Partially Formed Bonds In $HCN-SO_3$ and CH_3CN-SO_3: A Comparison between Donor−Acceptor Complexes of SO_3 and BF_3

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The gas-phase structures of $HCN-SO_3$ and CH_3CN-SO_3 have been determined by microwave spectroscopy in a supersonic jet. Both adducts are symmetric tops with the nitrogen bonded to the SO_3. In $HCN-SO_3$, the N−S distance is 2.577(6) Å and the NSO angle is 91.8(4)°. In CH_3CN-SO_3, the bond length and bond angle are 2.466(16) Å and 92.0(7)°, respectively. The N−S distances are significantly shorter than the sum of van der Waals radii, and the structures are indicative of N−S dative bonds which are in their early stages of development. ^{14}N nuclear hyperfine structure is consistent with this assessment. The bond length−bond angle relationship for a series of SO_3 complexes with amine and nitrile donors is examined and compared with that for a similar series of complexes of BF_3 and BH_3. The variation of bond angle with bond length is strikingly similar for both sets of systems despite the differing atomic sizes of boron and sulfur. With a given base, however, the degree of bond formation to SO_3 appears to lag that to BF_3.

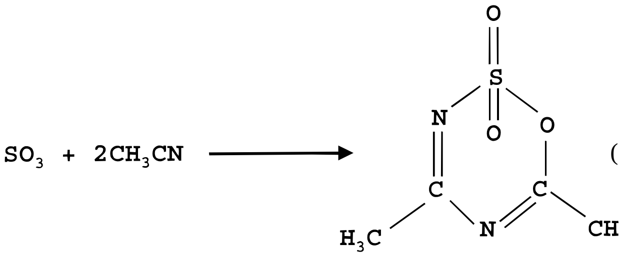
Introduction

The electron pair donor−acceptor bond has been an integral part of basic chemical theory ever since its introduction by G. N. Lewis in 1923.[1] Indeed, its far-reaching impact is now documented by an overwhelming literature on the reactivity,[2] thermodynamics,[3,4] spectroscopy,[5] and structures[6] of a wide range of donor−acceptor complexes. An important conceptual advance in our understanding of these systems came in the early 1960s, when Pearson introduced the hard and soft acid−base (HSAB) principle, which provided an organized albeit qualitative framework for understanding the relative stabilities of donor−acceptor adducts.[3] An empirical quantification of the HSAB theory by Drago and co-workers[4] appeared shortly thereafter. More recently, the distinction between covalent and dative bonds has been clearly enunciated by Haaland[7] and the number of theoretical investigations involving Lewis acid−base adducts appears to be on the rise.[8,9] A fundamental theoretical basis for the HSAB principle may be found in density functional theory.[3b,10]

In our own work, we have been concerned with the structure and bonding of Lewis acid−base complexes involving primarily BF_3[11−13] and SO_3.[14−16] We have found that with a suitably chosen series of Lewis bases, the dative linkages in these systems can vary from weak, van der Waals attractions to bona fide chemical bonds. Species in the middle portion of the range thus appear to be "partially bound". We have also seen that adducts which contain a partially formed bond in the gas phase are extraordinarily sensitive to the presence of neighboring molecules and therefore undergo large changes in structure upon crystallization.[11,12,15a,17,18] The ability of partially bound systems to access the intermediate regime between van der Waals and chemical bonding has also been used to investigate reaction paths for the formation of donor−acceptor bonds.[11,17,19]

In some ways, BF_3 and SO_3 are very similar. Indeed, both are trigonal planar species with a strongly acidic site at the central atom and both are generally categorized as "hard" Lewis acids.[20] Yet, despite these superficial similarities, significant differences can also be identified. The acidity of BF_3, for example, is usually attributed to electron deficiency at the boron and is readily visualized in terms of electron pair acceptance into an empty p_z orbital perpendicular to the molecular plane. In SO_3, however, the sulfur already has an octet and the exact nature of the acceptor orbital is not as apparent. In addition, while partial double bond character in the B−F bonds of BF_3 is often invoked as a means of satisfying the boron octet,[21] it comes at the expense of a partial positive charge on the fluorines. In contrast, at least one resonating double bond in SO_3[21−24] is a natural part of the "best" Lewis structure for this species. And further, while the valence shell on boron is rigorously limited to eight electrons, the octet on sulfur is expandable. The net result is that addition of an electron pair to the MX_3 unit breaks the partial double bond character of the M−X bonds in BF_3, but formation of a new bond to SO_3 is need not. A detailed comparison of the bonding in SO_3 and BF_3 has been given.[24]

Additional differences between BF_3 and SO_3 lie in reactivity. For example, while BF_3 readily forms donor−acceptor adducts with HCN and CH_3CN, bulk-phase chemistry with SO_3 apparently produces heterocycles according to reactions such as[25]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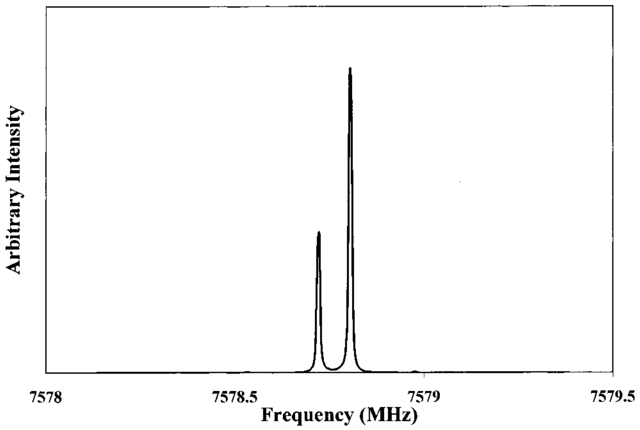

Figure 1. The $(F' \leftarrow F'') = (2 \leftarrow 1)$ and $(3 \leftarrow 2)$ components in the $J = 2 \leftarrow 1$ transition of $HC^{14}N{-}^{32}SO_3$.

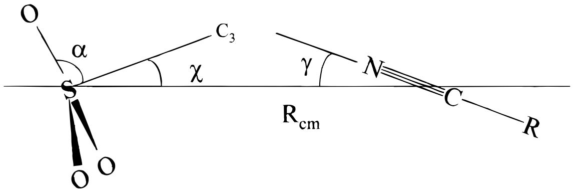

Figure 2. Definition of coordinates used to describe the structure of $RCN{-}SO_3$.

Though the likely first step in such processes is the formation of a donor−acceptor intermediate, it appears that no such complex has yet been isolated. The adducts are, of course, readily prepared in a supersonic jet and their comparison with the previously studied complexes of BF_3[11,12] would be interesting. In this paper, therefore, we report a microwave investigation of $HCN{-}SO_3$ and $CH_3CN{-}SO_3$ in the gas phase.

