van der Waals vs Covalent Bonding: Microwave Characterization of a Structurally Intermediate Case

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Abstract: The gas-phase adduct $CH_3CN–BF_3$ has been observed by rotational spectroscopy. The structure is that of a symmetric top with the nitrogen end of the CH_3CN toward the boron. The B–N bond length is 2.011 ± 0.007 Å, and the NBF angle is 95.6 ± 0.6°. The structure is reminiscent of the classical dative bond chemistry known for adducts of BF_3 with nitrogen-containing donors, and of related weakly bound complexes of BF_3, but is extremely unusual in that the bond length and bond angle are intermediate between the limits normally observed for van der Waals and covalently bonded systems. Moreover, the B–N bond length is 0.381 ± 0.011 Å longer and the N–B–F angle 10 ± 1° smaller than those determined in the solid state by X-ray crystallography, indicating a significant influence of neighboring molecules in the crystal on the structure of a single dimeric unit. We draw analogy with the well-known crystallographic work of Bürgi and Dunitz and co-workers and interpret the structure of this system as a gas-phase snapshot along the reaction path for the formation of the boron–nitrogen dative bond.

Introduction

The concepts of van der Waals and covalent interactions are thoroughly integrated into the conceptual foundations of chemistry.[1] Both structurally and energetically, these interactions are usually regarded as separate and distinct, and each important in its own way in shaping the nature and properties of matter. Such sharp distinction, for example, is epitomized by the separate (yet useful) definitions of van der Waals and covalent radii. In principle, however, there is no reason why a continuous range in behavior between these two limits should not be possible, though the identification of examples of intermediate cases, at least in the gas phase, has been rather elusive. Indeed, neither the large body of elegant work on the high-resolution spectroscopy of weakly bound molecular complexes[2] nor the even larger body of work on gas-phase, small-molecule spectroscopy[3] has enjoyed much opportunity to comment on the transition from van der Waals to covalent bonding.

The situation has been somewhat different in the solid state, however, where numerous X-ray crystallographic studies have been reported showing bond lengths and bond angles involving the same elements spanning values from those characteristic of nonbonded, van der Waals type interactions through those suggestive of incipient and ultimately fully-developed chemical bonds.[4] The classic study by Bürgi, Dunitz, and Shefter[4c] on amine–carbonyl interactions is a familiar case in point. In a series of compounds containing these groups, crystallographic data show N–C bond lengths varying from 1.5 Å (only slightly longer than an N–C covalent bond) to 3.0 Å (a typical van der Waals distance). Moreover, the shorter N–C distances correlate with longer C–O bond lengths and a more nearly tetrahedral geometry about the carbon. A key idea put forth in relation to these observations is that the locus of geometries produced by the series as a whole serves to map the reaction path for the corresponding nucleophilic addition of an amine to a carbonyl. A wide variety of systems have been studied in a similar manner, and the reaction paths determined show generally good qualitative agreement with expectations based on independent chemical evidence. The use of solid-state structure correlations has thus been widely regarded as a "static" means of observing "chemical dynamics".[4a]

An explicit assumption in the above use of structure correlations is that the perturbing effects of the crystal are negligible from the point of view of displacing the system from the reaction path.[4a] In this light, it is clear that the examination of a gas-phase

analogue of such a structure correlation would be of considerable interest if a suitable series of systems could be found. In view of the impressive advances made over the past decade in the microwave and infrared characterization of weakly bound molecular complexes,[2] such experiments should, in principle, be possible. Yet, as noted above, few, if any, species demonstrating intermediate characteristics have been observed. This is due, in part, to the extraordinary spectroscopic complexity which would be encountered if the same systems that have been studied crystallographically were to be examined at high resolution in the gas phase. Another reason is that many of the gas-phase complexes studied to date have been chosen specifically with an eye toward studying *weak* intermolecular interactions and, therefore, have been formed from unreactive binding partners which neither lend themselves to bond formation nor correspond to any known crystalline structures.[5]

In this work, we report the microwave spectrum and structure of the gas-phase complex $CH_3CN–BF_3$. At room temperature, acetonitrile and boron trifluoride react to form a crystalline solid, but at 50 °C, the solid forms a vapor which, in at least one report,[6] appears fully dissociated into the starting materials. X-ray crystallography has shown the solid to consist of discrete molecular donor–acceptor complexes, with a 1.630 (4) Å B–N bond length and N–B–F angle of 105.6 (6)°.[7] This structure is quite typical of the well-known dative bonding of nitrogen donors to BF_3,[8] but

(1) Pauling, L. C. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(2) See, for example: (a) Novick, S. E.; Leopold, K. R.; Klemperer, W. In *Atomic and Molecular Clusters*; Bernstein, E. R.; Ed.; Elsevier: Amsterdam, 1990. (b) Nesbitt, D. J. *Chem. Rev.* **1988**, *88*, 843. (c) *Structure and Dynamics of Weakly Bound Systems*, Weber, A., Ed.; Reidel: Dordrecht, 1987. (d) Miller R. E. *J. Phys. Chem.* **1986**, *90*, 3301.

(3) See, for example: (a) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; van Nostrand Reinhold: New York, 1979. (b) Hollas, J. M. *High Resolution Spectroscopy*; Butterworths: London, 1982. (c) Levine, I. N. *Molecular Spectroscopy*; Wiley: New York, 1975.

(4) (a) Bürgi, H. G.; Dunitz, J. D. *Acc. Chem. Res.* **1983**, *16*, 153 and references therein. (b) Bent, H. A. *Chem. Rev.* **1968**, *68*, 587. (c) Bürgi, H. G.; Dunitz, J. D.; Shefter, E. *J. Am. Chem. Soc.* **1973**, *95*, 5065.

(5) There has, however, been some work on reactive chemical intermediates. See, for example: (a) Gillies, J. Z.; Gillies, C. W.; Suenram, R. D.; Lovas, F. J.; Stahl, W. *J. Am. Chem. Soc.* **1989**, *111*, 3073. (b) Gillies, C. W.; Gillies, J. Z.; Suenram, R. D.; Lovas, F. J.; Kraka, E.; Cremer, D. *J. Am. Chem. Soc.* **1991**, *113*, 2412.

(6) Laubengayer, A. W.; Sears, D. S. *J. Am. Chem. Soc.* **1945**, *67*, 164.

(7) (a) Hoard, J. L.; Owen, T. B.; Buzzell, A.; Salmon, O. N. *Acta Crystallogr,.* **1950**, *3*, 130. (b) Swanson, B.; Shriver, D. F.; Ibers, J. A. *Inorg. Chem.* **1969**, *8*, 2183. (c) The crystal shows two slightly different kinds of B–F bonds, with NBF bond angles of 105.8 (2)° and 105.3 (3)°, respectively. The average value is given in the text and is suitable for the purposes of comparison.

