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Articles

Molecular Structures of Sulfur Cyanide Trifluoride, SF$_3$CN, and Sulfinyl Cyanide Fluoride, FS(O)CN

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General valence force fields for SF$_3$CN and FS(O)CN are derived from vibrational data taken from the literature and from theoretical calculations. Gas phase electron diffraction studies on both molecules yield the following geometric parameters (r_a distances and angles with 3σ uncertainties). SF$_3$CN: $r(\mathrm{S-F_e}) = 155.2(4)$ $r(\mathrm{S-F_a}) = 165.7(3)$, $r(\mathrm{S-C}) = 173.6(8)$, $r(\mathrm{C{\equiv}N}) = 115.9(4)$ pm; $\angle(\mathrm{F_aSF_e}) = 86.9(3)$, $\angle(\mathrm{F_aSC}) = 86.0(4)$ $\angle(\mathrm{F_eSC}) = 98.7(8)$, $\angle(\mathrm{F_aSF_a}) = 169.0(6)$, $\angle(\mathrm{SCN}) = 171(4)°$. FS(O)CN: $r(\mathrm{S-F}) = 159.8(3)$, $r(\mathrm{S{=}O}) = 143.2(2)$, $r(\mathrm{S-C}) = 178.3(3)$, $r(\mathrm{C{\equiv}N}) = 115.0(3)$ pm; $\angle(\mathrm{FSO}) = 104.9(4)$, $\angle(\mathrm{FSC}) = 93.9(4)$, $\angle(\mathrm{CSO}) = 105.3(5)$, $\angle(\mathrm{SCN}) = 176(4)°$. These experimental results are compared to ab initio values (HF/3-21G*, HF/6-31G*, and MP2/6-31G*), and the bonding properties in these sulfur (IV) cyanides are discussed.

Introduction

Sulfur cyanides are an interesting class of compounds with respect to their bonding properties, because of possible interactions of the cyanide group with the sulfur atom:

$$\mathrm{S-C{\equiv}N} \leftrightarrow \mathrm{S^{+}{=}C{=}N^{-}}$$

The contribution of such a mesomeric structure, which corresponds to an interaction between the sulfur lone pair and the π^* orbital of the C≡N bond (lp(S) → π^*(C≡N)), depends strongly on the oxidation state of sulfur. In SCN$^-$, with sulfur in the formal oxidation state −2, the π-bond interaction is maximized as demonstrated by the short S−C bond length of 168 pm in NaSCN.[1] In sulfur dicyanide, S(CN)$_2$, with sulfur in the oxidation state +2, this interaction is slightly weaker, thus the S−C bond length is 170.1(3) pm.[2] No π-bond interaction occurs in the S(VI) compound SF$_5$CN, and the observed S−CN distance of 176.5(5) pm is the longest known.[3] So far, no S−C bond lengths for analogous S(IV) derivatives have been reported.

Recently, sulfur cyanide trifluoride, SF$_3$CN, and sulfinyl cyanide fluoride, FS(O)CN, have been synthesized.[4] These novel sulfur cyanides in the oxidation state +4 were characterized by IR, Raman, ^{19}F-NMR, UV, and mass spectroscopy. In order to learn more about their bonding properties, we report now valence force fields and gas phase structures for these compounds. The experimental studies were supplemented by ab initio calculations. The geometric structures of both compounds were optimized with the three widely used standard methods HF/3-21G*, HF/6-31G*, and MP2/6-31G*. A set of six d-functions was used for all atoms with orbital exponents of 0.8 and 0.65 for second-row atoms and sulfur, respectively. The calculated parameters are compared with the experimental values in the respective tables. The vibrational frequencies were calculated with the MP2/6-31G* method, using analytical gradients, and the force constants were used as starting parameters in the normal coordinate analyses. All calculations were performed with the Gaussian 92 program system[5] on a Cray YMP computer (Research Center, KFA Jülich, Germany).