Experimental Section

Spectra were recorded using a Balle−Flygare type pulsed nozzle Fourier transform microwave spectrometer[26] the details of which have been presented elsewhere.[27] For both systems studied, the complexes were produced by injecting the nitrile via a hypodermic needle into the early phase of a supersonic expansion of SO_3 seeded in argon. The expansion was prepared by passing argon over a solid sample of SO_3 held at 0 °C, at a pressure of about 2 atm. In experiments involving $HCN{-}SO_3$, a 32% mixture of HCN in argon was placed behind the injection needle at a backing pressure of 0.3 atm, whereas for the production of $CH_3CN{-}SO_3$ the acetonitrile was transported to the needle by bubbling a small amount of argon through a sample of the neat liquid. Optimum signals were achieved in this case using rather large needles (0.010″ or 0.012″ i.d.) with a backing pressure only a few Torr higher than the room-temperature vapor pressure of acetonitrile (78 Torr). For both complexes, ^{15}N and ^{34}S species were observed in natural abundance, as was the spectrum of $HC^{14}N{-}^{33}SO_3$. For experiments on $DCN{-}SO_3$, a sample of DCN was prepared by reaction of KCN with dry D_3PO_4.

Results

The observed rotational transitions of $HCN{-}SO_3$ and $CH_3CN{-}SO_3$ are given in Tables 1 and 2, respectively. A sample spectrum is shown in Figure 1. The spectra are characteristic of symmetric tops with equivalent off-axis oxygens and were readily fit to an expression of the form

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

Here, D_{eff} is an effective distortion constant which is equal to D_{JK} for $HCN{-}SO_3$, but contains additional contributions due to internal rotation for $CH_3CN{-}SO_3$ (see below). ΔE_{quad} is the difference in the quadrupole hyperfine energies for the upper and lower states and other symbols have their usual meanings.[28] ^{14}N hyperfine structure, when present, was observed and analyzed according to the usual first-order expression.[28] Hyperfine structure due to the deuterium nucleus was also analyzed in the case of $DC^{14}N{-}^{32}SO_3$ and $DC^{14}N{-}^{34}SO_3$ using standard methods for systems with two coupling nuclei.

The effect of the equivalent oxygens in both complexes was apparent. For $HCN{-}SO_3$, the $K = 0$ spectra were intense but the $K = \pm1$ and ±2 spectra were absent. This is consistent with the application of Bose−Einstein statistics to the equivalent spinless oxygen atoms, which restricts values of K to integral multiples of 3. Although higher values of $K = \pm 3n$ states are in principle present in the jet, their population is significantly reduced relative to that of the $K = 0$ states and their analysis was not pursued. Thus, D_{eff} was not determined.

For $CH_3CN{-}SO_3$, the spin statistics produce effects similar to those previously discussed for $CH_3F{-}NH_3$[29] and $H_3N{-}SO_3$.[15a] In addition to the quantum numbers J and K, rotational states of the complex are described by m, which gives the component of angular momentum of the CH_3CN unit about its symmetry axis in the limit of free internal rotation. At infinite separation of the monomers, m and $K - m$ correlate with k_{CH_3CN} and k_{SO_3}, respectively, where the k's are the ordinary K quantum numbers for the free monomers and $k_{SO_3} + k_{CH_3CN} = K$. Thus, to the extent that the internal rotation is free, m describes the contribution of the CH_3CN moiety to the overall K of the complex, which appears in eq 2. For k_{SO_3}, values are restricted to integral multiples of 3 as noted above. For the CH_3CN, no such restriction exists, but cooling in the jet effectively limits the values of m to 0 and ±1. Although the $m = \pm1$ states are energetically well above kT in the jet, these states remain populated since the interconversion of the $k = 0$ and ±1 states has a vanishingly small collisional cross section.

Since only $K = 0$ and ±1 states are observed in this work, and since $K = k_{SO_3} + k_{CH_3CN}$, only values of $K = m$ are observed. Without this restriction, the D_{JKm} distortion term used by Fraser et al.[29] splits the $K = \pm1$ transitions into a doublet whose components correspond to $mK > 0$ and $mK < 0$. In the present case, however, with $m = K$, only the $mK > 0$ component is observed and D_{eff} in eq 2 is related to the constants of Fraser et al. by $D_{\text{eff}} = D_{JK} + D_{JM} + D_{JKm}$. As in the case of $HCN{-}SO_3$, states correlating with $k_{SO3} = \pm3$ were not analyzed. Spectroscopic constants resulting from least-squares fits of the data in Tables 1 and 2 are presented in Table 3. Residuals from the fits are also given in Tables 1 and 2.

Structure Analysis

For both complexes studied, the symmetric top spectrum together with the magnitudes of the isotope shifts in the rotational constants confirm the expected geometry, namely that in which the nitrogen bonds to the sulfur with the symmetry axis of the nitrile along the C_3 axis of the SO_3. Furthermore, preliminary analysis of the rotational constants indicates that the nitrogen−sulfur bond lengths are about 2.6 and 2.5 Å for the HCN and CH_3CN complexes, respectively. These values are significantly shorter than the 2.9 Å distance expected for a van der Waals distance, yet still much longer than the sum of

TABLE 1: Observed Transitions of HCN−SO$_3$[a]