(8) (a) Muetterties E. L. *The Chemistry of Boron and its Compounds*; Wiley: New York, 1967. (b) Booth, H. S.; Martin, D. R. *Boron Trifluoride and its Derivatives*; Wiley: New York, 1949.

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sharply contrasts the 2.6–2.8 Å bond lengths and 90° N–B–F angles previously determined in a molecular beam for the van der Waals complexes N_2–BF_3[9] and NCCN–BF_3.[10] The present study was initiated to explore whether the *gas-phase* complex CH_3C-N–BF_3, formed by expansion of the vapor in a supersonic jet, would have the same geometry found in the solid or whether it would more closely resemble the N_2 and NCCN species. Much to our surprise, the B–N bond length has neither the 1.6-Å value found in the solid nor the 2.6–2.8-Å van der Waals distance, but rather, it has an intermediate value of 2.0 Å. An N–B–F angle of 96° is also determined, representing a significant but incomplete deformation of the BF_3 toward a tetrahedral geometry. The system is thus an unusual example of intermediacy between van der Waals and covalent bonding in a gas-phase adduct. The structure is compared with that of other donor–acceptor adducts of BF_3 and is discussed, in the spirit of Bürgi and Dunitz et al., as a snapshot along the reaction path for the formation of the boron–nitrogen dative bond. The relationship of these results to the underlying assumption of negligible environmental perturbations in the X-ray structure correlation method is also discussed, and prospects for further studies of this type are considered.

Experimental Section

Spectra were observed using a Balle–Flygare[11a] type pulsed-nozzle Fourier transform microwave spectrometer, which has been described previously.[11b–d] Initial spectral searches were conducted by entraining the vapor of a heated sample of CH_3CN–BF_3 (synthesized by reacting CH_3CN with BF_3[6]) in a flowing stream of argon or by on-line mixing of 1% mixtures of CH_3CN and BF_3 in argon immediately prior to the expansion.[12] All initial searches were conducted near frequencies predicted assuming either a 1.6- or 2.6-Å B–N bond length. These searches yielded spectra of the previously uncharacterized complex Ar–CH_3CN[13] as well as known transitions of Ar–BF_3, BF_2OH, and CH_3CN, but they did not succeed in locating transitions of the desired CH_3CN–BF_3 adduct.

While these searches were in progress, an ab initio study by Jurgens and Almlöf[14] was completed in which a single potential energy minimum was determined, corresponding to a C_{3v} symmetric structure and a boron–nitrogen bond length of 2.17 Å. Guided by these results, we continued to search at frequencies predicted for intermediate bond lengths and eventually observed spectra assignable to the [11]B species of the desired complex. Optimum signals were obtained using the on-line mixing source[12] with equal flow rates of 1% mixtures of CH_3CN and BF_3 in argon, at a total stagnation pressure of 1.2 atm. Time domain signals were averaged for 500–4000 pulses (depending on the transition strength) and were Fourier transformed into the frequency domain to obtain line centers. In most cases, 256 or 512 data points were taken per pulse, providing resolution of 8 or 4 kHz, respectively.

Spectra were initially identified as originating from CH_3CN–BF_3 by the requirement that both BF_3 and CH_3CN be present and by the complex hyperfine pattern expected for this system due to the nuclear spins of both [11]B ($I = 3/2$) and [14]N ($I = 1$). Confirmation that the complex did not contain argon was readily obtained by observing the spectra using neon as the carrier gas. The final, unambiguous identification of the absorbing species was made possible, however, by the observation of a rotational progression of the [11]B species, as well as by the prediction and subsequent observation of spectra due to CH_3CN–[10]BF_3 and the [10]BF_3 and [11]BF_3 complexes with CH_3C[15]N and CD_3C[14]N.

Results

To a first approximation, the observed rotational transitions of CH_3CN–BF_3 were found to fall into the familar pattern expected for the $\Delta J = 1$, $\Delta K = 0$ transitions of a symmetric top.[15]

$$\nu = 2B(J + 1) \tag{1}$$

This immediately confirms the expected geometry of the complex, in which the symmetry axis of the CH_3CN is coincident with that of the BF_3. Due to the relatively large moment of inertia of BF_3, states of the complex with $K = 0$, ± 1, and ± 2 are populated, even at the estimated[11d] 1 K temperature of the jet. Moreover, since the $K = 0$ and ± 1 states of acetonitrile correlate with the $m = 0$ and ± 1 internal rotor states of the complex, respectively, and since their interconversion is a nuclear spin forbidden process, both the $m = 0$ and ± 1 will be populated as well. J-, K-, and m-dependent centrifugal distortion terms such as those observed in the complex CF_3H–NH_3[16] split each rotational transition into a series of components whose K and m quantum numbers differ, and each component thus produced is further split by the boron and nitrogen nuclear quadrupole interactions (except in the case of ^{15}N species for which only the boron hyperfine structure is present). As a result, each rotational transition appears as an extremely complex multiplet, spread over approximately 1–2 MHz.

Although a complete analysis of the nuclear hyperfine structure was not undertaken, an analysis of the $K = 0$ spectra was carried out for all but the deuterated species in order to obtain accurate rotational and centrifugal distortion constants as well as the nuclear quadrupole coupling constant for the boron and nitrogen nuclei. Two sets of $K = 0$ spectra were identified by their characteristic hyperfine pattern and corresponded to the $m = 0$ and ± 1 internal rotor states of the complex. Although an unambiguous assignment of the m quantum numbers is not rigorously possible without the observation of $K \neq 0$ states, probable assignments were made on the basis of relative intensities. While the interconversion of the $m = 0$ and ± 1 states is strictly a nuclear spin forbidden process, kinetic factors in the jet may still influence the final populations of the $m = 0$ and ± 1 states of the complex. Since the higher frequency set of spectra was found to be uniformly more intense than the lower frequency counterpart, we have chosen the higher frequency set to correspond to $m = 0$. Fortunately, we may note that since D_{Jm} (defined below) is small, this choice will have negligible effect on the results of the structural analysis. The frequencies of the $K = 0$ transitions and their assignments are listed in Tables I and II.

The frequencies were readily fit using an expression of the form

$$\nu = 2(J + 1)\{B - D_{Jm}m^2\} - 4(J + 1)^3 D_J + \Delta W_Q \tag{2}$$

where B and D_J are the usual rotational and centrifugal distortion constants,[15] D_{Jm} is an m-dependent distortion constant,[16] and ΔW_Q is the difference in hyperfine energies between the upper and lower states. For the ^{15}N species, for which only a boron hyperfine structure was present, the hyperfine energies were well approximated by the usual first-order expression[15] for a single quadrupolar nucleus on the axis of a symmetric top. For the ^{14}N species, the usual treatment for two quadrupolar nuclei was applied.[15] Spectroscopic constants resulting from a least-squares fit for each isotopic derivative are given in Table III, and rotational line centers determined from the analysis are listed in Table IV. Approximate line centers and rotational constants derived from eq 1 for the deuterated derivatives are also included in the tables.

