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LETTERS

Structural Change at the Onset of Microsolvation: Rotational Spectroscopy of HCN···HCN−SO_3

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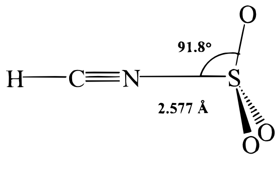
The structure and dipole moment of HCN···HCN−SO_3 have been determined by rotational spectroscopy. The N−S bond distance is 2.470(20) Å, which is 0.107(21) Å shorter than that in HCN−SO_3. In contrast, the N···H distance, 2.213(29) Å, is the same to within experimental uncertainty as that in $(HCN)_2$. The dipole moment of $HC^{15}N$···$HC^{15}N$−$^{32}SO_3$ is 8.640(19) D, representing an enhancement of 1.238(19) D over the sum of the dipole moments of HCN and HCN−SO_3. The results indicate significant changes in the HCN−SO_3 subunit upon interaction with a single HCN "solvent" molecule, with relatively little change in the HCN−HCN interaction. The hypersensitivity of the HCN−SO_3 moiety to the presence of an additional HCN arises because the dative bond is partially formed, and we suggest that partially bound systems may offer sensitive probes of microsolvation.

Introduction

The effect of solvent on molecular energetics and reactivity is a subject of immense importance in chemistry.[1] For this reason, in recent years much experimental and computational effort has been expended on the elucidation of the role of solvent in molecular systems.[2] Cluster science provides a microscopic view of molecules in their early phases of aggregation[3−8] and can thus offer a detailed picture of the early stages of solvation. In this vein, the study of microsolvated species constitutes an important bridge between molecular clusters and solution phase chemistry.

In recent years, we have been concerned with a class of molecules that are best described as "partially bound".[9,10] In general, these have been Lewis acid−base adducts in which the constituent moieties are chosen to produce a dative linkage that is intermediate between a van der Waals interaction and a fully formed chemical bond. We have shown that such systems undergo enormous changes in structure upon crystallization and are thus extraordinarily sensitive to the presence of near neighbors. It is reasonable to speculate, therefore, that partially bonded molecules may offer sensitive probes of microsolvation. The purpose of this study is to ascertain whether a single "solvent" molecule can produce a measurable effect on the structure and bonding of such systems.

In a previous paper,[11] we reported the microwave spectrum and structure of the complex HCN−SO_3, shown below.



The 2.577(6) Å bond length is slightly shorter than the 2.9 Å distance expected for a van der Waals interaction but is significantly longer than the sum of ordinary covalent bond radii for nitrogen and sulfur (1.74 Å). Correspondingly, the SO_3 unit is distorted (but only minimally) from its normally planar configuration. The system can thus be regarded as containing a nitrogen−sulfur bond in its early stages of formation and as

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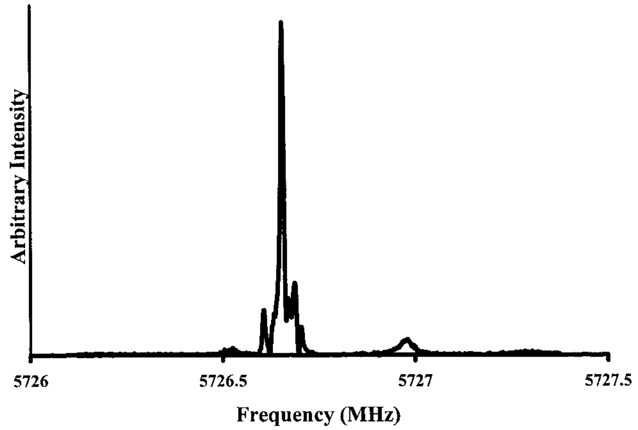

Figure 1. 7 ← 6 transition of $HC^{14}N\cdots HC^{14}N-^{32}SO_3$. This spectrum is the average of data taken in ~400 gas pulses over a period of ~60 s. The broad feature at the right is ringing of the microwave cavity, not a molecular transition.

such represents a viable candidate for testing the effect of microsolvation.

