3	2	4	1	12898.389	0.001
1	4	2	4	0	12899.203	0.000

[a] All values in MHz. [b] Measurement uncertainties are typically 4−6 kHz. See text for discussion.

which probably arise, therefore, from additional spin−spin and/ or spin−rotation interactions of the BF$_3$. Because of these partially resolved splittings, neither the deuterium quadrupole coupling constant in the DF species nor the HF spin−spin coupling constant in the protonated form were determined. The data given in Tables 1−4 represent weighted averages of the resolved and partially resolved components. Based on the reproducibility of frequencies of clean transitions, and taking into account the effect of compounding errors in the averaging

Table 4. Observed Transitions of DF−^{11}BF$_3$[a]

J''	F''	J'	F'	K	freq[b]	obs − calc
0	1.5	1	0.5	0	6433.157	−0.005
0	1.5	1	2.5	0	6433.710	0.001
0	1.5	1	1.5	0	6434.398	0.003
1	0.5	2	0.5	1	12866.092	−0.003
1	1.5	2	0.5	0	12866.205	0.003
1	0.5	2	1.5	1	12866.442	0.004
1	2.5	2	3.5	1	12866.615	0.001
1	1.5	2	1.5	0	12866.886	−0.002
1	2.5	2	2.5	1	12866.954	−0.003
1	1.5	2	1.5	1	12867.055	0.000
1	1.5	2	2.5	1	12867.298	−0.002
1	2.5	2	3.5	0	12867.377	0.000
1	1.5	2	2.5	0	12867.377	0.000
1	2.5	2	2.5	0	12868.060	−0.003

[a] All values in MHz. [b] Measurement uncertainties are typically 4−6 kHz. See text for discussion.
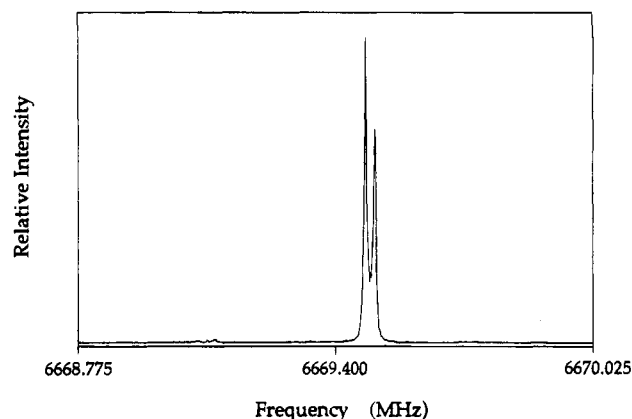

Figure 2. The $J = 0$, $F = 3$ to $J = 1$, $F = 4$ transition in HF−^{10}BF$_3$. This signal was averaged for approximately 60 s, and contains 4500 individual FID's. The observed splitting is due to the Doppler effect. The weaker signal at the left is the $J = 0$, $F = 3$ to $J = 1$, $F = 2$ transition.

procedure, we estimate a typical uncertainty of 4−6 kHz in the reported numbers. Further analysis of these extra hyperfine effects was not pursued.

The observed spectrum is that of a symmetric top. This was evident, initially, from the absence of asymmetry doubling in the $K = 1$ component of the $J = 2 \leftarrow 1$ transition, and later from the failure of any structure reasonably consistent with the *ab initio* calculations to reproduce the observed separation between the $K = 0$ and 1 components (see next section). Thus, transition frequencies were fit to the usual expression for a symmetric rotor with J- and K-dependent distortion terms and a single quadrupolar nucleus,[27] viz.

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

Here ΔE_{Quad} is the difference in quadrupole energy for the upper and lower rotational states, which was calculated via the usual first-order treatment,[27] and the other symbols have their usual meanings. Spectroscopic constants determined from a least-squares fit of the observed frequencies are displayed in Table 5. Residuals from these fits are shown with the transition frequencies in Tables 1−4.