It should be noted that for the [14]N–[11]B species, values of eqQ(N) and eqQ(B) are not listed in Table III. Although the quantum number assignments for this species appear firm, the limited number of assignable transitions renders the resulting values of the quadrupole coupling constants somewhat uncertain. Specifically, using the data given in Table II, the values of eqQ(^{14}N) = –3.93 (28) MHz and eqQ([11]B) = 1.86 (20) MHz were obtained for the [14]N–[11]B complex. However, while the former value appears quite reasonable, the latter does not, as is apparent upon comparison with the corresponding value of 2.377 (9) MHz for the more thoroughly analyzed species CH_3C[15]N–[11]BF_3.

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Table I. Assigned $K = 0$ Transitions of $CH_3C^{15}N-BF_3$[a,b]

	^{11}B			^{10}B		
$J'-J''$	$F' - F''$	freq	obs − calc	$F' - F''$	freq	obs − calc
			m = 0 States			
3-2	3/2 − 3/2	7464.785	0.002	5 − 4	7491.396	−0.002
	5/2 − 5/2	7464.955	0.002	6 − 5	7491.457	0.000
	9/2 − 7/2, 7/2 − 5/2	7465.224	−0.006	4 − 3, 1 − 1	7491.624	0.002
	5/2 − 3/2, 3/2 − 1/2	7465.375	−0.003	3 − 2	7491.892	0.000
	7/2 − 7/2	7465.830	0.005			
4-3	5/2 − 5/2	9953.044	0.010	6 − 5	9988.508	0.004
				7 − 6	9988.539	−0.002
	11/2 − 9/2, 9/2 − 7/2	9953.541	−0.011	5 − 4	9988.592	−0.003
	7/2 − 5/2, 5/2 − 3/2	9953.609	−0.012	4 − 3	9988.717	0.001
	9/2 − 9/2	9954.159	0.013			
5-4	7/2 − 7/2	12441.202	−0.001	7 − 6	12485.500	0.005
	9/2 − 9/2	12441.597	0.009	8 − 7	12485.512	−0.005
				5 − 4	12485.613	0.000
	13/2 − 11/2, 11/2 − 9/2	12441.755	−0.001			
	9/2 − 7/2, 7/2 − 5/2	12441.790	−0.007			
6-5	15/2 − 13-2, 13/2 − 11/2	14929.842	−0.005			
	11/2 − 9/2, 9/2 − 7/2	14929.880	0.005			
			m = ±1 States			
3-2	3/2 − 3/2	7464.658	0.003	5 − 4	7491.266	0.000
	5/2 − 5/2	7464.825	0.000	6 − 5	7491.325	0.000
	9/2 − 7/2, 7/2 − 5/2	7465.102	0.000			
	7/2 − 7/2	7465.693	−0.003			
4-3	7/2 − 7/2	9953.158	−0.007	6 − 5	9988.336	0.004
	11/2 − 9/2, 9/2 − 7/2	9953.374	0.001	7 − 6	9988.365	−0.004
	7/2 − 5/2, 5/2 − 3/2	9953.448	0.006			
5-4	13/2 − 11/2, 11/2 − 9/2	12441.550	0.002	8 − 7	12485.299	−0.008
				6 − 5	12485.340	0.006
				5 − 4	12485.409	0.006
	9/2 − 7/2, 7/2 − 5/2	12441.587	−0.002	4 − 3	12485.448	−0.004
6-5	15/2 − 13/2, 13/2 − 11/2	14929.594	−0.005			
	11/2 − 9/2, 9/2 − 7/2	14929.631	0.005			

[a] All frequencies in MHz. [b] Uncertainties in observed frequencies are estimated to be ±0.004 MHz.

Table II. Assigned $K = 0$ Hyperfine Transitions of $CH_3C^{14}N-^{11}BF_3$ and $CH_3C^{14}N-^{10}BF_3$[a]

				freq, MHz	
$J'-J''$	F'	$F_1' - F''$	F_1''	*m* = 0	*m* = ±1
		$CH_3C^{14}N-^{11}BF_3$			
3-2	9/2	3 − 7/2	2	7467.987 (4)	7467.868 (4)
	11/2	4 − 9/2	3	7468.045 (4)	7467.928 (4)
	9/2	4 − 7/2	3	7468.079 (4)	
	7/2	3 − 5/2	2	7468.118 (4)	
4-3	11/2	4 − 9/2	3	9957.246 (4)	
	5/2	4 − 3/2	3	9957.268 (4)	9957.087 (4)
	13/2	5 − 11/2	4	9957.281 (4)	9957.107 (4)
	7/2	5 − 5/2	4	9957.293 (4)	9957.119 (4)
		$CH_3C^{14}N-^{10}BF_3$			
3-2	6	3 − 5	2	7494.390 (4)	
	6	4 − 5	3	7494.478 (4)	7494.351 (4)
	7	4 − 6	3		
	5	3 − 4	2	7494.544 (4)	
5-4	8	5 − 7	4	12490.488 (4)	
	7	5 − 6	4	12490.512 (4)	12490.273 (4)
	8	6 − 7	5		
	9	6 − 8	5		

[a] $F_1 = I_1 + J$, $F = F_1 + I_2$, where I_1 and I_2 are the nitrogen and boron nuclear spins, respectively.

Table III. Spectroscopic Constants (MHz) for Isotopic Derivatives of CH_3CN-BF_3

$CH_3C^{14}N-^{11}BF_3$		$CH_3C^{14}N-^{10}BF_3$	
B	1244.690 (1)	B	1249.101 (2)
D_J	0.001021 (14)	D_J	0.000967 (4)
D_{Jm}	0.0209 (5)	D_{Jm}	0.0232 (11)
$CH_3C^{15}N-^{11}BF_3$		$CH_3C^{15}N-^{10}BF_3$	
B	1244.228 (1)	B	1248.603 (1)
D_J	0.00102 (1)	D_J	0.000958 (9)
D_{Jm}	0.0211 (5)	D_{Jm}	0.0214 (3)
eq $Q(^{11}B)$	2.377 (9)	eq $Q(^{10}B)$	4.947 (42)
$CD_3C^{14}N-^{11}BF_3$		$CD_3C^{14}N-^{10}BF_3$	
B	1123.57 (7)	B	1127.78 (6)