J'	F_1'	F'	J''	F_1''	F''	frequency (MHz)	(obs − calc) (MHz)
$HC^{14}N-^{32}SO_3$							
1		1	0		1	3788.385	−0.001
1		2	0		1	3789.580	0.001
1		0	0		1	3791.369	0.000
2		2	1		2	7577.526	0.000
2		1	1		0	7577.725	0.000
2		2	1		1	7578.719	0.000
2		3	1		2	7578.806	0.001
2		1	1		2	7579.515	0.000
2		1	1		1	7580.708	0.000
3		3	2		3	11366.695	−0.002
3		2	2		1	11367.777	0.001
3		3	2		2	11367.978	0.003
3		4	2		3	11368.021	−0.002
3		2	2		3	11368.488	0.001
3		2	2		2	11369.764	−0.001
$HC^{14}N-^{34}SO_3$							
1		1	0		1	3771.390	0.000
1		2	0		1	3772.584	0.001
1		0	0		1	3774.373	−0.001
2		2	1		2	7543.533	-0.001
2		1	1		0	7543.733	0.000
2		2	1		1	7544.727	0.000
2		3	1		2	7544.813	0.000
2		1	1		2	7545.523	0.000
2		1	1		1	7546.717	0.000
3		3	2		3	11315.709	0.000
3		2	2		1	11316.788	−0.001
3		3	2		2	11316.992	0.004
3		4	2		3	11317.033	−0.002
3		2	2		2	11318.778	0.000
$DC^{15}N-^{32}SO_3$							
1		2	0		1	3537.631	0.000
1		1	0		1	3537.687	0.000
2		1	1		1	7075.150	−0.001
2		3	1		2	7075.243	0.003
2		2	1		1	7075.243	−0.001
2		1	1		0	7075.290	−0.001
3		4	2		3	10612.773[b]	0.000
$DC^{14}N-^{32}SO_3$[c]							
1	0	1	0	1	2	3574.635	−0.001
1	0	1	0	1	1	3574.635	−0.001
1	0	1	0	1	0	3574.635	−0.001
1	2	2	0	1	2	3574.665	−0.002
1	2	2	0	1	1	3574.665	−0.002
1	1	0	0	1	0	3574.708	−0.002
1	1	0	0	1	1	3574.708	−0.002
1	2	1	0	1	0	3575.829	−0.001
1	2	1	0	1	1	3575.829	−0.001
1	2	1	0	1	2	3575.829	−0.001
1	2	3	0	1	2	3575.852	0.000
1	1	2	0	1	1	3575.894	−0.001
1	1	2	0	1	2	3575.894	−0.001
$DC^{14}N-^{32}SO_3$[c] (cont.)							
1	1	1	0	1	1	3577.660	0.001
1	1	1	0	1	2	3577.660	0.001
1	1	1	0	1	0	3577.660	0.001
2	1	1	1	1	2	7150.029	0.001
2	1	2	1	1	2	7150.072	−0.003
2	3	3	1	2	3	7150.089	0.000
2	1	0	1	1	1	7150.239	0.002
2	2	2	1	1	1	7150.280	−0.001
2	2	1	1	1	1	7150.311	0.001
2	1	1	1	1	0	7151.214	0.001
2	3	3	1	2	2	7151.273	−0.001
2	1	1	1	0	1	7151.290	0.003
2	1	2	1	2	2	7151.309	0.005
2	1	2	1	0	1	7151.336	0.002
2	3	4	1	2	3	7151.366	−0.001
2	2	3	1	1	2	7151.380	0.002
2	2	2	1	2	3	7152.088	−0.002
2	2	1	1	1	0	7153.258	−0.002
2	2	2	1	2	2	7153.274	−0.001
2	2	1	1	2	2	7153.303	−0.001
$DC^{14}N-^{34}SO_3$[c]							
1	0	1	0	1	2	3558.035	0.000
1	0	1	0	1	1	3558.035	0.000
1	0	1	0	1	0	3558.035	0.000
1	2	2	0	1	2	3558.063	−0.003
1	2	2	0	1	1	3558.063	−0.003
1	1	2	0	1	1	3559.294	0.000
1	1	2	0	1	2	3559.294	0.000
1	1	1	0	1	1	3561.057	−0.002
1	1	1	0	1	2	3561.057	−0.002
1	1	1	0	1	0	3561.057	−0.002
2	1	2	1	1	2	7116.867	−0.004
2	3	3	1	2	3	7116.884	0.000
2	2	2	1	1	1	7117.073	−0.003
2	1	1	1	1	0	7118.009	0.002
2	3	3	1	2	2	7118.071	0.002
2	1	2	1	0	1	7118.131	0.001
2	3	4	1	2	3	7118.162	0.001
2	2	3	1	1	2	7118.177	0.004
2	2	3	1	2	3	7118.216	−0.001
$HC^{14}N-^{33}SO_3$[d]							
2	2.5	2.5	1	1.5	1.5	7560.994	−0.005
2	0.5	1.5	1	0.5	1.5	7561.202	0.004
2	3.5	3.5	1	2.5	2.5	7561.680	0.000
2	3.5	4.5	1	2.5	3.5	7561.960	0.002
2	2.5	3.5	1	1.5	2.5	7562.147	−0.004
2	3.5	2.5	1	2.5	1.5	7562.186	0.001
3	3.5	3.5	2	2.5	2.5	11342.094	0.000
3	4.5	4.5	2	3.5	3.5	11342.273	0.003
3	4.5	3.5	2	3.5	2.5	11342.273	−0.002
3	4.5	5.5	2	3.5	4.5	11342.409	0.004
3	3.5	4.5	2	2.5	3.5	11342.491	−0.003

[a] All transitions correspond to $K = 0$. Measurements are accurate to ±3 kHz. [b] Unresolved triplet of hyperfine components. [c] $\mathbf{F}_1 = \mathbf{I}(\mathbf{N}) + \mathbf{J}$; $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}(\mathbf{D})$. [d] $\mathbf{F}_1 = \mathbf{I}(\mathbf{S}) + \mathbf{J}$; $\mathbf{F} = \mathbf{F}_1 + \mathbf{I}(\mathbf{N})$.

covalent radii[22] for nitrogen and sulfur (1.74 Å). Thus, the analysis follows closely that used for other partially bonded complexes. Briefly, the individual monomer geometries are assumed to remain unchanged upon complexation *except* that the SO$_3$ is allowed to distort from its initially planar configuration. The validity of this approach has been discussed elsewhere.[11−16]

The coordinates used to describe the structure of RCN−SO$_3$ (R═H, CH$_3$) are illustrated in Figure 2. R_{cm} is the distance between the centers of mass of the RCN and SO$_3$ units and R(NS) is the nitrogen−sulfur bond length. The monomers are allowed to undergo large-amplitude angular vibrations (as in weakly bound complexes), and the instantaneous angular deviations from the equilibrium geometry are given by γ and χ for the RCN and SO$_3$ moieties, respectively. The degree of out-of-plane distortion of the SO$_3$ is given by α, which is equal to the NSO angle when $\gamma = \chi = 0$. In terms of these coordinates, the moment of inertia about the b-inertial axis, $\langle I_{\mathrm{bb}}\rangle = h^2/8\pi^2 B$, may be written as

$$\langle I_{\mathrm{bb}}\rangle = M_{\mathrm{s}}\langle R_{\mathrm{cm}}{}^2\rangle + ({}^1/_2)I_{\mathrm{bb}}(\mathrm{SO_3})[1 + \langle\cos^2\chi\rangle] + ({}^1/_2)I_{\mathrm{cc}}(\mathrm{SO_3})\langle\sin^2\chi\rangle + ({}^1/_2)I_{\mathrm{bb}}(\mathrm{RCN})[1 + \langle\cos^2\gamma\rangle] + ({}^1/_2)I_{\mathrm{aa}}(\mathrm{RCN})\langle\sin^2\gamma\rangle \quad (3)$$

where $M_{\mathrm{s}} = m(\mathrm{RCN})m(\mathrm{SO_3})/[m(\mathrm{RCN}) + m(\mathrm{SO_3})]$, the I_{gg}'s are the moments of inertia of the indicated monomer units about their *g*th inertial axes, and the angular brackets denote averaging over the ground vibrational state. The dependence of $\langle I_{\mathrm{bb}}\rangle$ on α

TABLE 2: Observed Transitions of $CH_3CN{-}SO_3$[a]