Structure Analysis

The *ab initio* structure places the hydrogen off the C_3 axis of the BF$_3$, but the observed spectrum is that of a symmetric rotor. Strictly speaking, the failure to observe asymmetry splitting in the $K = \pm 1$ levels, as noted above, provides only negative

Table 5. Spectroscopic Constants for Isotopic Derivatives of $HF-BF_3{}^a$

	$HF-{}^{10}BF_3$	$HF-{}^{11}BF_3$	$DF-{}^{10}BF_3$	$DF-{}^{11}BF_3$
$\langle(B+C)/2\rangle$	3334.9065(58)	3327.3370(70)	3224.6627(82)	3216.9446(29)
D_J	0.01123(93)	0.0112(11)	0.0109(12)	0.01071(30)
D_{JK}	0.05037(22)	0.0490(30)	0.1628(16)	0.1638(16)
$eqQ(B)$	5.726(29)	2.777(17)	5.727(33)	2.742(16)

^{a} All values in MHz. Uncertainties quoted are two standard errors in the fit.

evidence for the lack of an asymmetric structure. We note, however, that the transitions observed in this study were generally quite strong and we expect that an additional component, if present, would have been easy to locate within the spectral range scanned. Moreover, preliminary calculations indicate that the separation between the $2_{02} \leftarrow 1_{01}$ and the $2_{12} \leftarrow 1_{11}$ transitions for a rigid asymmetric rotor vary from 17.9 to 8.5 MHz as the ^{10}B--F−H angle is varied from 90° to 134°, whereas the observed separation between the linecenters of the $K = 0$ and ± 1 components is only about 200 kHz (for the protonated species). Thus, the observed spectrum is not even approximately consistent with that of an asymmetric top rigidly constrained to the theoretical structure. The observed separation, however, is of the magnitude expected for D_{JK} centrifugal distortion effects of a symmetric rotor. For example, the corresponding separation in $HCN-BF_3$ is about 64 kHz.[18] These observations, taken together, suggest that the symmetric top character of the spectrum arises from rapid torsional averaging of the relative $HF-BF_3$ orientation at or near the theoretically predicted B--F−H angle. In effect, the complex appears as the symmetric top analog of a quasi-linear molecule. Both the strong H/D isotopic dependence of D_{JK} seen in Table 5 and the low barrier to HF internal rotation obtained from the ab initio calculations are fully consistent with the occurrence of such a large amplitude motion in the complex.

Further preliminary observations indicate that the complex is also essentially weakly bound. Rough calculation of the intermolecular B--F bond length from the measured rotational constants gives an estimate of about 2.5 Å, which is much longer than the 1.43 Å B−F distance in $BF_4{}^-$.[7,16] In addition, the observed values of $eqQ(B)$ are very near that in the weakly-bound Ar--BF_3.[26] From an ab initio standpoint, the complex is certainly weakly bound, with a binding energy of only 3−4 kcal/mol and only minor changes in the HF and BF_3 equilibrium bond lengths. Thus, in the determination of the structure of the complex, we invoke the usual approximation in which the B−F and H−F bond lengths are constrained to their experimental values for the ground vibrational states of the monomers (1.3102 Å[28] and 0.925595 Å,[29] respectively). The out-of-plane distortion in the BF_3 unit, however, is retained as an adjustable parameter. This is appropriate in view of previous results for BF_3 adducts in which significant angular distortion is observed[17,18] and in light of the present ab initio results which predict a 1.7° out-of-plane deformation. It is also quite reasonable, since distortion of the BF_3 is much more sensitive than the monomer bond lengths to incipient bond formation. For example, in the crystalline $HCN-BF_3$ adduct, in which the BF_3 unit is distorted by 14°, the B−F bond is lengthened by only 0.051 Å relative to that in free BF_3.[19]