Table IV. Hyperfine Free Rotational Frequencies for Isotopic Species of $CH_3CN-BF_3{}^a$

species	J',	m	–	J'',	m	$^{11}BF_3$	$^{10}BF_3$
$CH_3C^{14}N$	3,	0	–	2,	0	7468.032 (10)	7494.495 (10)
	3,	±1	–	2,	±1	7467.907 (10)	7494.367 (10)
	4,	0	–	3,	0	9957.260 (10)	9992.6
	4,	±1	–	3,	±1	9957.082 (10)	
	5,	0	–	4,	0	12446.397 (10)	12490.527 (10)
	5,	±1	–	4,	±1	12446.190 (10)	12490.290 (10)
	6,	0	–	5,	0	14935.395 (20)	
	6,	±1	–	5,	±1	14935.150 (20)	
$CH_3C^{15}N$	3,	0	–	2,	0	7465.259 (4)	7491.516 (4)
	3,	±1	–	2,	±1	7465.130 (4)	7491.384 (4)
	4,	0	–	3,	0	9953.570 (4)	9988.578 (4)
	4,	±1	–	3,	±1	9953.391 (4)	9988.407 (4)
	5,	0	–	4,	0	12441.769 (4)	12485.547 (4)
	5,	±1	–	4,	±1	12441.561 (4)	12485.337 (4)
	6,	0	–	5,	0	14929.857 (4)	14982.418 (10)
	6,	±1	–	5,	±1	14929.608 (4)	
	7,	0	–	6,	0	17417.777 (10)	17479.117 (20)
	7,	±1	–	6,	±1	17417.490 (10)	
CD_3CN	5		–	4		11235.8	11277.9
	6		–	5		13482.6	13533.3
	7		–	6		15729.4	

^{a} All frequencies in MHz. Frequencies for which no uncertainty is given are those for which the hyperfine structure was not analyzed. For these transitions, the estimated uncertainties are ±0.5 MHz.

Presumably, an increased number of assigned transitions would bring the quadrupole coupling constant of the boron in the ^{14}N species into agreement with that determined for the ^{15}N species, but additional assignments were hampered by severe spectral conjestion as well as low signal-to-noise ratios. Fortunately, however, the quadrupole interaction of the boron remains well-characterized through the analysis of the ^{15}N complex, for which the spectra were considerably simpler.

Structural Analysis

The rotational constants in Table III may be used to evaluate the structure of the complex once a number of simplifying assumptions have been made. Depending upon whether the species is regarded as a covalently bonded molecule or a weakly bound van der Waals complex, slightly different (though essentially equivalent) approaches seem appropriate. To retain maximum flexibility, we adopt a viewpoint similar to that normally taken in the analysis of weakly bound systems, in which the complex is viewed as two separate, interacting monomer units whose instantaneous angular orientations may differ significantly from the vibrationally averaged geometry of the complex.

Although the usual structural analysis of weakly bound systems further assumes that the monomer geometries are unchanged upon complexation, such an assumption must be relaxed in the present case. In particular, both the N–B–F angle of 105.6° observed in the crystal[7b,c] and the results of ab initio calculations on the gas-phase adduct[14] suggest that the BF_3 subunit is likely to be nonplanar, and we therefore allow the N–B–F angle to vary in the analysis. In principle, we may also expect the formation of the complex to lengthen the B–F bond slightly, as evidenced by
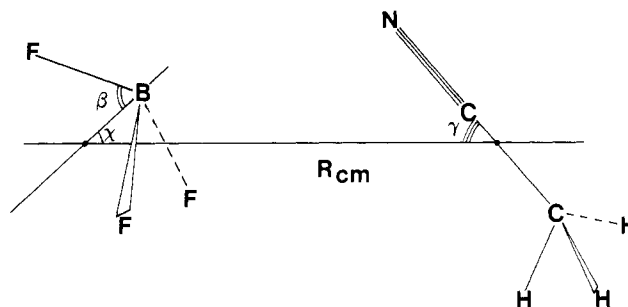

Figure 1. Definition of coordinates used to describe the geometry of CH_3CN-BF_3. The observation of a symmetric rotor spectrum for the complex indicates that $\langle \chi \rangle = \langle \gamma \rangle = 0$.

its increase from 1.3102 (12) Å[17] in free BF_3 to 1.344 (15) Å in the solid crystalline adduct.[7b] In the absence of available fluorine isotopes, however, its gas-phase value is difficult to determine experimentally. Fortunately, however, we may note that since the B–F bond length is not likely to be longer than that observed in the crystal, the lengthening upon complex formation in the gas-phase species is expected to be small. Moreover, since the moment of inertia of the complex is only weakly dependent on its value, the precise bond length chosen is of little consequence. Thus, we will constrain the B–F bond length to be equal to that of free BF_3 and later test the sensitivity of the resulting structure to this approximation.

Similarly, for the acetonitrile, chemical intuition suggests that the structural changes which occur upon complexation will be small. This is supported by noting that the geometry of the CH_3CN subunit determined in the crystalline complex with BF_3[7b] is reasonably close to that for free CH_3CN, with the N≡C and C—C bond lengths decreased from their gas-phase values[18] by 0.0217 and 0.0227 Å, respectively. Thus, in our analysis, we will further assume that the N≡C and C—C bond lengths, as well as the C—H distance and C—C—H angle, are the same in the complex as those observed in free CH_3CN. As discussed below, this, too, has little effect on the final structure determined for the complex.

As a final point concerning changes in the monomer geometries upon complexation, it is of interest to examine the gas-phase species BH_3-NH_3, for which extensive isotopic substitution has made possible a complete structural determination.[19] In this molecule, the B–H bond lengths are 1.216 Å (compared with 1.160 Å for uncomplexed BH_3), while the H–B–H angle is 113.8° (compared with 120° for the free monomer). These values indicate a small increase in the B–H distance and a substantial angular deformation of the BH_3 upon formation of the dative bond.[20] The N–H bond length, however, is 1.014 Å for both complexed and uncomplexed NH_3, and the H–N–H angles are 107.06° and 108.7° for free and complexed ammonia, respectively. These numbers thus reaffirm the notion that the N–B–F angle must be allowed to vary in the structure determination but that the remaining structural parameters of the monomer units may be reasonably constrained to their values observed in the uncomplexed species.

In light of the above discussion, the coordinates needed to describe the complex CH_3CN-BF_3 are defined in Figure 1. R_{cm} is the distance betwen the centers of mass of the acetonitrile and the pyramidally distorted BF_3, and β is the acute angle formed between the B–F bond and the C_3 axis of the BF_3. The angles χ and γ denote the instantaneous angles that the C_3 axes of the BF_3 and CH_3CN moieties make with R_{cm}, respectively. In terms

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(20) For BF_3, the elongation of the B–F bond upon complexation may be more significant than in the BH_3 case, due to loss of the partial double bond character present with fluorine but not hydrogen. However, as noted above, the gas-phase and crystal-phase bond lengths are actually quite similar.

of these coordinates, the vibrationally averaged moment of inertia of the complex about its b-inertial axis, $\langle I_{bb} \rangle$, may be written[21]

$$\langle I_{bb} \rangle = M_s \langle R_{cm}^2 \rangle + \tfrac{1}{2} I_{bb}(BF_3)[1 + \langle \cos^2 \chi \rangle] +$$
$$\tfrac{1}{2} I_{cc}(BF_3) \langle \sin^2 \chi \rangle + \tfrac{1}{2} I_{bb}(CH_3CN)[1 + \cos^2 \gamma] +$$
$$\tfrac{1}{2} I_{aa}(CH_3CN) \langle \sin^2 \gamma \rangle \quad (3)$$