J'	F'	J''	F''	K	frequency (MHz)	(obs − calc) (MHz)
$CH_3C^{14}N{-}^{32}SO_3$						
2	2	1	2	0	4062.319	0.001
2	2	1	1	1	4062.416	0.000
2	1	1	0	0	4062.490	−0.001
2	2	1	2	1	4062.927	−0.006
2	1	1	1	1	4063.278	0.000
2	2	1	1	0	4063.351	−0.002
2	3	1	2	0	4063.428	0.001
2	3	1	2	1	4063.488	0.000
2	1	1	2	1	4063.793	−0.003
2	1	1	2	0	4064.045	0.002
2	1	1	0	1	4064.573	0.001
2	1	1	1	0	4065.077	−0.001
3	3	2	3	0	6093.901	0.000
3	3	2	3	1	6094.128	0.001
3	3	2	2	1	6094.683	0.001
3	2	2	1	0	6094.835	−0.002
3	2	2	1	1	6094.991	0.007
3	4	2	3	1	6094.991	0.001
3	3	2	2	0	6095.013	0.003
3	4	2	3	0	6095.052	0.001
3	2	2	2	1	6095.845	−0.002
3	2	2	2	0	6096.562	−0.001
4	4	3	4	0	8125.491	−0.002
4	4	3	4	1	8125.543	−0.001
4	4	3	3	1	8126.407	0.000
4	3	3	2	1	8126.499	0.000
4	5	3	4	1	8126.544	0.000
4	3	3	2	0	8126.567	−0.002
4	4	3	3	0	8126.645	0.002
4	5	3	4	0	8126.669	0.000
4	3	3	3	1	8127.663	−0.001
4	3	3	3	0	8128.122	0.000
$CH_3C^{14}N{-}^{34}SO_3$						
2	2	1	1	1	4037.235	0.000
2	1	1	0	0	4037.309	0.000
2	1	1	0	1	4039.399	0.005
2	1	1	1	1	4038.097	−0.001
2	2	1	1	0	4038.168	−0.005
2	3	1	2	0	4038.247	0.000
2	3	1	2	1	4038.306	−0.002
2	1	1	1	0	4039.898	−0.003
3	3	2	3	0	6056.128	−0.001
3	3	2	3	1	6056.360	0.004
3	3	2	2	1	6056.909	−0.002
3	2	2	1	0	6057.066	0.000
3	4	2	3	1	6057.220	0.000
3	3	2	2	0	6057.242	0.003
3	4	2	3	0	6057.281	0.001
4	4	3	4	0	8075.129	0.000
4	4	3	4	1	8075.181	0.000
4	4	3	3	1	8076.046	0.001
4	3	3	2	1	8076.136	−0.001
4	5	3	4	1	8076.183	0.001
4	3	3	2	0	8076.203	−0.004
$CH_3C^{14}N{-}^{34}SO_3$ (cont)						
4	4	3	3	0	8076.280	−0.001
4	5	3	4	0	8076.307	0.000
$CD_3C^{14}N{-}^{32}SO_3$						
2	2	1	2	0	3670.912	−0.001
2	2	1	1	1	3671.035	0.000
2	1	1	0	0	3671.084	−0.003
2	2	1	1	0	3671.956	0.001
2	3	1	2	0	3672.029	0.000
2	3	1	2	1	3672.117	0.003
2	1	1	1	0	3673.693	0.002
3	3	2	3	0	5506.802	0.002
3	3	2	3	1	5507.063	−0.001
3	3	2	2	1	5507.622	0.000
3	2	2	1	0	5507.741	−0.001
3	4	2	3	1	5507.934	0.002
3	4	2	3	0	5507.953	−0.004
3	2	2	2	1	5508.787	−0.007
3	2	2	2	0	5509.478	0.000
4	4	3	4	0	7342.703	0.002
4	4	3	4	1	7342.802	0.001
4	4	3	3	1	7343.665	−0.004
4	3	3	2	1	7343.764	0.002
4	3	3	2	0	7343.782	−0.002
4	5	3	4	1	7343.804	−0.003
4	4	3	3	0	7343.859	0.001
4	5	3	4	0	7343.886	0.001
4	3	3	3	1	7344.935	0.002
4	3	3	3	0	7345.346	0.000
$CD_3C^{14}N{-}^{34}SO_3$						
3	3	2	2	1	5471.584	0.008
3	2	2	1	0	5471.699	0.001
3	2	2	1	1	5471.880	0.001
3	4	2	3	1	5471.891	0.005
3	4	2	3	0	5471.913	0.000
4	4	3	4	0	7294.644	0.000
4	4	3	3	1	7295.609	0.001
4	3	3	2	0	7295.714	−0.012
4	5	3	4	1	7295.744	−0.002
4	4	3	3	0	7295.799	−0.001
4	5	3	4	0	7295.826	0.000
4	3	3	3	1	7296.871	0.000
5	5	4	4	1	9119.528	0.000
5	6	4	5	1	9119.603	−0.001
5	4	4	3	0	9119.664	0.002
5	5	4	4	0	9119.701	−0.002
5	6	4	5	0	9119.724	0.003
$CH_3C^{15}N{-}^{32}SO_3$						
3		2		1	6078.129	0.001
3		2		0	6078.240	−0.001
4		3		1	8104.133	0.000
4		3		0	8104.284	0.000
5		4		1	10130.105	−0.001
5		4		0	10130.294	0.000

[a] Estimated uncertainties in spectral frequencies is ±3 kHz.

is contained in the expressions for the $I_{gg}(SO_3)$[28b] and may be extracted from $^{32}S/^{34}S$ isotopic substitution.

The implementation of eq 3 to determine R_{cm} and α requires estimates of $\langle \cos^2 \chi \rangle$ and $\langle \cos^2 \gamma \rangle$. While these can often be obtained from hyperfine structure in the case of weakly bound systems, the possibility of a partial chemical interaction complicates the problem to some extent here. Detailed arguments, together with the final structures are given for each complex below.

$HCN{-}SO_3$. Initially, values of $\langle \cos^2 \gamma \rangle$ (and hence $\gamma_{eff} \equiv \cos^{-1} \langle \cos^2 \gamma \rangle^{1/2}$) were calculated from the tensor projection formula

$$eQq_{complex} = eQq_0 \langle P_2 \cos(\gamma) \rangle = eQq_0 [3 \langle \cos^2 \gamma \rangle - 1]/2 \quad (4)$$

using both ^{14}N and deuterium quadrupole coupling constants. Here, $eQq_{complex}$ is the quadrupole coupling constant of a particular nucleus observed in the complex and eQq_0 is that of the free monomer. Using the literature values for $eQq_0(HC^{14}N) = -4.70789(8)$ MHz[30] and $eQq_0(DC^{14}N) = -4.7030(12)$ MHz,[31] the values of γ_{eff} obtained from the five ^{14}N coupling constants in Table 3 range from 18.5° to 18.9°. On the other hand, values obtained using the deuterium coupling constants and the literature values of $eQq_0(DC^{14}N) = 0.1944(22)$ MHz[31] and $eQq_0(DC^{15}N) = 0.207(4)$ MHz[32] are 6.2(+3.5/−6.2)°, 4.0(+5.1/−4.0)°, and 14.7(+3.8/−5.4)° for the $DC^{14}N{-}^{32}SO_3$, $DC^{14}N{-}^{34}SO_3$, and $DC^{15}N{-}^{32}SO_3$ derivatives, respectively. Since eq 4 is valid only to the extent that the electric field gradient at the coupling nucleus is unchanged upon complex-