In view of the above, the most natural coordinates for the structural analysis of rotational constants are displayed in Figure 1b. The out-of-plane distortion of the BF_3 unit is represented by α, the angle between the C_3 axis and the B−F bonds of BF_3. The average angular excursion of the C_3 axis of the BF_3 about the "pseudo-C_3" axis of the complex (the vertical dotted

line) is given by χ. The intermolecular distance can be represented by either of two distinct coordinates, R_{cm}, the usual center of mass separation of the moieties, or R(B--F), the *effective* B--F bond distance. The former is most convenient for analysis of the moments of inertia of individual isotopomers (eq 3, below), while the latter is expected to be more nearly isotopically invariant and is more useful in specifying the structure of the complex. Similarly, the angular orientation of the HF unit is represented by either $\gamma_{R_{cm}}$, the angle between the H−F bond and R_{cm}, or γ, the *effective* B--F−H bond angle. The torsional averaging described above is represented by the conical figure upon which the HF is drawn.

With the coordinates defined in this manner, the vibrationally averaged moment of inertia of the complex can be expressed in simple analytical terms. According to the theoretical structure, the complex is asymmetric and thus the instantaneous a-axis does not coincide with R_{cm}. However, when the moments of inertia are averaged over the free or nearly free torsional motion of the HF, and with $\langle\chi\rangle = 0$, the average values of I_{bb} and I_{cc} become equal. Moreover, the products of inertia vanish in a coordinate system with R_{cm} along z and hence the experimentally determined moment of inertia of the complex, $\langle I_{bb}\rangle$, is given by[30]

$$\langle I_{bb}\rangle = h^2/4\pi^2\langle(B+C)\rangle = M_s\langle R_{cm}\rangle^2 + (1/2)I_{bb}(BF_3)\{1 + \langle\cos^2\chi\rangle\} + (1/2)I_{cc}(BF_3)\langle\sin^2\chi\rangle + (1/2)I_{bb}^{H(D)F}\{1 + \langle\cos^2\gamma_{R_{cm}}\rangle\} \quad (3)$$

Here, M_s is the pseudo-diatomic reduced mass, m(HF)m(BF₃)/m(HFBF₃), and the I_{gg}'s represent the monomer moments of inertia. Since the BF_3 unit is allowed to distort from the planar configuration, $I_{bb}(BF_3)$ and $I_{cc}(BF_3)$ contain the α-dependence of $\langle I_{bb}\rangle$,[27] viz.,

$$I_{bb}(BF_3) = (3/2)m_F r^2 \sin^2\beta + [3m_B m_F/(m_B + 3m_F)]r^2 \cos^2\beta \quad (4)$$

$$I_{cc}(BF_3) = 3m_F r^2 \sin^2\beta \quad (5)$$

where r is the B−F bond length in the BF_3 moiety and $\beta = 180° - \alpha$.

Since the complex is essentially weakly bound, we invoke the usual approximation that the reduction of $eqQ(B)$ from its values in free $^{10}BF_3$ and $^{11}BF_3$ is primarily projective, viz.,

$$eqQ(B)_{complex} = eqQ(B)_0\langle(3\cos^2\chi - 1)/2\rangle \quad (6)$$

Hence, with the 3.002(13) MHz[31] value of $eqQ(B)_0$ for $^{11}BF_3$, and the known ratio of the $^{10}B/^{11}B$ quadrupole moments, equal to 2.084(2),[27b,32] values of $\cos^{-1}(\langle\cos^2\chi\rangle^{1/2})$ can be determined for all isotopic species studied. These range from 12.9° to 13.9°

(28) Brown, C. W.; Overend, J. *Can. J. Phys.* **1968**, *46*, 977.

(29) Guelachvili, G. *Opt. Commun.* **1976**, *19*, 150.

(30) Fraser, G. T.; Leopold, K. R.; Klemperer, W. *J. Chem. Phys.* **1984**, *80*, 1423.

(31) (a) Dreizler, H. Z. *Naturforsch.* **1992**, *47a*, 342. (b) Vormann, K. Dissertation, Kiel, 1991.

(32) Dawent, B. NBS Publication NSRDS-NBS-31, 1970.