In this Letter, we report the rotational spectrum of $HCN\cdots HCN-SO_3$, which represents an $HCN-SO_3$ adduct microsolvated by a single HCN unit. The structure and dipole moment of the complex are determined and indeed demonstrate a significant, quantifiable effect of the additional HCN on the nature of the $HCN-SO_3$ moiety. The results are considered in the general context of medium effects in partially bonded systems.

Experimental Section

Rotational spectra were observed using a pulsed nozzle Fourier transform microwave spectrometer[12,13] equipped with aluminum Stark plates[14] for the determination of dipole moments. To produce the complex, a molecular injection source similar to previously reported designs[15−19] was used to inject HCN into an expansion of SO_3 seeded in argon. Approximately 2 atm of argon were passed over a polymerized sample of SO_3 and expanded through an 0.8 mm orifice. A mixture of 32% HCN in Ar was flowed through a 0.016 in. i.d. stainless steel needle into the early stages of the expansion at a backing pressure of 125 Torr. Spectra of eight isotopic derivatives were recorded, with ^{34}S-containing species observed in natural abundance. Isotopic substitution on the HCN moieties was accomplished using enriched samples. DCN was prepared by reaction of KCN with dry D_3PO_4 while $HC^{15}N$ was prepared by reacting 99 atom % $KC^{15}N$ (Icon Services) with dry H_3PO_4.

Results and Analysis

The observed spectra were characteristic of symmetric tops, and only levels with $K = 0$ and ± 3 were observed, consistent with Bose−Einstein statistics for equivalent splinless oxygens. Tables of experimental data are lengthy and are provided as Supporting Information. A sample spectrum is shown in Figure 1. With the exception of the doubly substituted ^{15}N derivative, all spectra exhibit the expected ^{14}N nuclear hyperfine structure, which was readily fit using standard methods for one or two nuclei, as appropriate.[20] Assignment of the nuclear quadrupole coupling constants to the inner and outer nitrogens was determined from the singly substituted ^{15}N derivatives. Deuterium hyperfine structure was not well resolved, and when present, broadened the observed transitions but did not preclude the determination of the nitrogen quadrupole coupling constants. Spectroscopic constants are given in Table 1.

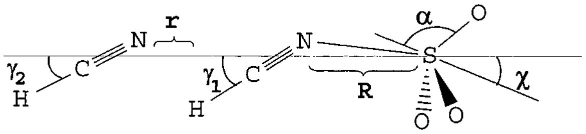

Figure 2. Definition of angles used to describe the structure of $HCN\cdots HCN-SO_3$. γ_1 and γ_2 give the instantaneous deviations of HCN_1 and HCN_2 from the equilibrium C_3 axis of the complex. χ is the analogous angle for the C_3 axis of the SO_3. α measures the distortion of the SO_3 unit from planarity and is equal to the NSO angle at the equilibrium geometry of the complex. R is the N−S distance and r is the length of the $HCN\cdots HCN$ hydrogen bond.

The dipole moment of $HC^{15}N\cdots HC^{15}N-^{32}SO_3$ was measured by observing the Stark effect on the $J = 6 \leftarrow 5$, $7 \leftarrow 6$, and $8 \leftarrow 7$, $K = 0$ transitions. The distance between the Stark electrodes was calibrated using the first-order Stark effect on the $J = 4 \leftarrow 3$, $K = \pm 3$ transition of $Ar-SO_3$,[21] as also described previously.[14] Only moderate electric field strengths (up to 127.6 V/cm) were applied, as the intensity of the observed components diminished with increased voltage. Transitions were observed mainly in the perpendicular ($\Delta M_J = \pm 1$) configuration and were readily fit to within experimental uncertainties using the usual second-order Stark formula.[20] A table of transition frequencies at various electric fields is also included as Supporting Information and the resulting dipole moment is given in Table 1.