In this expression, $M_s = m(CH_3CN)m(BF_3)/m(CH_3CN-BF_3)$ is the pseudodiatomic reduced mass, I_{gg} refers to the moment of inertia of the indicated monomer unit about its g-inertial axis, and the angular brackets denote vibrational averaging. In addition, we employ the usual approximation that $\langle I_{bb} \rangle = h^2/8\pi^2 B$, where B is the measured rotational constant of the complex. The moments of inertia of the acetonitrile are taken as those obtained from the rotational constants of Damaison et al.,[18] while those for the distorted BF_3 are calculated from $r(B-F)$ (the boron-fluorine bond length) and β using standard expressions for a pyramidal XY_3 molecule.[15b] Since the moments of inertia of the complex do not depend upon rotation angles of the BF_3 and the CH_3CN about their respective symmetry axes, these angles may be ignored in the analysis.

The value of $\langle \cos^2 \gamma \rangle$ may be estimated using the approximate ^{14}N nuclear quadrupole coupling constant discussed above, assuming that the measured value in the complex is the tensor projection of the free monomer value onto the a axis of the complex, viz.,

$$eqQ(^{14}N) = eqQ(CH_3CN) \langle 3 \cos^2 \gamma - 1 \rangle / 2 \quad (4)$$

While this relation is generally applicable for weakly bound systems, the unusual nature of this complex necessitates some additional comments about its use here. In particular, as discussed below, there are compelling reasons to regard this complex as being somewhere *between* the weakly bound and covalently bonded limits, suggesting that at least some of the changes in the observed quadrupole coupling constants upon complexation might be electronic in origin. Interestingly, however, for the CH_3CN, we may estimate $\langle \cos^2 \gamma \rangle$ in the van der Waals limit by noting that in nitrogen bonded van der Waals complexes of HCN the value of $\cos^{-1} [\langle \cos^2 \gamma \rangle^{1/2}]$ is typically about $17°$ [22] and that in an approximation in which the angular vibration is treated as harmonic γ scales roughly as the fourth root of the rotational constant of the submolecule.[16] Thus, the known rotational constants of HCN[23] and CH_3CN[18] give a scaled estimate of $12°$ for the bending amplitude of the acetonitrile. This value is remarkably close to the value of $12.4°$ obtained from eq 4, above, using the known value of $eqQ(CH_3CN)$[18b] and the approximate value of $eqQ(^{14}N)$ determined in the complex, suggesting that the approximation of negligible electronic distortion of the CH_3CN implied by the use of eq 4 is reasonable. Moreover, since I_{bb} in eq 3 is dominated by the $M_s R_{cm}^2$ term, errors in the choice of $\langle \cos^2 \gamma \rangle$ have little effect on the final geometry determined for the complex, and the structural calculations for the ^{14}N isotopic species may thus be carried out with the approximation that $\langle \cos^2 \gamma \rangle \sim \cos^2 (12.4°)$. For the other isotopic derivatives of CH_3CN, small corrections to vibrational averaging are readily made by scaling the angle with the fourth root of the known rotational constants of the substituted monomers.

The effects of the angular averaging of the BF_3 subunit are more difficult to assess since considerably less information is available with which to estimate $\langle \cos^2 \chi \rangle$. We note, however, that in Ar-BF_3, the measured value of $eqQ(^{11}B) = 2.70$ (5) MHz is about the same as the solid-state monomer value of 2.64 (4) MHz,[24] indicating that the projective reduction in $eqQ(^{11}B)$ upon complexation is rather small. We therefore choose to perform the structural calculations with $\langle \cos^2 \chi \rangle = 1$ and check the sensitivity

Table V. Calculated Structures for CH_3CN-BF_3[a]

CH_3CN isotopic deriv	$R(B-N)$, Å	$\alpha(NBF)$, deg
$CH_3C^{14}N$	2.017793	95.35
$CH_3C^{15}N$	2.004665	95.92
$CD_3C^{14}N$	2.008 ± 0.020	95.4 ± 1.2

[a] Structure on the right is that determined from the ^{10}B and ^{11}B isotopes complexed with the indicated isotopic form CH_3CN. For the CD_3CN species, errors given are those arising from uncertainties in the observed rotational constants. For the $CH_3C^{14}N$ and $CH_3C^{15}N$ species, errors due to uncertainties in the rotational constants are deceptively small and are therefore not listed. See text for discussion.

of the results to this approximation later. We note here, though, that a crude upper limit to χ may be obtained from the measured value of $eqQ(^{11}B) = 2.377$ MHz for the $^{15}N-^{11}B$ species discussed above and the solid-state value of 2.64 MHz,[24] using a relation analogous to eq 4. If the reduction in eqQ upon complex formation were *entirely* projective, these numbers would give a value of $\langle \cos^2 \chi \rangle$ corresponding to χ of only about $14°$. Since, as discussed below, the BF_3 is observed to be significantly distorted upon complexation, this value is likely to be less accurate than that correspondingly determined for the acetonitrile, but at least it provides a rough upper bound to $\langle \cos^2 \chi \rangle$. Fortunately, again, the $\langle \cos^2 \chi \rangle$ term also introduces only a small correction to I_{bb} of the complex, and hence the precise value chosen for χ is of relatively minor consequence.

With these choices of the angular expectation values, only two structural parameters of the complex, R_{cm} and β, remain to be calculated. Thus, the six rotational constants in Table III permit several independent determinations of the molecular geometry. These may be obtained by finding a locus of points (R_{cm}, β) which reproduce the observed rotational constant for each isotopic form studied. The intersections of these loci for the ^{10}B and ^{11}B species complexed with each isotopic derivative of acetonitrile yields an independent determination of the molecular geometry. The boron-nitrogen bond length, $R(B-N)$, is readily determined from R_{cm} and the known structure of CH_3CN, while $\alpha(N-B-F)$, the N-B-F angle at the equilibrium configuration, is simply given by $(180° - \beta)$. Values of $R(B-N)$ and $\alpha(NBF)$ determined by this procedure are listed in Table V. For the ^{14}N and ^{15}N species, the uncertainties in the structures arising from the measurements of the rotational constants are quite small (on the order of 10^{-6} Å for $R(B-N)$ and $0.01°$ for α) and are not listed, as they do not provide realistic estimates of the true uncertainties in the structure of the complex. Rather, changes in the monomer geometries upon complexation, as well as uncertainties regarding the angular vibrational averaging, are likely to be the dominant sources of error, and ultimately limit the accuracy of the structure determination. This issue is considered in more detail below.