Table 6. Selected Properties of HF−BF$_3$

	ab initio	microwave[a]
R(B- -F) (Å)	2.45−2.55	2.544(2)[b]
γ (deg)	107.1	104.1(1)
χ (deg)		13.6(4)[c]
α (deg)	91.8	90.1[d]
ΔE (kcal/mol)	3−4	
k_s (mdyn/Å)	0.118	0.089(1)[e]
μ (D)	2.093[f]	

[a] Quoted uncertainties in the structural parameters represent sensitivity to approximations and model errors, not standard errors from the least-squares fit. See text for discussion. [b] Zero-point vibrationally averaged value. The anharmonic zero-point extension of the intermolecular bond is estimated to be 0.0097 Å. See text for additional details. [c] This value is the average of four determinations from the nuclear quadrupole coupling constants of the boron and was constrained in the fit. [d] The least-squares fit gives an unreasonably precise determination of 90.090(2). See text for discussion. [e] Quoted uncertainty represents the scatter among isotopic determinations. The true uncertainty arising from model errors cannot be estimated with the available information. [f] Oriented 57° from the intermolecular B- -F bond axis. See text for discussion.

with an average value of 13.6°. This scatter is more likely due to measurement and model errors than to actual variations in vibrational amplitude between isotopic species, as the moments of inertia of BF$_3$ are only weakly dependent on the boron mass. Therefore, the value of χ is constrained to 13.6° in the subsequent analysis.

Because the moments of inertia of HF and DF are significantly different, the zero-point vibrational amplitudes of these moieties in their respective complexes are not the same. In linear complexes, this normally leads to different vibrationally averaged excursion angles away from the a-inertial axis of the complex. For a bent equilibrium geometry, however, the oscillations are about a *different* axis (defined here by the equilibrium orientation of the HF bond), and thus isotopic differences in the average angle that the H(D)F bond makes with the a-axis of the complex are a result of subtle aspects of the shape of the HF bending potential. In short, it is not immediately clear to what degree the average angular position of the H(D)F will be consistent between the isotopomers, i.e., whether it is appropriate to use a single value of γ to describe the complex. Unfortunately, in the absence of any information from hyperfine constants, H/D substitution is the only measure of this orientation. Thus, to check the consistency of γ between the protonated and deuterated forms, the four pairs of observed rotational constants which represent H/D substitution were used to determine values of R(B- -F) and γ with the values of α and χ constrained to 90° and 13.6°, respectively. The resulting values are remarkably consistent among the pairs, with R(B- -F) ranging only from 2.5464 to 2.5466 Å, and γ ranging from 104.05° to 104.21°. This, together with the very close agreement with theory, suggests that a single angle can be used to describe both the protonated and deuterated forms and that this angle is reasonably well determined by H/D substitution. It is satisfying to note that at this angle, both the HF spin−spin and deuterium quadrupole hyperfine structure are expected to be seriously convoluted with the BF$_3$ hyperfine interactions noted above, and that this is consistent with our inability to assign individual HF- or DF-related hyperfine components.

With these assumptions, the final structure of the complex can be derived from a least-squares fit of the four observed rotational constants to R(B- -F), γ, and α. The results are given in Table 6. The uncertainty in χ is quoted as the standard deviation in the four redundant determinations. For R(B- -F), although the standard error in the fit was only 0.0002 Å, constraint of χ to the extreme values encompassed by its

uncertainty produced a range of R(B- -F) of ±0.0015 Å about the best fitted value. Similarly, while the standard error in γ was only 0.0047°, the values corresponding to the uncertainty in χ varied by ±0.1° about its best value. The uncertainties in Table 6 reflect these ranges. We note, however, that small systematic *shifts* in the reported values can arise from changes in the monomer bond lengths upon complexation. In the case of the BF$_3$, an increase in r_{BF} by an amount equal to the average elongation in equilibrium bond length determined from the *ab initio* calculations (0.0023 Å) lowers R(B- -F) by 0.002 Å and increases γ by 0.11°. Similarly, the effect of an analogous elongation of the HF bond (0.003 Å) decreases R(B- -F) by only 0.0001 Å, but increases γ by 0.08°.