The important structural parameters of the complex are defined in Figure 2. As in the case of $HCN-SO_3$, we account for the possibility of large amplitude vibration of the HCN and SO_3 subunits by including the angles χ, γ_1 and γ_2 in the analysis. Since the complex is a symmetric top, $\langle\chi\rangle = \langle\gamma_1\rangle = \langle\gamma_2\rangle = 0$. For $HCN-SO_3$, we argued that $\gamma_{\mathrm{eff}} \equiv \cos^{-1}\langle\cos^2\gamma\rangle^{1/2} = 8.3 \pm 4.6°$ and that $\chi_{\mathrm{eff}} \equiv \cos^{-1}\langle\cos^2\chi\rangle^{1/2} = 7.8 \pm 7.8°$.[11]

Several methods of fitting the structure were investigated, all of which resulted in essentially the same values for the relevant structural parameters. As in the case of $HCN-SO_3$, the H−C, C≡N, and S−O bond distances were fixed to those in free HCN[22] and SO_3,[23] respectively. The NSO angle, which at equilibrium is equivalent to α, was expected to differ from 90° but preliminary fits confirmed the expectation that α and χ were highly correlated thus not independently determinable from the rotational constants. Moreover, preliminary fits revealed a strong correlation of both α and χ with R. Consequently, α was estimated to be 92.2(6)° using $R_{N-S} = 2.47$ Å and the bond length − bond angle relationship

$$R_{N-S}\,(\text{Å}) = (1.621\ \text{Å}) - (0.449\ \text{Å})\log(9\cos^2\alpha) \quad (1)$$

which has been previously established for nitrogen−SO_3 adducts.[11] Equation 1 was found to accurately reproduce the NSO bond angles (α) for SO_3 complexes across a wide range of bond lengths and is expected to be reliable here. The quoted uncertainty of 0.6° is the rms deviation in predicted bond angles among the complexes used to derive eq 1. The value of χ was taken to be 7.8° ± 7.8°, which guarantees its value not to exceed the 15.6° value obtained for the more weakly bound complex $Ar-SO_3$.[24] For γ_2, a Kraitchman analysis of the hydrogen and nitrogen coordinates gave 9.4°, though for γ_1, a similar analysis failed since the inner nitrogen lies within 0.1 Å of the center of mass of the complex. For this reason, the value of γ_2 (9.4°) was utilized as a conservative upper limit for γ_1, which seems reasonable since the N−S bond is likely to be stronger than the $N\cdots H$ hydrogen bond and since the inner HCN is constrained by binding partners on both ends.

TABLE 1: Spectroscopic Constants of $HCN_2\cdots HCN_1-SO_3$[a]

isotopomer	B (MHz)	D_J (Hz)	D_{JK} (kHz)	$eQq(N_1)$[b]	$eQq(N_2)$[c]	μ (D)
$HC^{14}N-HC^{14}N-{}^{32}SO_3$	409.05358(16)	61.9(17)	5.191(13)	−3.882(15)	−4.053(15)	
$HC^{14}N-HC^{15}N-{}^{32}SO_3$	409.05958(16)	62.0[d]	e		−4.051(9)	
$HC^{15}N-HC^{14}N-{}^{32}SO_3$	401.750(1)	55(12)	e	−3.885(16)		
$HC^{15}N-HC^{15}N-{}^{32}SO_3$	401.76559(28)	55(4)	5.020(40)			8.640(19)
$HC^{15}N-HC^{15}N-{}^{34}SO_3$	398.8989(35)	63(39)	e			
$DC^{14}N-HC^{14}N-{}^{32}SO_3$	393.67411(7)	62.0[d]	e	−3.853(35)	−4.060(34)	
$HC^{14}N\text{-}DC^{14}N-{}^{32}SO_3$	406.93065(8)	53.87(50)	e	−3.866(34)	−4.042(41)	
$DC^{14}N\text{-}DC^{14}N-{}^{32}SO_3$	391.79521(6)	62.0[d]	e	−3.871(24)	−4.053(29)	

[a] Uncertainties are one standard error in the least-squares fit. [b] Inner nitrogen. [c] Outer nitrogen. [d] Held constant in fit. [e] This constant was not determined because only $K = 0$ lines were observed.