First, the influence of uncertainties in the estimation of the large-amplitude angular oscillations of the two moieties may be explored by repeating the structural determination using different values of $\langle \cos^2 \chi \rangle$ and $\langle \cos^2 \gamma \rangle$. For the acetonitrile, for which $\cos^2 (12.4°)$ was used above, the sensitivity of the final structure to the choice of γ may be checked by repeating the calculation for the extreme case of a rigid molecule, in which $\langle \cos^2 \gamma \rangle$ is unity. The result, using the $CH_3C^{15}N$ species as an example, is that the B-N bond length and the N-B-F angle are decreased by only 0.003 Å and 0.2°, respectively, from those obtained using $\gamma = 12.4°$, confirming that the calculated structure is fairly insensitive to the precise value of γ chosen. Similarly, for the BF_3, if $\langle \cos^2 \chi \rangle$ is replaced by the upper limit of $\cos^2 (14°)$ discussed above, the calculated value of $R(B-N)$ is reduced by only 0.006 Å, and the value of $\alpha(NBF)$ changed by less than 0.2° compared with the calculation using $\chi = 0°$. Thus, it is apparent that reasonable (and even, perhaps, extreme) estimates of the uncertainties in the angular expectation values introduce uncertainties in the calculated structure which are small. These errors, however, are significantly greater than those produced by the uncertainties in the measured rotational constants of the nondeuterated species.

The effect of using the bond lengths of the free monomers in the analysis may similarly be tested. Changing the value of $r(B-F)$

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from the gas-phase value of 1.3102 Å[17] to that observed in the crystal (1.344 Å),[7] for example, decreases the calculated values of R(B–N) and α(NBF) for the ^{15}N species by only 0.011 Å and 0.4°, respectively. Similarly, for the acetonitrile, if the C≡N and C—C bond lengths are replaced with those determined in the crystalline complex,[7] the calculated B–N bond length and the N–B–F angle increase by 0.027 Å and 0.2°, respectively. In light of the large difference between the structures of the gas phase and crystalline complexes, however, it seems unlikely that the monomer structures observed in the solid would truly be appropriate choices for analysis of the gas-phase species. Rather, the above calculations may again be taken to provide only an upper limit to the effect of bond length changes in the BF_3 and CH_3CN subunits on the calculated geometry of the adduct.

In summary, the measured rotational constants for six isotopically substituted forms of CH_3CN–BF_3 have been used to provide three redundant determinations of the B–N bond length and NBF angles in the complex. The approximations used in deriving the structure have been examined in detail and shown to introduce errors into the final calculated geometry which are small, but larger than those due to the estimated uncertainties in the rotational constants for the ^{14}N and ^{15}N species. For the case of the CD_3CN derivatives, we may note that measurement errors and model errors appear comparable. Rigorous estimates of the true uncertainties in R(B–N) and α(NBF) are difficult to make since the monomer structural changes upon complexation and the angular vibrational amplitudes in the complex are not known. However, a reasonable procedure would be to take the algebraic sum of the upper limits of uncertainty as discussed in the paragraphs above, yielding conservative estimates of about ±0.007 Å in the bond length and ±0.6° in the angle. It is satisfying to note that these values are comparable to the scatter among the three independent structure determinations. Thus, with reference to Table V, we will take the boron–nitrogen bond length and N–B–F angle in the gas-phase species to be the average of the ^{14}N and ^{15}N determinations, with uncertainties as quoted above, viz. 2.011 (7) Å and 95.6 (6)°. The CD_3CN values are seen to agree well with these values, though they are not included in the average due to the additional source of uncertainty arising from the measurements.

Discussion

The structure determined above for the complex CH_3CN–BF_3 is seen to be in reasonably good agreement with the results of ab initio calculations, which predict values of R(B–N) = 2.17 Å and α(NBF) = 98°.[14] The structure is quite striking in two important respects. First, the observed values for R(B–N) and α(N–B–F) (2.011 ± 0.007 Å and 95.6 ± 0.6°, respectively) are seen to be significantly different from the corresponding values of 1.630 (4) Å and 105.6 (5)° observed in the solid state.[7] The 0.381 ± 0.011 Å contraction of the B–N bond and the 10.0 ± 1.1° increase in the N–B–F angle upon crystallization are, by any measure, very large effects indeed. Although correspondingly large differences in bond lengths are certainly known (for example, between gas-phase ionic species[25] and their crystalline counterparts[26]), the present system differs in that a single dimeric unit in the gas phase retains its independent integrity in the solid. The observed differences, therefore, are a direct reflection of the influence of the crystalline environment on the structure of a single, identifiable molecular unit. While the origin of this influence is difficult to assess, it might be speculated to arise from the cooperative effect of adjacent dipole moments, whose values are enhanced as the bond formation proceeds. It is interesting to note that similar behavior has recently been observed in the complex $(CH_3)_3N$–SO_2, in which the S–N bond length is found to be 0.205 Å shorter in the crystal than it is in the gas-phase complex.[27]

Table VI. Comparison of Boron–Nitrogen Bond Lengths and NBF Angles in Donor–Acceptor Complexes of BF_3 and BH_3

adduct	R(B–N), Å	α(NBF), deg	phase
N_2–BF_3[a]	2.875 (2)	90.5 (5)	gas; molecular beam
NCCN–BF_3[b]	2.647 (3)	90–100	gas; molecular beam
HCN–BF_3[c]	2.52 (3)	90–91.5	gas; molecular beam
CH_3CN–BF_3[d]	2.011 (7)	95.6 (6)	gas; molecular beam
H_3N–BH_3[e]	1.6576 (16)	104.69 (11)	gas
$(CH_3)_3N$–BF_3[f]	1.636 (4)	106.4 (3)	gas
$(CH_3)_3N$–BH_3[g]	1.638 (10)	105.3 (2)	gas
CH_3CN–BF_3[h]	1.630 (4)	105.6 (6)	crystal
H_3N–BF_3[i]	1.60 (2)	107 (2)	crystal
$(CH_3)_3N$–BF_3[j]	1.59 (3)	112 (2)	crystal
CH_3H_2N–BF_3[k]	1.57 (2)	108.5 (20)	crystal

[a] Microwave spectroscopy, ref 9. [b] Microwave spectroscopy, ref 10. [c] Microwave spectroscopy, ref 28. [d] This work. [e] Microwave spectroscopy, ref 19. [f] Microwave spectroscopy, ref 29. [g] Microwave spectroscopy, ref 30. [h] X-ray diffraction, ref 7b. [i] X-ray diffraction, ref 31. [j] X-ray diffraction, ref 32; uncertainty in the angle is unavailable, but has been estimated by analogy with other related crystal structures. [k] X-ray diffraction, ref 33.
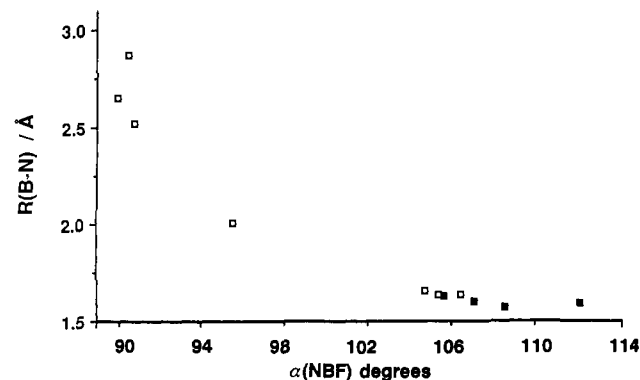

Figure 2. A plot of the B–N bond length vs the N–B–F (or N–B–H) angle for the addition complexes of BF_3 and BH_3 with nitrogen donors listed in Table VI. Open squares represent gas-phase data, and solid squares correspond to crystallographic data. Error bars have not been plotted in order to avoid clutter, but reference to Table VI shows that they are, in general, small, and that consideration of the uncertainties in the experimental structures does not change any of the qualitative conclusions drawn from the plot. See text for discussion.