It is interesting to note that the fitted value of the out-of-plane distortion angle of the BF$_3$, α, is very close to 90°. We have shown previously, however, that α becomes increasingly difficult to measure for values near 90°[18] and thus we expect that the 0.002° standard error obtained in the fit described above is unrealistic.[33] Nonetheless, it is clear that the spectra indicate an out-of-plane distortion of the BF$_3$ which is small, and it is satisfying that experiment and theory concur in this regard as well.

Finally, the stretching force constant for the intermolecular bond can be estimated from D_J in the usual manner[34] assuming that it is the only bond which contributes significantly to the centrifugal stretching of the molecule, viz.,

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

The observed values of D_J for the four observed isotopomers yield values of k_s in the range 0.088 to 0.090 mdyn/Å, with an average value of 0.089 mdyn/Å.

Discussion

Table 6 summarizes the salient features of the HF−BF$_3$ complex determined in this study, and it is clear that the present theoretical and experimental results are in excellent agreement. Moreover, it is apparent that the overall picture of the HF−BF$_3$ complex obtained here is in marked disagreement with that of earlier work.[14] Specifically, the intermolecular B--F distance is 0.7 Å longer, the out-of-plane distortion of the BF$_3$ is substantially less, and the binding energy is five to six times smaller than previously reported. Clearly the system is more weakly bound. Thus, although the heterolytic dissociation energies have not been calculated in the present study, it seems unlikely that the HF bond in the complex is substantially weakened, as previously suggested.[12,14]

That the complex is bound fairly weakly can be further seen by inspection of Table 7, which compares the new data obtained in this work with similar results for other complexes of BF$_3$. k_s is the stretching force constant for the intermolecular bond, $eqQ(^{11}B)$ is the nuclear quadrupole coupling constant of the boron in the ^{11}B isotopomer, and ΔE is the calculated binding energy of the complex. It is clear from the force constants that, in terms of bond rigidity, the B- -F bond in the HF complex is slightly less rigid than the B--N bond in the nitrile complexes, and somewhat more rigid than the corresponding bond in the Ar and HCl species. The binding energies for the HF and nitrile complexes reflect this trend. The quadrupole coupling constant of the boron in HF−BF$_3$ is similar to those in Ar−BF$_3$, HCl−

(33) We note, however, that fits with α constrained to 90° satisfactorily reproduce the observed moments of inertia, whereas fits with α constrained to larger angles (e.g., 91°) are of significantly poorer quality.

(34) (a) Fraser, G. T.; Suenram, R. D.; Lovas, F. J. *J. Chem. Phys.* **1987**, *86*, 3107. (b) Fraser, G. T.; Lovas, F. J.; Suenram, R. D.; Nelson, D. D., Jr.; Klemperer, W. *J. Chem. Phys.* **1986**, *84*, 5983.

Microwave and ab Initio Investigation of HF−BF₃

J. Am. Chem. Soc., Vol. 117, No. 50, 1995 12555

Table 7. Comparison of Physical Properties of Selected BF_3 Complexes

donor	k_s (mdyn/Å)	$eqQ(^{11}B)$	$-\Delta E$ (kcal/mol)
Ar	0.029[a]	2.70(5)[a]	
HCl	0.051[b]	2.672(25)[b]	
HF	0.089[c]	2.777(17)[c]	3−4[c]
HCN	0.103[d]	2.813(16)[d]	4.6[e]
CH₃CN	0.094[f]	2.377(9)[f]	5.7[g]
NH₃	4.14[h]	1.21[i]	19.2[e]

[a] Reference 26. [b] Reference 35. [c] This work. [d] Reference 18. [e] Reference 20. [f] Reference 17. [g] Reference 21. [h] Reference 36. [i] Reference 37.