TABLE 3: Spectroscopic Constants of $HCN-SO_3$ and CH_3CN-SO_3[a]

species	B (MHz)	D_J (kHz)	D_{eff} (kHz)	eQq(N) (MHz)	eQq(D) (MHz)	eQq(S) (MHz)
$HC^{14}N-^{32}SO_3$	1894.6937(8)	1.730(52)	b	−3.9779(49)		
$HC^{14}N-^{33}SO_3$	1890.3904(6)	1.742(21)	b	−3.965(14)		−17.15(14)
$HC^{14}N-^{34}SO_3$	1886.1956(8)	1.717(56)	b	−3.9785(49)		
$DC^{14}N-^{32}SO_3$	1787.8339(1)	1.578(9)	b	−3.9960(12)	0.1905(14)	
$DC^{14}N-^{34}SO_3$	1779.5335(2)	1.685(25)	b	−3.9945(21)	0.1930(20)	
$DC^{15}N-^{32}SO_3$	1768.8230(11)	1.519(92)	b		0.1872(85)	
$CH_3C^{14}N-^{32}SO_3$	1015.8409(2)	0.3305(51)	18.71(17)	−3.4506(24)		
$CH_3C^{14}N-^{34}SO_3$	1009.5460(3)	0.3417(71)	18.69(21)	−3.4552(47)		
$CD_3C^{14}N-^{32}SO_3$	917.9908(3)	0.2644(82)	12.88(29)	−3.4720(32)		
$CD_3C^{14}N-^{34}SO_3$	911.9833(2)	0.2599(45)	13.19(21)	−3.4676(83)		
$CH_3C^{15}N-^{32}SO_3$	1013.0462(8)	0.336(17)	18.83(51)			

[a] Uncertainties are one standard error in the least-squares fits. [b] Not determined.

ation, the sharp disagreement between the ^{14}N and deuterium results almost certainly signals electronic rearrangement on the HCN. A similar effect has been observed in $(HCN)_2$.[33] The deuterium atom in $HCN-SO_3$ is most remote from the site of the intermolecular interaction and thus we take γ_{eff} to be the average value of the three deuterium-based determinations, 8.3-(4.6)°. The 4.6° uncertainty is the standard deviation among the three experimental values, which seems appropriate since the scatter among them is comparable to their individual uncertainties.

For the SO_3, the corresponding expectation value, $\langle \cos^2 \chi \rangle$, is harder to evaluate. Interestingly, the ^{33}S quadrupole coupling constant in $HCN-^{33}SO_3$ is essentially identical to the ab initio value of −17.14 MHz obtained for the $^{33}SO_3$ monomer.[34] However, we cannot interpret this as representing a value of unity for $\langle \cos^2 \chi \rangle$ since a negligible angular vibrational amplitude would only arise in the case of significant bonding between the nitrogen and the sulfur. This would present an inconsistency, however, since in such a scenario the electric field gradient at the sulfur would necessarily be different from that in free SO_3. Thus, we surmise that the similarity between the quadrupole coupling constants in $HCN-^{33}SO_3$ and free $^{33}SO_3$ is accidental, resulting from a combination of electronic and vibrational effects in the complex. That significant electronic rearrangement takes place upon complexation is consistent with the results of the ^{14}N hyperfine structure. The implication, however, is that the eQq(^{33}S) should not be used in the estimation of $\langle \cos^2 \chi \rangle$.

Fortunately, $\langle I_{bb} \rangle$ in eq 3 is only weakly dependent on $\langle \cos^2 \chi \rangle$ and only a rough estimate is needed. Since both the bond length and the hyperfine structure indicate some degree of chemical interaction in the complex, the range of plausible values of χ_{eff} is easily bracketed by the minimum value of zero and a maximum value equal to the characteristic vibrational amplitude of weakly bound SO_3. The latter has recently been estimated for $Ar-^{33}SO_3$ to be 15.6°,[34] and thus we take a nominal value of $\chi_{eff} = 7.8 \pm 7.8°$. Moreover, we can bracket the effects of χ_{eff} on the calculated structure of the complex by performing the analysis at $\chi_{eff} = 0°$ and 15.6°, thereby encompassing the full range of reasonable values.

R(NS) and α for $HCN-SO_3$ were initially determined by a least-squares fit of the six observed moments of inertia with γ_{eff} and χ_{eff} constrained to the values chosen above, viz, 8.3° and 7.8°, respectively. To estimate the effects of uncertainties in these angles, the fits were then repeated with these parameters constrained to all combinations of the maximum and minimum values implied by their error bars. The minimum and maximum values of R(NS) obtained were 2.5709 and 2.5831 Å, respectively, with an average value of 2.577 Å. The resulting values of α ranged from 91.42° to 91.64°.

To test the effect of constraining the monomer bond lengths to their free-molecule values, we applied the notion that the changes in monomer geometries upon forming a *partially* bound complex will not be more that those observed when the monomers participate in a fully developed chemical bond. For the HCN subunit, we used the −0.103 and −0.033 Å changes in the HC and CN bond lengths observed when HCN forms crystalline $HCN-BF_3$.[12b] Using these values to make the appropriate changes in the HCN rotational constants and refitting the moments of inertia of the complex causes R(NS) and α to change by 0.0004 Å and 0.58°, respectively. Similarly, for the SO_3 moiety, the crystal structure of H_3N-SO_3[35] was used to estimate the maximum plausible elongation of the S−O bond (0.0225 Å). The corresponding changes in R(NS) and α were −0.010 Å and −0.12°, respectively.

TABLE 4: Structural Results for $HCN-SO_3$ and CH_3CN-SO_3[a]

parameter	$HCN-SO_3$	CH_3CN-SO_3
R(NS) (Å)	2.577(6)	2.466(16)
α (deg)	91.8(4)	92.0(7)

[a] See text for discussion of uncertainties.

Clearly, the effects of the assumptions in the analysis are small. While the uncertainties in γ and χ are very realistic, the monomer distortions, in all likelihood, represent the worst-case scenario. This is apparent since the values of R(NS) and α indicate that $HCN-SO_3$, while partially bound, is more like a weakly bound complex than a chemically bonded adduct. Thus, considering the entire assortment of fits describe above, we settle on values of $R(NS) = 2.577(6)$ Å and $\alpha = 91.8(4)°$. These results are reported in Table 4.