The second aspect of this system which makes its structure particularly remarkable is its intermediacy between that expected for a van der Waals and covalently bonded species. Table VI compares the B–N bond lengths and N–B–F (or N–B–H) angles observed for a series of BF_3 and BH_3 adducts with nitrogen donors. It is readily seen that the B–N bond length and N–B–F angle of 2.011 Å and 95.6°, respectively, for the gas-phase CH_3CN–BF_3 are quite intermediate between the limiting cases represented in the table. It is particularly interesting to note here, too, that the calculated binding energy of the complex is only 5.7 kcal/mol.[14] Thus, while the system is *structurally* quite intermediate between a covalent molecule and a weakly bound complex, it is energetically much more like a van der Waals molecule.

The question might be raised as to whether the extreme values of the B–N bond length and N–B–F angle found in the table represent true covalent and van der Waals limits for the boron–nitrogen interaction. Muetterties gives the covalent radii of boron and nitrogen as 0.88 and 0.70 Å, respectively,[8a] implying that a

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B–N covalent bond should be about 1.58 Å in length. Noting that the shortest B–N bonds in Table VI are very close to this value, and that the geometry at the boron is nearly tetrahedral for species exhibiting those bond lengths, we are left with little doubt that the covalent limit is well-represented in the series of complexes listed.

For the limiting van der Waals bond length, a similar estimate may be made. Although a van der Waals radius for boron is difficult to find, a value of 1.41 Å may be derived from the observed Ar–B distance in Ar–BF$_3$ (3.325 Å[9]) and the usual van der Waals radii of argon (1.92 Å). Together with a 1.5 Å van der Waals bond length of nitrogen, we expect a limiting van der Waals distance for the boron–nitrogen bond to be about 2.91 Å, in close agreement with the 2.88-Å value observed in N$_2$–BF$_3$. The conclusion that N$_2$–BF$_3$ is truly a van der Waals bonded species is in good agreement with chemical intuition.

A graphical representation of the data in Table VI is further revealing. Figure 2 shows a plot of the B–N bond length vs the N–B–F angle for the species listed and graphically illustrates the strong correlation between these parameters. If one considers the general addition reaction F$_3$B + donor → F$_3$B–donor and defines a reaction path in terms of the coordinates R(B–N) and α(NBF), it is natural to draw analogy with the crystallographic structure correlations of Bürgi and Dunitz and co-workers[4a] and to regard each point on the plot as a snapshot along that path. If such a viewpoint is legitimate, these results show that an angular deformation of the BF$_3$ of only 5° has occurred by the time the nitrogen atom has reached a distance halfway between the van der Waals and covalent bond lengths.

Figure 2 illustrates several additional points of interest. First, it is evident that adducts of both amines and nitriles of BF$_3$, as well as related complexes of BH$_3$, fall on the same curve. Also, it may be seen that the gas-phase points span a significant portion of the plot and that they smoothly connect with those points representing solid-state structures. For the particular case of CH$_3$CN–BF$_3$, which is plotted twice (once for the solid and once for the gas-phase complex), we observe that both points lie on the smooth curve defined by the collective body of data. This would seem to indicate that although the formation of the crystal clearly perturbs the system significantly (as evidenced by the large structural change incurred upon crystallization), the perturbation is one which drives the system *along* the reaction path but does not cause it to deviate from that path. A similar conclusion may be drawn by comparison of the gas-phase and crysal-phase points for (CH$_3$)$_3$N–BF$_3$. Thus, while solid-state data at long bond lengths would certainly be desirable, the smooth splicing of the gas-phase and crystal-phase structures would appear to provide the first direct evidence in support of the stated assumption[4a] underlying the use of crystal structure correlations to map reaction paths, namely that the perturbing effects of the crystal do not displace the system significantly from the presumed reaction path.

In the context of a reaction path, it is of interest to consider the evolution of other properties of the system as the B–N bond formation proceeds. In particular, we may, from the data acquired in this work, consider (1) the stretching force constant for the B–N bond, (2) the attenuation of the large amplitude angular vibrations of the CH$_3$CN as the system proceeds toward the rigid molecule limit, and (3) the electronic changes in the BF$_3$ accompanying its structural deformation.

First, the stretching force constant for the complex may be estimated, assuming that the predominant contribution to the purely *J*-dependent distortion constant of the complex (D_J) arises from centrifugal stretching of the intermolecular bond. Using the usual approximate formula[16]

$$k_s = \frac{(4\pi)^4 (M_s R_{cm})^2 B^4}{2hD_J} \quad (5)$$

we obtain a stretching force constant for the B–N bond of 0.094 mdyn/Å. This value is somewhat larger than though surprisingly comparable to those determined for the complexes Ar–BF$_3$ (0.03 mdyn/Å),[9] CO–BF$_3$ (0.05 mdyn/Å,[9] or HCl–BF$_3$ (0.051

mdyn/Å),[34] for which the out of plane distortion of the BF$_3$ was determined[9] or assumed[34] to be less than 1°.

This situation along the acetonitrile bending coordinate (γ) is seen to be quite similar. As we have already noted in the course of the structure determination, the bending vibrational amplitude of the CH$_3$CN, as measured by $\langle\cos^2\gamma\rangle$, is readily predicted by a scaling procedure, using nitrogen bound van der Waals complexes of HCN as a reference. Stated differently, the zero-point bending amplitude of the CH$_3$CN subunit is quite comparable to that predicted on the basis of a van der Waals type bending force constant, though we must emphasize that the value of eqQ(^{14}N) used in the calculation is quite approximate. Nonetheless, it appears that while the *structure* of the system is quite intermediate between the van der Waals and covalent limits, the rigidity of the bond, along both the bending and stretching coordinates, is reminiscent of those in weakly bound molecular complexes.