BF_3, and even $HCN−BF_3$. Since the former two are essentially weakly bound complexes, for which no electronic rearrangement is expected, the similarity of the quadrupole coupling constants indicates comparable angular excursion amplitudes and hence a comparable degree of angular non-rigidity of the BF_3 moiety.

It is interesting to note, however, that although the system appears weakly bound in most regards, the intermolecular B- -F bond is slightly shorter than that expected for an ordinary van der Waals complex. This is readily seen by subtracting the difference in the van der Waals radii of chlorine and fluorine from the 3.17 Å B- -Cl distance in HCl- -BF_3.[35] The difference in radii between the two halogens can be estimated by using either the known structures of HF- -HCl[38] and (HCl)₂[39] or those of HCl- -HF[38] and (HF)₂.[40] In the former case, one obtains an estimate of 2.67 Å for the B- -F bond length in HF−BF_3, while in the latter case, the estimate is 2.69 Å. The use of standard van der Waals radii for fluorine and chlorine[41] gives 2.72 Å. Thus, the 2.544(2) Å B- -F distance in HF- -BF_3 is one to two tenths of an angstrom shorter than anticipated for an ordinary van der Waals bond. We note, of course, that this difference is small in comparison with the precision with which van der Waals radii are typically meaningful, and that indeed the definition of a van der Waals radius for boron is particularly tenuous due to electron deficiency. However, the consistency among several estimates suggests that the difference is probably real. Moreover, the small but finite angular distortion obtained theoretically is fully consistent with this result. That these trends are not reflected by the force constants or quadrupole coupling constant is not surprising, as similar results have been obtained in the case of the nitrile complexes[18,42] which are even more strongly bound.

In this light, it is interesting to make note of some apparent differences in interaction between HCl and HF with BF_3 in solution. Although the sum of appropriate van der Waals radii for HF−BF_3 exceeds the gas-phase B- -F distance by 0.1−0.2 Å, an analogous calculation for HCl−BF_3 correctly predicts the measured B- -Cl distance[35] to within 0.034 Å. This agrees with

the previously stated conclusion[35] that HCl−BF_3 is truly a weakly bound complex, and somewhat contrasts the present situation for HF−BF_3, for which the intermolecular bond distance suggests the beginnings of a new bond. Interestingly, in solution, a low-temperature examination of a liquid HCl/ BF_3 mixture showed no sign of any interaction between the species.[43] However, as described above, BF_3 is quite active in liquid HF, and indeed subtle indications of complex formation have even been observed. For example, a marked increase in the solubility of BF_3 in HF at temperatures below 0 °C has been reported, and the possibility of complex formation has been noted.[9] Thus, while these observations do not rigorously point to complexation in solution, they are indeed rather intriguing in light of the gas-phase results and suggest that perhaps the role of complex formation in HF/BF_3 solutions should be reexamined.

Finally, in light of the above results, it is interesting to speculate on the role that solvents may play in synthetically useful reactions involving this and related complexes. With a fluorine-bound structure, the system is clearly of the donor− acceptor type frequently invoked in Friedel−Crafts chemistry. However, in the gas phase the binding is quite weak. Nonetheless, the intermolecular B- -F bond is somewhat short and the BF_3 is probably deformed out of plane slightly, indicating the incipient formation of a new bond. We have shown previously[17−19,42,44] that for such systems which lie precariously on the edge between bonding and nonbonding, it is the creation of an environment which to a large extent drives the formation of the dative bond. For example, the B−N bond lengths in CH₃CN− and HCN−BF_3 are shorter by 0.381(11) and 0.835(31) Å, respectively, in the solid state than they are in the gas-phase adducts, and the NBF angles are 10(1)° and 14.1(18)° larger.[45] Thus, it is reasonable to expect that the effect of solvent on Friedel−Crafts intermediates could be significant. In the particular case of HF−BF_3, the formation of $BF_4^-H^+$ leaves behind a bare proton, and this may be too energetically costly to occur without the formation of a genuine bond to a proton acceptor. However, for alkyl fluorides, which leave behind more stable carbocations, it is interesting to speculate that the solvent may indeed have a substantial effect on the nature of the F- -B bond. Thus, the suggestion by Silla and co-workers[14] that the HF bond is considerably weakened in the complex, though unlikely for HF−BF_3 in the gas phase, may assume greater importance for alkylated intermediates in solution.