It should be noted that, in the above analysis, the correlation coefficients between R(NS) and α were high. Thus, as a final check of the calculated structure, we applied a Kraitchman analysis[28b] to determine the N−S bond length. The result, 2.574 Å is in excellent agreement with the 2.577(6) Å value given above. Double substitution on the HCN also affords a measure of $\langle \cos \gamma \rangle$ [33] and gives an effective bending amplitude of 5.5°. This too is in remarkable agreement with the above results. We retain as our “preferred structure”, however, that obtained from the fitting of moments of inertia, since the Kraitchman formalism does not explicitly include the angular vibrations of the subunits.[36]

CH_3CN-SO_3. The methods of analysis were similar to those described above for $HCN-SO_3$. Using the literature value of eQq($CH_3C^{14}N$) = −4.2243(40) MHz[37] in eq 4, the ^{14}N quadrupole coupling constants in Table 3 yield values of γ_{eff} ranging from 20.2° to 20.5°. These values, though consistent among isotopomers, seem excessive on several counts. For example, in CH_3CN-HF, a weakly bound complex, the corre-

TABLE 5: Comparison of Selected Sulfur−Nitrogen and Boron−Nitrogen Complexes

SO_2 and SO_3					BF_3 and BH_3				
complex[a]	R(SN) (Å)	α(NSO) (deg)	ΔE[b] (kcal/mol)	ref[c]	complex[a]	R(BN) (Å)	α(NBX) (deg)	ΔE[b] (kcal/mol)	ref[c]
$HCN-SO_2$(g)	2.98		3.6[d]	42					
					N_2-BF_3(g)	2.875(20)	90.5(5)		52
					$NCCN-BF_3$(g)	2.647(3)	93[j]	3.6[i]	54
$HCN-SO_3$(g)	2.577(6)	91.8(4)	4.8[e]	*f*	$HCN-BF_3$(g)	2.473(29)	91.5(15)	4.6[k] 5.8[l]	12a
CH_3CN-SO_3(g)	2.466(16)	92.0(7)	8.4[e]	*f*	CH_3CN-BF_3(g)	2.011(7)	95.6(6)	5.7[j] 7.2[l]	11
Me_2HN-SO_2(g)	2.34(3)		10.3[g]	45					
Me_3N-SO_2(g)	2.26(3)		13.4[g]	46					
Me_2HN-SO_2(c)	2.00(1)			18					
Me_3N-SO_2(c)	2.046(4)			46					
H_3N-SO_3(g)	1.957(23)	97.6(4)	19.1[h]	15a	H_3N-BF_3(g)	1.673(10)	103.6[k]	19.2[k]	55
					H_3N-BH_3(g)	1.658(2)	104.7(1)	33.7[l]	56
					Me_3N-BH_3(g)	1.638(10)	105.3(2)	43.6[l]	57
					Me_3N-BF_3(g)	1.636(4)	106.4(3)	33.3[l]	58
Me_3N-SO_3(g)	1.912(24)	100.04(4)		48					
Me_2HN-SO_3(c)	1.790(6)	102.1(3)		49					
MeH_2N-SO_3(c)	1.779(8)	102.4(7)		50					
					CH_3CN-BF_3(c)	1.630(4)	105.6(6)		59
H_3N-SO_3(c)	1.7714(3)	102.46(2)	32.6[i]	35	H_3N-BF_3(c)	1.60(2)	107(2)		60
Me_3N-SO_3(c)	1.844(2)	101.8(1)		51	Me_3N-BF_3(c)	1.585(5)	112(2)		61
					MeH_2N-BF_3(c)	1.58(2)	108.3(20)		62

[a] Symbol in parentheses gives the phase: g = gas; c = crystal. [b] Binding energy (D_e). [c] References are for the experimental structures. [d] Reference 41. [e] Reference 43. [f] This work. [g] Reference 44. [h] Reference 47. [i] SCRF calculation of ref 47. [j] Theoretical results of ref 53. [k] Reference 19. [l] Reference 8.

sponding value is somewhat smaller (16° from eq 4, 8° from a force constant analysis).[38] Moreover, the shorter bond length for CH_3CN-SO_3 relative to that $HCN-SO_3$ would be inconsistent with the larger angular anisotropy implied by a 20° excursion angle. Indeed, having established that the quadrupole coupling constant in $HCN-SO_3$ is affected by electronic rearrangement at the nitrogen, it would be unreasonable to expect a similar effect to be absent in CH_3CN-SO_3. Again, however, only a rough estimate of γ_{eff} is needed and thus, it is more reasonable to simply scale the corresponding range from $HCN-SO_3$ by the fourth root of the ratio of the HCN and CH_3CN moments of inertia.[39] Though not strictly correct, we note that the bonding in the two complexes is not vastly different (as indicated by bond lengths and bond angles) and thus, such a procedure should be adequate. The resulting range is $\gamma_{\text{eff}} = 6 \pm 3°$. $\langle \cos^2 \chi \rangle$ is chosen as in the case of $HCN-SO_3$.

Values of R(NS) and α were obtained from a series of fits similar to those described for $HCN-SO_3$, with the moments of inertia of free acetonitrile taken from the literature.[40] The results are also given in Table 4. A Kraitchman analysis yielded an N−S bond length of 2.435 Å, which is again in acceptable agreement with the reported value.

Discussion

Molecular and Electronic Structure. The structures of $HCN-SO_3$ and CH_3CN-SO_3 are indicative of dative bonds which are in their early stages of formation. This is clear from the N−S bond lengths which, as noted above, are much longer than the sum of covalent bond radii (1.74 Å) but still considerably shorter than the estimated van der Waals distance of 2.9 Å. The small but finite angular distortions of the SO_3 unit also represent the start of a progression from the trigonal planar arrangement of free SO_3 to the tetracoordinate geometry of its adducts. The shorter bond length in the CH_3CN complex is consistent with the greater basicity of CH_3CN relative to that of HCN.

The progression between weak bonding and chemical interactions in complexes containing a sulfur−nitrogen bond is examined more broadly in Table 5. Except as indicated, bond distances and bond angles come from microwave spectroscopy and X-ray crystallography. Binding energies are from ab initio theory. For the purposes of later comparison, the table also includes data for related complexes of BF_3 and BH_3.

It is clear from the table that a wide range of N−S distances is represented, spanning the 1.77 Å bond length in solid H_3N-SO_3 to the 2.98 Å van der Waals distance in $HCN-SO_2$. For complexes of SO_3, where α(NSO) truly represents a disortion of the SO_x moiety, the decrease in bond distance is seen to be accompanied by an increase in bond angle. Thus, from a structural perspective, this series clearly represents a transition from van der Waals to chemical bonding. The binding energies are consistent with this assessment.

The ordering of compounds is also generally in accord with chemical sensibilities. For example, methylation of the gas-phase electron pair donors increases their basicity and shortens the dative bond distances. This is seen not only in the case of the $HCN-SO_3$ and CH_3CN-SO_3 noted above but in gas-phase H_3N-SO_3 and $(CH_3)_3N-SO_3$ as well. A similar effect is observed upon comparing the dimethylamine and trimethylamine complexes of SO_2 in the gas phase. The greater acidity of SO_3 compared with SO_2 is also apparent from its HCN and $(CH_3)_3N$ complexes. Small anomalies are seen in the case of the solid adducts of methylamines with SO_3 and are probably related to the details of the forces which act on the molecules in the crystal.