Finally, the nuclear quadrupole coupling constant for the ^{11}B may be used as a rough indicator of changes in the electronic structure at the boron. Specifically, the value of eqQ(^{11}B) in CH$_3$C^{15}N–BF$_3$ (2.37 MHz) is seen to be almost identically equal to the average of that observed in the van der Waals complex Ar–BF$_3$ (2.7 MHz)[9] and in the covalently bound species (CH$_3$)$_3$N–BH$_3$ (2.064 MHz).[30b] Since it seems unlikely that the projective reduction in the quadrupole coupling constant in CH$_3$CN–BF$_3$ would be larger than that in Ar–BF$_3$, this intermediacy is quite likely an expression of the electronic reorganization accompanying the 6° distortion from planarity. We hesitate to apply simplistic models to describe the electronic structure, however, as such models have been shown to be inadequate for boron trihalides.[24] An ab initio calculation of eqQ(B) would be most interesting in this regard.

The differences between the complexes NCCN–BF$_3$ and CH$_3$CN–BF$_3$ can easily be rationalized in simple chemical terms. Since the CN group in cyanogen is a more electron withdrawing substituent than the CH$_3$ group in acetonitrile, NCCN is a poorer donor than CH$_3$CN. Indeed, a recent study of the related system (CH$_3$)$_3$N–BF$_3$ has concluded that the orbital which is classically regarded as the "donor orbital" on the nitrogen is actually delocalized over the entire (CH$_3$)$_3$N,[35] making large substituent effects in these types of systems especially reasonable. It is interesting to note that large substituent effects have also recently been observed in complexes of the type R$_3$N–HBr. The complex H$_3$N–HBr is essentially a weakly bound, hydrogen bonded system while the species (CH$_3$)$_3$N–HBr is more accurately described as the ion pair, (CH$_3$)$_3$NH$^+$Br$^-$.[36]

Finally, it is of some interest to reflect on why this system exhibits such unusual behavior, while the myriad of other weakly bound complexes studied to date do not. The answer, clearly, is that it is possible to form a bond to BF$_3$ without violating the octet rule, whereas for the binding partners involved in many "typical" weakly bound complexes (e.g. molecules like HF, CO$_2$, HCCH, etc.) the addition of another electron pair cannot occur while still comforming the normal valency rules. In this sense, BX$_3$ species are the exception rather than the norm for stable compounds of the second-row elements. This suggests, however, that systems with expandable octets, such as compounds of third-row elements, may be more prone to exhibiting intermediate behavior and that complexes of these systems might be generally useful in examining gas-phase reaction paths by the method originally proposed by Bürgi and Dunitz in the solid state. Such a use of rotational spectroscopy to explore chemical reaction dynamics would provide an intriguing complement to structural work on reactive chemical intermediates such as O$_3$–C$_2$H$_4$,[5] in which weakly bonded species corresponding to local minima along a reaction path can be characterized in detail. The large difference between the solid-

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state and gas-phase structures recently noted for $(CH_3)_3N-SO_2{}^{27}$ (0.21 Å) is encouraging in this respect, as it demonstrates the possibility of a substantial "dynamic range" in N–S bond lengths.

Conclusion

Microwave spectroscopy has been used to observe the gas-phase adduct formed between CH_3CN and BF_3. The structure has been determined to be intermediate between the limits normally expected for van der Waals and covalent interactions and is significantly different from that observed in the crystalline material. The correlation between the boron–nitrogen bond length and the N–B–F angle in a series of BX_3 species with nitrogen donors provides the first gas-phase example of a structure correlation

analogous to those used frequently to map reaction paths in crystalline systems.

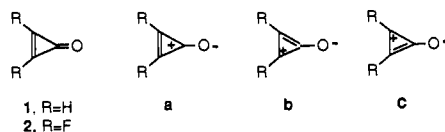# Synthesis, Microwave Spectrum, and ab Initio Calculations for Difluorocyclopropenone

Carolyn A. Jacobs,[†] John C. Brahms,[†] William P. Dailey,*,[†] Kyle Beran,[‡] and Marlin D. Harmony*,[‡,§]

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Abstract: Difluorocyclopropenone was prepared by gas-phase photolysis of difluoromaleic anhydride and was characterized spectroscopically. It is unstable at room temperature but may be stored for long periods of time at −78 °C. Microwave spectra of the normal and ^{18}O isotopomer for difluorocyclopropenone were measured. The structural parameters were determined to be $r(C_1O) = 1.192$ Å, $r(C_1C_2) = 1.453$ Å, $r(C_2C_3) = 1.324$ Å, and $r(CF) = 1.314$ Å, and the electric dipole moment was found to be 2.32 D. Ab initio calculations at the CISD/6-31G* level are reported for cyclopropenone, difluorocyclopropenone, and related cyclopropenes and are in good agreement with the experimental results. The experimental geometry and ab initio computations indicate that difluorocyclopropenone enjoys a resonance energy comparable to that of the parent compound.

Cyclopropenone (**1**) has received considerable attention because of its potential aromaticity based on Huckel's $4N + 2$ rule.[1] This stability is predicted to arise because of the relative importance of resonance structures such as **1a–c**. In accord with this reasoning, cyclopropenones have high dipole moments and low pK_b values.[1] Staley and co-workers have recently used several criteria to quantify the degree of aromaticity enjoyed by cyclopropenone and concluded that it is a moderately aromatic compound.[2] Although the exact value is still in question, the resonance energy of cyclopropenone is in the range of 14–24 kcal/mol.[3]

Substitution of hydrogen by fluorine often causes remarkable changes in the structures, relative energies, and kinetic stabilities of organic molecules.[4] Our recent synthesis[5] of difluorocyclopropenone (**2**) under matrix-isolation conditions prompted our interest in how fluorine substitution might affect the degree of aromaticity in this compound compared with that in **1**. On the basis of the high electronegativity of fluorine, one might expect that resonance structures such as **2a–c** might be less important for **2** than for **1**. This would then serve to decrease the aromaticity in **2**. On the other hand, if fluorine were able to efficiently donate π-electron density to the cyclopropenone using one of its lone pairs

1, R=H
2, R=F

of electrons,[6] it may serve to enhance the stability and relative importance of resonance structures **2a–c**. To address these questions, we report the details of the isolation, structural characterization by microwave spectroscopy, and high-level ab initio calculations for difluorocyclopropenone. A comparison with the properties of the parent cyclopropenone will also be made. The sensitivity of various criteria for the determination of aromaticity in **2** will be examined.

Experimental Section

Synthesis of Difluorocyclopropenone. Difluoromaleic anhydride[7] (85 mg) was transferred into an evacuated 2.5-L gas-tight photolysis well fitted with a water-cooled quartz immersion well containing a 450-W medium-pressure mercury vapor lamp and a Vycor filter. The whole assembly was cooled in ice water, and the lamp was operated for 45 min. The volatile products were isolated by vacuum transfer through a series of three U-traps cooled to −40, −78, and −196 °C. The middle trap

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