Conclusion

The HF−BF_3 complex has been examined via *ab initio* methods and the spectra of four of its isotopomers were observed via pulsed nozzle Fourier transform microwave spectroscopy. The experimental and theoretical results are in excellent agreement. The experimental structure places the fluorine of the HF near the C_3 axis of the BF_3 moiety, with an intermolecular B−F separation of 2.544(2) Å. The proton is off the intermolecular axis, but rapid vibrational averaging renders the complex effectively symmetric in the ground vibrational

(35) LoBue, J. M.; Rice, J. K.; Blake, T. A.; Novick, S. E. *J. Chem. Phys.* **1986**, *85*, 4216.

(36) Taylor, R. C. In *Boron-Nitrogen Chemistry. Adv. Chem. Ser.* **1964**, *42*, 59.

(37) (a) Legon, A. C.; Warner, H. E. *J. Chem. Soc., Chem. Commun.* **1991**, 1397. (b) Fujiang, D.; Fowler, P. W.; Legon, A. C. *J. Chem. Soc., Chem. Commun.* **1995**, 113

(38) (a) Janda, K. C.; Steed, J. M.; Novick, S. E.; Klemperer, W. *J. Chem. Phys.* **1977**, *67*, 5162. (b) Fraser, G. T.; Pine, A. S. *J. Chem. Phys.* **1989**, *91*, 637.

(39) (a) Ohashi, N.; Pine, A. S. *J. Chem. Phys.* **1984**, *81*, 73. (b) Blake, G. A.; Busarow, K. L.; Cohen, R. C.; Laughlin, K. B.; Lee, Y. T.; Saykally, R. J. *J. Chem. Phys.*, **1988**, 89, 6577.

(40) (a) Dyke, T. R.; Howard, B. J.; Klemperer, W. *J. Chem. Phys.* **1972**, *56*, 2442. (b) Howard, B. J.; Dyke, T. R.; Klemperer, W. *J. Chem. Phys.* **1984**, *81*, 5417.

(41) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 3rd ed.; Interscience: New York, 1972; p 120.

(42) K. R. Leopold In *Advances in Molecular Structure Research*; Hargittai, I., Hargittai, M., Eds.; JAI Press, Vol. II, in press.

(43) (a) Booth, H. S.; Martin, D. A. *J. Am. Chem. Soc.* **1942**, *64*, 2198. (b) Booth, H. S.; Martin, D. A. *Chem. Rev.* **1943**, *33*, 57.

(44) Leopold, K. R.; Fraser, G. T.; Novick, S. E.; Klemperer, W. *Chem. Rev.* **1994**, *94*, 1807.

(45) The results cited for HCN−BF_3 and CH₃CN−BF_3 pertain to the formation of a crystalline environment, but recent results on CH₃CN−BF_3 indicate that even in disordered media (i.e., solvents of low dielectric constant, including an argon matrix), the formation of the bond is nearly complete. Beattie, I., private communication.

state. The average B- -F—H angle determined from moments of inertia is 104°. The *ab initio* calculations indicate that the staggered configurations represent the only minima in the intermolecular potential energy surface, and that the barrier to 3-fold internal rotation (torsion) is about 100 cm^{-1}. In addition, a 2° out-of-plane distortion of the BF$_3$ moiety is indicated theoretically. While the complex is essentially weakly bound, careful examination of its structure indicates an incipient dative bond and suggests a possible role of solvents in determining the nature of Friedel—Crafts intermediates in general. The current picture of this complex differs markedly from that put forth by previous studies, but the importance of HF- -BF$_3$

complexes in solution cannot be ruled out on the basis of the gas-phase properties of the complex.

JA952827C