In light of the notion of a "partially formed" bond, it is of some interest to attempt to quantify the degree of electron transfer which occurs upon complexation. In principle, such information can be obtained from the ^{14}N nuclear hyperfine structure. The quadrupole coupling constant of a single p_z electron in atomic nitrogen is approximately −9.0 MHz,[63] while the free monomer values for HCN[30] and CH_3CN[37] are

$-4.70789(8)$ and $-4.2243(40)$ MHz, respectively. Using these numbers, and assuming that the lone pair of electrons on the nitrile is in a pure sp hybrid orbital, a Townes and Dailey analysis[28] of the ^{14}N quadrupole coupling constants in Table 3 gives 0.16 and 0.17 e transferred for the HCN and CH_3CN complexes, respectively.

It should be noted that, since the above calculation uses the observed values of eQq, the purely projective reduction in the quadrupole coupling constant described by eq 4 has been ignored. The calculation can be easily be modified, however, to account for angular vibrations by dividing the observed quadrupole coupling constant of each complex by the appropriate value of $\langle P_2(\cos \gamma_{\mathrm{eff}})\rangle$. The resulting "zero-point corrected" constants may be interpreted as the "$(eQq)_0$'s" of the electronically reorganized RCN, whose values in their respective complexes are reduced still further by angular zero-point motion. Using the estimates of γ_{eff} discussed in the previous section, the Townes and Dailey analysis gives zero-point corrected electron-transfer values of 0.13 and 0.16 e for the HCN and CH_3CN complexes, respectively. The vibrational corrections turn out to be small because $P_2(\cos \gamma_{\mathrm{eff}})$ is very near unity for both systems.

It is satisfying that the degree of electron transfer obtained for both complexes is substantially less than the 0.36 e value previously determined for H_3N-SO_3, where the N$-$S bond distance is only 1.957 Å.[15a] We caution, however, in the case of H_3N-SO_3, the N$-$S bond is short and the observed quadrupole coupling constant is significantly different from that of free ammonia. Thus, it is reasonable to apply the Townes and Dailey model. But in the case of $HCN-SO_3$ and CH_3CN-SO_3, the dative bond is considerably less developed and the changes in the quadrupole coupling constants upon complexation are not as large. In this regard, we note that, even in *weakly* bound complexes, small changes in quadrupole coupling constants can occur without electron transfer.[64] Thus, the above calculations may not yield quantitatively accurate measures of the degree of electron transfer. Nevertheless, the small but finite values obtained are consistent with bonds that are in the early stages of their formation.

One of the most interesting features of partially bonded systems is that their structures change dramatically upon crystallization.[17] Indeed, bond contractions of many tenths of an angstrom have been observed upon comparison of gas-phase and solid-state structures for partially bonded systems. While we are unaware of any previous reports of the crystalline complexes $HCN-SO_3$ and CH_3CN-SO_3, the formation of such compounds should, in principle, be possible if conditions could be arranged to crystallize the adduct before further chemistry takes place (e.g., such as that depicted in eq 1). On the basis of the results of this study, we predict that the N$-$S bonds in these crystals will be significantly shorter than those reported here. In support of this idea, we note that self-consistent reaction field calculations for both adducts indicate that the N$-$S bonds are substantially shorter in a dielectric medium than they are in a vacuum.[43]

Structure Correlation. The observation of "intermediate" structures such as those described above has been widely used to examine the reaction paths for simple chemical transformations. The idea is that if a systematic correlation between structural parameters, say q_1 and q_2, is observed across a series of related compounds, the locus of points (q_1,q_2) provides a qualitative depiction of the reaction path for some simple chemical reaction. This idea was first suggested by Bürgi and Dunitz and co-workers and later applied to a myriad of cases involving crystallographically determined structures.[65]

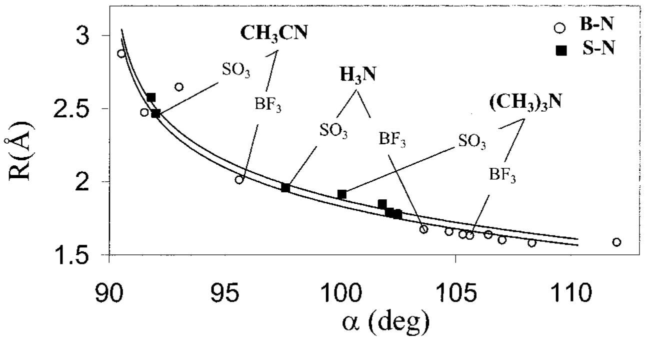

Figure 3. Structure correlation plot for S$-$N and B$-$N donor acceptor complexes. Circles represent boron$-$nitrogen data, and squares represent sulfur$-$nitrogen data. The solid curves are drawn as described in the text. Several gas-phase complexes with the same donor molecule are noted. Data for these plots are found in Table 5.

While most such studies have involved molecules in the solid state, at least one example of a *gas-phase* structure correlation has also been reported.[11] Specifically, in a series of BF_3 and BH_3 adducts with amine and nitrile donors, a gradual shortening of the B$-$N bond length (R) was observed to be accompanied by a systematic increase in the NBF or NBH angle (α). Thus, the series of points (R,α) was interpreted as a representation of the "reaction path" for the formation of a dative B$-$N bond. Ab initio methods were subsequently used to test the notion that the reaction path thus determined is in reasonable accord with reality.[19]

The series of nitrogen$-SO_3$ complexes contained in Table 5 can be used to generate a similar "reaction path". The data are plotted in Figure 3, which also includes the boron$-$nitrogen systems for comparison. Clearly, as in the case of the BX_3 complexes, an increase in the NSO angle accompanies a shortening of the donor$-$acceptor bond. This is not particularly surprising. But what is remarkable, at least initially, is that despite the different atomic sizes of boron and sulfur, the two sets of data are nearly coincident.

Bond length$-$bond angle relationships such as those shown in Figure 3 have been widely scrutinized by chemists.[65,66] Perhaps most closely related to the present results are the observations by Murray-Rust, Bürgi, and Dunitz[67] that the Y$-$M bond lengths (r) and Y$-$M$-$X angles (θ) in a collection of nearly 200 different YMX_3 molecular fragments all fall on the same curve when referenced to a common origin. Murray-Rust et al. analyzed these data by starting with Pauling's empirical bond length$-$bond order relation,[68]

$$r_n = r_1 - c \log(n) \tag{5}$$

and converting it to a bond length$-$bond angle relationship via the formula

$$n = (-3 \cos \theta)^m \tag{6}$$

In these equations, r_n is the bond length for a bond of order n, r_1 is the bond length for $n = 1$, and m was chosen as 2. It should be noted that both the form of eq 6 and the choice of $m = 2$ are unfounded on any fundamental theoretical basis but reproduce the expected bond angles at $n = 0$ and $n = 1$. Moreover, when combined with equivalent formulas involving the MX bond length and XMX bond angle, eqs 5 and 6 preserve the total "bond number" about the central atom. Thus, they offered a simple (albeit simplistic) picture of the bonding and provided a compact means of correlating the structures of a large number of molecular fragments.