TABLE 2: Structural Parameters for $HCN\cdots HCN-SO_3$

parameter[a]	value
$R(N-S)$	2.470(20) Å
$r(N_2\cdots H)$	2.213(29) Å
$\alpha(NSO)$[b]	92.2(6)°
γ_2[c]	9.4°

[a] Numbering of the nitrogens is according to the formula $HCN_2\cdots HCN_1-SO_3$. [b] Estimated value. See text for discussion. [c] Determined from double-substitution Kraitchman analysis.

The "preferred" structural parameters of the complex were obtained from a series of least-squares fits in which R and r were varied with γ_2 fixed at 9.4° and γ_1, α, and χ constrained to values representing the maximum and minimum values implied by their uncertainties above (0° and 9.4° for γ_1; 91.6° and 92.8° for α; 0° and 15.6° for χ). The resulting ranges of values for R and r were small and the average value for each parameter is reported in Table 2. The uncertainties given encompass the full set of values obtained in the fits. These uncertainties are small, indicating that those parameters, which are not well determined from the rotational constants, have little effect on the determination of the important structural features of the system. This situation is typical of partially bound complexes.[9−11]

Finally, it should be noted that, in addition to the procedures described above, a broader series of least-squares fits were performed in order to test the stability of the resulting parameters to changes in the method of solving the structure. In these fits, different combinations of parameters were freed. The results were essentially the same as those in Table 2 but were found to be somewhat sensitive to initial estimates used in the least squares routine. With the constraints described above, however, this sensitivity was removed and thus the values given in Table 2 were deemed the most reliable.

Discussion

The spectroscopic and structural parameters determined above can be used to examine the effect of microsolvation on $HCN\cdots HCN-SO_3$. To do so, Table 3 compares the structural and electronic properties of the system with those of several closely related species. The N−S bond in $HCN-SO_3$ is seen to contract by 0.107(21) Å upon addition of the extra HCN unit, which is probably the most striking result of this work. The N···H distance, on the other hand, differs from that in $(HCN)_2$[25] by only 0.017(29) Å, which represents essentially no change within the experimental uncertainty. Thus, while the nitrogen−sulfur interaction is significantly affected by the presence of the remote HCN, the HCN···HCN interaction is relatively unaltered by the SO_3. The values of γ_2 in $HCN_2\cdots HCN_1-SO_3$ (9.4°) and γ_1 in $HCN_1\cdots HCN_2$ (13.7°) suggest a slight alignment of the terminal HCN in the trimer, but are nevertheless consistent with an HCN···HCN interaction which is not too different from that in $(HCN)_2$.

TABLE 3: Comparison of Structural and Electronic Properties for $HCN\cdots HCN-SO_3$ and Related Complexes

HCN_1-SO_3[a]	$HCN_2-HCN_1-SO_3$[b]
$R(N_1-S) = 2.577(6)$ Å	$R(N_1-S) = 2.470(20)$ Å
$\alpha(NSO) = 91.8(4)°$	$\alpha(NSO) = 92.2(6)°$
$\gamma_1 = 8.3(4.6)°$	$r(N_2\cdots H) = 2.213(29)$
	$\gamma_2 = 9.4°$
$eQq(N_1) = -3.9779(49)$ MHz	$eQq(N_1) = -3.882(15)$ MHz
	$eQq(N_2) = -4.053\ (15)$ MHz
$\mu = 4.4172(31)$ D[c]	$\mu = 8.640(19)$ D
$HCN_1\cdots HCN_2$[c]	$HCN_1\cdots HCN_2\cdots HCN_3$[d]
$r(N_1\cdots H) = 2.230$ Å	$r(N_1\cdots H) = 2.17$ Å
	$r(N_2\cdots H) = 2.18$ Å
$\gamma_1 = 13.7°$	$\gamma_1 = 12.6°$
$\gamma_2 = 9.0°$	$\gamma_2 = 6°$[e]
	$\gamma_3 = 8.6°$
$eQq(N_1) = -4.097(20)$ MHz	$eQq(N_1) = -4.049(2)$ MHz
$eQq(N_2) = -4.440(19)$ MHz	$eQq(N_2) = -4.251(2)$ MHz
	$eQq(N_3) = -4.375(1)$ MHz
$\mu = 6.552(35)$ D	$\mu = 10.6(1)$ D

[a] Reference 11. [b] This work. [c] Reference 25. [d] Reference 26. [e] Assumed value of ref 26.