In a previous paper, we showed that eqs 5 and 6 also reproduce the bond length−bond angle relationship for the series of BX_3 complexes contained in Figure 3.[19] The lower curve, drawn through the open circles (BF_3 complexes), thus has the form

$$R(\mathrm{BN}) = R_1(\mathrm{BN}) + c_{\mathrm{BN}} \log[9 \cos^2 \alpha]$$

where α is the N−B−F angle and R(BN) is the boron−nitrogen bond length. The curve is drawn using the parameters R_1(BN) = 1.580(44) Å and $c_{\mathrm{BN}} = -0.441(35)$ Å, which were determined from a least-squares fit to the bond lengths and bond angles of the complexes included in the figure. The upper curve drawn through the sulfur−nitrogen data (squares) was drawn using R_1(SN) = 1.621(11) Å and $c_{\mathrm{SN}} = -0.449(1)$ Å, which were determined from a similar fit. Note that the constants c_{BN} and c_{SN} depend on an arbitrary choice of m and cannot be used to calculate bond orders from eq 5.

Clearly, the two curves in Figure 3 are very similar. If we adopt the interpretation[65] that they represent the response of the BF_3 or SO_3 acceptor to the approach of a "generalized" nitrogen donor, it would appear that the formation of the boron−nitrogen and sulfur−nitrogen bonds occurs along similar "paths". This is similar to the observation by Murray-Rust et al.[67] that the identity of the central atom has little effect on the bond angle−bond length relationship in valence bonded systems.

Despite the obvious similarities between the boron−nitrogen and sulfur−nitrogen series, however, there are some significant differences. In particular, we observe that for complexes which lie in the "partially bonded" regime (i.e., the middle of the diagram), the degree of bond formation for a particular donor with SO_3 appears to lag that for the same donor with BF_3. For example, in the complexes with HCN, CH_3CN, H_3N, and $(CH_3)_3N$ (the complexes in Table 5 for which direct comparison is possible), we find that R(NS) − R(NB) has values of 0.104, 0.455, 0.284, and 0.276 Å, respectively. Moreover, for a given donor, the angular distortion of BF_3 exceeds that of the equivalent complex of SO_3. The data corresponding to the gas-phase structures of the CH_3CN, H_3N, and $(CH_3)_3N$ complexes have been indicated in the figure, but the HCN points (which lie immediately to the left of $CH_3CN{-}SO_3$) have not in order to avoid clutter.

A portion of the bond length differences noted above certainly arises from the relative sizes of the central atom. However, we note that the difference in covalent radii for sulfur[21] and boron[69] is only 0.16 Å.[21] Also, it is interesting to observe that the van der Waals distances in $Ar{-}SO_3$[70] and $Ar{-}BF_3$[53] are 3.350 and 3.325 Å, differing by only 0.025 Å! If the 1.92 Å radius of argon is subtracted from these distances, we conclude that the "van der Waals radii of BF_3 and SO_3" are both 1.4 Å. This is about equal to the nonbonded radii of fluorine and oxygen, suggesting that in forming weak bonds to these acids, it is the crown formed by the oxygens or fluorines which sets the van der Waals contact distance. The relative similarity between $HCN{-}BF_3$ and $HCN{-}SO_3$ may reflect this idea. On the other hand, in the limit of a fully formed bond, R(NS) − R(BF) must approach the difference in covalent bond radii. The trend toward this limit is seen in the CH_3CN, H_3N, $(CH_3)_3N$ part of the series but is not fully realized. The intermediate bonding regime, in which the MX_3 unit is distorted but bonding is incomplete, is evidently more complex.

The question arises, "Is BF_3 more or less acidic than SO_3?". An enlightening discussion of this matter has been presented by Deakyne and Liebman[24] who argue that simple chemical reasoning using resonance structures and formal charges does not yield an unambiguous answer. However, using ab initio methods together with a limited amount of thermochemical data, they conclude that, with a series of anionic bases, SO_3 is the stronger acid. Whether this conclusion remains valid for the neutral amine and nitrile bases considered here is not clear. For example, in cases where direct comparison is possible (viz., the gas-phase complexes with HCN, CH_3CN, and NH_3), Table 5 indicates that the binding energies for the SO_3 and BF_3 complexes are fairly similar. From a structural perspective, the systematic lag in the bond lengths and bond angles of the SO_3 complexes noted above could arguably indicate that BF_3 is the stronger of the two acids. However, such an assessment would not be in keeping with the usual energetic criterion for evaluating acid strength. It is possible that SO_3, for which the π bonding presumably persists even after complexation, is less susceptible to out-of-plane distortion. Indeed the force constants for the umbrella mode of SO_3 are significantly larger than those for BF_3.[71] A broader, systematic investigation of the energetics of BF_3 and SO_3 complexes with neutral donors should prove fruitful.

Conclusion

The complexes $HCN{-}SO_3$ and $CH_3CN{-}SO_3$ have been studied in the gas phase by microwave spectroscopy. The N−S bond distances are shorter than expected for a van der Waals interaction, yet longer than the sum of covalent bond radii. This, together with the small but finite angular distortion of the SO_3 moiety, indicates that the N−S bond in these systems is partially formed. The observed nuclear quadrupole coupling constants further support this conclusion.

A series of complexes of SO_3 with amine and nitrile donors shows a distinct correlation between the N−S bond length and the degree of angular distortion of the SO_3 subunit. In the spirit of *crystallographic* structure correlations, the locus of points defined by the values of R(SN) and α(NSO) for members of the series is thus interpreted as a depiction of the reaction path for the formation of an N−S dative bond. It is shown that the path can be well described by combining Pauling's empirical bond length−bond order relation with a simple formula relating bond order to bond angle.

Complexes of SO_3, BF_3, and BH_3 show some interesting similarities and differences. The locus of points consisting of bond lengths and bond angles for complexes of BF_3 and BH_3 is very similar to (indeed nearly superimposable on) that for complexes of SO_3. This is true, despite the differing atomic sizes of sulfur and boron. Nevertheless, while the curves themselves are similar, the location of the complex corresponding to a particular electron pair donor differs between the two sets of data. Bond formation to SO_3 appears to lag that to BF_3. Although most measures of Lewis acidity are based on energetics (rather than structure), the structural results suggest that BF_3 may be a stronger acid when combined with neutral amines and nitriles. A systematic ab initio investigation of the relative acidities of BF_3 and SO_3 with neutral Lewis bases would be interesting.

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