The nitrogen quadrupole coupling constants are consistent with this picture. The value of $eQq(N_2)$ in $HCN_2\cdots HCN_1-SO_3$, for example, is nearly identical to $eQq(N_1)$ in $HCN_1\cdots HCN_2$, indicating that the hydrogen bonds in the two complexes are similar. However, $eQq(N_1)$ in $HCN_2\cdots HCN_1-SO_3$ is significantly less than any of the nitrogen coupling constants observed in $(HCN)_2$, $(HCN)_3$, or $HCN-SO_3$. Particularly noteworthy is the reduction in magnitude of $eQq(N_1)$ in $HCN_2-HCN_1-SO_3$ (−3.882(15) MHz) relative to that in $HCN-SO_3$ (−3.978(5) MHz). The change is in the direction opposing that expected to accompany a decreased vibrational amplitude and seems likely to reflect actual electronic rearrangement at the inner nitrogen.[27]

Both the structure and nuclear quadrupole coupling constants of the complex are consistent with an advancement of the dative interaction upon addition of the extra HCN. It is well established that *crystallization* of partially bonded systems drives their dative bonds toward completion[9,10] and such an effect, therefore, is not unexpected. Its magnitude, however, is somewhat dramatic. As a comparison, several complexes with the general formula HCN−HCN−Y (Y = HF, HCl, HCF_3, and CO_2) have also been investigated,[28] and shrinkage of the N−Y bonds relative to those of HCN−Y were found to be in the range 0.04−0.06 Å. These values, while significant, are still somewhat less than the 0.11 Å observed here for $HCN\cdots HCN-SO_3$. Undoubtedly, the ability of SO_3 to expand its octet and form true donor−acceptor complexes produces a heightened sensitivity of the $HCN-SO_3$ fragment to near neighbor interactions. Interestingly, contractions of the HCN···HCN *hydrogen bond* lengths in the HCN···HCN···Y systems (relative to HCN···HCN) are somewhat larger than those of $HCN\cdots HCN-SO_3$, falling in the range 0.004−0.07 Å. A similar range of values is observed for the

TABLE 4. Induced Dipole Components at the HF/aug-cc-pVDZ Level Using BLW-ED[a]

	$HCN\cdots HCN-SO_3$	$HCN-SO_3$
μ_{HF}	8.88	4.5
$\Delta\mu_{pol}$	1.13	0.908
$\Delta\mu_{CT}$	0.17	0.122
$\Delta\mu_{dist}(SO_3)$	0.23	0.183
$\Delta\mu_{dist}(HCN)$		0
$\Delta\mu_{dist}(HCN\cdots HCN)$	0.05	
μ(exp)	8.640(19)[b]	4.4172(31)[c]

[a] All values in Debye. $\Delta\mu_{pol}$ and $\Delta\mu_{CT}$ are the contributions to the induced dipole moment ($\Delta\mu_{ind}$) due to polarization and charge transfer, respectively, as defined in ref 33. $\Delta\mu_{dist}$ is the contribution due to distortion of the indicated moiety. [b] This work. [c] Reference 32.

$X\cdots H$ distances in the series $X\cdots HCN\cdots HCN$ (X = OC, N_2, H_3N, H_2O).[29]

A previous self-consistent reaction field calculation for $HCN-SO_3$ indicates a 0.22 Å contraction of the N−S bond accompanied by a 2.2° widening of the NSO bond angle in a medium described by a bulk dielectric constant of 78.5.[30] Although a single HCN by no means constitutes a bulk environment, we can draw some analogy between the electric field of the remote HCN and the reaction field produced by polarization of a dielectric medium surrounding a single molecule of $HCN-SO_3$. The substantial contraction of the N−S bond brought about by a single molecule of HCN demonstrates that a significant portion of the response to environment is brought about by the addition of a single molecular "microsolvent". Being small and therefore inexpensive, partially bonded molecules thus offer promising "test" systems for quantum mechanical solvation models.

The dipole moment of $HCN\cdots HCN-SO_3$ is 8.640(19) D, which represents an enhancement of 1.238(19) D relative to HCN + $HCN-SO_3$. This value is large, but its magnitude is reasonable in the following sense: The dipole moment of $(HCN)_2$ is 6.552(35) D,[25d] which is 0.58 D larger than that of two HCN monomers.[31] Thus, the $HCN\cdots HCN$ interaction in the trimer should contribute about this much to the induced moment. On the other hand, recent ab initio calculations of $\mu(R)$ for $HCN-SO_3$[32] give a value of $d\mu/dR = -3.0$ D/Å at $R = 2.47$ Å (the bond length observed in $HCN\cdots HCN-SO_3$.) An increase of 0.33 D in the $HCN-SO_3$ moiety, therefore, should accompany the observed 0.11 Å contraction of the N−S bond. The sum of these values (0.58 D + 0.33 D) gives an induced moment of 0.91 D for $HCN\cdots HCN-SO_3$. This result falls about 27% short of the observed value, but the agreement is probably as good as can be expected from a crude additivity model. The calculation further suggests that a significant portion of the induced moment in the trimer arises from advancement of the N−S bond.

In this light, it is also of interest to explore a more complete decomposition of the observed dipole moment. While the quadrupole coupling constants in HCN_1-SO_3 and $HCN_2\cdots HCN_1-SO_3$ are indicative of electronic rearrangement at N_1, the induced moment of the complex certainly arises from an admixture of monomer distortion, charge transfer, and polarization terms. In order to separate these contributions, calculations were carried out for $HCN-SO_3$ and $HCN\cdots HCN-SO_3$ at the HF/aug-cc-pVDZ level of theory/basis set using the block-localized wave function energy decomposition scheme (BLW-ED) developed by Mo, Gao, and Peyerimhoff.[33] The results are given in Table 4. From the table, it is apparent that for $HCN\cdots HCN-SO_3$ at this level of theory/basis set, the polarization contribution to the induced moment ($\Delta\mu_{pol}$) is 6.65 times greater than that of the charge-transfer component ($\Delta\mu_{CT}$), while for $HCN-SO_3$, the ratio is 7.44. The difference between these numbers is too small to interpret, but it seems clear that the major contribution to the induced dipole moment in both adducts arises from electronic polarization of the respective fragments and not from charge transfer[34] (i.e., about 7 times more of a contribution from polarization than from charge transfer). In addition, taking the observed induced moments for both complexes, less the calculated contributions from monomer distortion, and using R(N−S) as a crude approximation to the distance for electron transfer, the calculated ratios of $\Delta\mu_{pol}/\Delta\mu_{CT}$ yield electron-transfer values of 0.012 and 0.020 e for $HCN-SO_3$ and $HCN\cdots HCN-SO_3$, respectively. Interestingly, these estimates are about an order of magnitude smaller than those obtained from a simple Townes and Dailey type analysis of the quadrupole coupling constants. Nevertheless, while the absolute magnitude of the electron transfer is imprecise, an increase upon addition of a single HCN unit appears discernible. The relation between charge transfer and induced moments in partially bound Lewis acid−base adducts will be discussed in a future publication.[32]

In conclusion, the results presented above indicate that the $HCN\cdots HCN$ interaction in $HCN\cdots HCN-SO_3$ is largely unaltered from that in $(HCN)_2$, but the $HCN-SO_3$ interaction is driven measurably in the direction of bond formation. Thus, in the "solvent−solute interaction" studied here, *weak closed-shell interactions remain weak but incipient chemistry is promoted by even the slightest degree of solvation.* It is interesting to comment that the binding energy of $(HCN)_2$ is 4.2 kcal/mol[35] while that of $HCN-SO_3$ is 7.1 kcal/mol.[36] Although these results were obtained at different levels of calculation, it is unlikely that the true values are widely disparate. Thus, the separation between inter- and intramolecular energetics is not sharp, as is normal for valence bonded systems. Such a situation should be general for partially bound complexes, making them sensitive probes of their local environment.

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Supporting Information Available: Tables of transition frequencies at zero and nonzero electric fields. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

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