Assignment of the Vibrational Bands. SF$_3$CN. Infrared spectra of gaseous and of matrix-isolated SF$_3$CN as well as Raman spectra of neat liquid samples have been measured, and a preliminary assignment of the bands has been given.[4] The 12 fundamental vibrations of the SF$_3$CN molecule transform as 8 a′ (IR, Ra p) + 4 a″ (IR, Ra dp). The assignment according to symmetry classes presented here (Table 1) is assisted by the observed IR gas band contours, and a comparison with calculated (MP2/6-31G*) band positions or with characteristic group frequencies of related molecules. The band at 2214 cm^{-1} (gas phase values are given throughout) can be assigned unambiguously to ν_1 (ν(CN)) due to its occurrence in the characteristic CN stretching region. Comparison of the SF stretching vibrations of SF$_4$, where the equatorial fluorines absorb at 892 and 867 cm^{-1} and the axial fluorines at 730 and

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[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1996.

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Table 1. Observed and Calculated Vibrational Wavenumbers (cm^{-1}) for Sulfur Cyanide Trifluoride

IR (gas)[a]	int[b]	calcd[c]	int[d]	assignment		
2214	17	2177	45	ν_1	a′	ν(CN)
(40.6)						(^{13}C)
849	33	871	109	ν_2	a′	$\nu(SF_e)$
(9.1)						(^{34}S)
714	100	808	421	ν_9	a″	$\nu_{as}(SF_{2a})$
(13.1)						(^{34}S)
693	4	732	79	ν_3	a′	ν(SC)
558	2	598	10	ν_4	a′	$\nu_s(SF_{2a})$
518	4	499	11	ν_{10}	a″	δ(SCN)
492	0.1	485	9	ν_5	a′	δ(SCN/FSC)
		452	0.3	ν_{11}	a″	twist
334	6	334	18	ν_6	a′	$\delta(SF_{2a})$
289	4	292	15	ν_7	a′	δ(SCN/FSC)
172	1	165	3	ν_{12}	a″	$\tau(F_e-S-CN)$
149	0.4	141	1.3	ν_8	a′	$\delta(F_e-S-CN)$

[a] Reference 4, isotopic shifts in parentheses. [b] Relative integrated band intensity, ref 4, Ne matrix. [c] Ab initio MP2/6-31G*. [d] Intensities in km mol^{-1}.

Table 2. Observed and Calculated Vibrational Wavenumbers (cm^{-1}) for Sulfinyl Cyanide Fluoride

IR (gas)[a]	int[b]	calcd[c]	int[d]	assignment	
2184	44	2108	87	ν_1	ν(CN)
(51.5)					(^{13}C)
(33.2)					(^{15}N)
1265	100	1299	122	ν_2	ν(SO)
(13.2)					(^{34}S)
752	83	766	145	ν_3	ν(SF)
(9.1)					(^{34}S)
627	91	649	128	ν_4	ν(SC)
(8.3)					(^{34}S)
480	13	482	20	ν_5	
		433	0.8	ν_6	
359	3	341	5	ν_7	
190	9	183	10	ν_8	
151	4	138	6	ν_9	

[a] Reference 4, isotopic shifts in parentheses. [b] Relative integrated band intensity, ref 4, Ne matrix. [c] Ab initio MP2/6-31G*. [d] Intensities in km mol^{-1}.

558 cm^{-1},[6] suggests an assignment for the strong infrared band at 849 cm^{-1} of SF_3CN to ν_2 ($\nu(SF_e)$) and at 714 cm^{-1} to the a″ mode ν_9 ($\nu_{as}(SF_a)$). For the other a″ modes the same band contours like those for ν_9 are expected. They are located at 518 and 172 cm^{-1} and assigned to the a″ modes ν_{10} (δ SCN) and ν_{12} (τ F_e-S-CN), respectively. The remaining a″ mode ν_{11} (twist SF_{2a}/F_eSCN), analogous to the infrared and Raman inactive a_2 mode of SF_4, was not observed due to its low intensity. This assignment into the symmetry class is in accordance with predictions based on the ab initio calculations. The third SF stretching mode is most likely the band at 548 cm^{-1} (ν_4, ν_s (SF_a)), because it should be of similar energy as the respective mode in SF_4 (558 cm^{-1}). The last unassigned band in the region above 500 cm^{-1} is a weak IR absorption and medium strong Raman band at ~690 cm^{-1}, which can be attributed to the S−CN stretching vibration. An exact assignment of the a′ deformation modes proves difficult, because of vibrational coupling between the SF_3CN skeleton and S−C−N deformation modes. They are described by the potential energy distribution presented in Table 3 which results from a normal coordinate analysis.

FS(O)CN. As in the case of SF_3CN, the vibrational wavenumbers of FS(O)CN were measured in the gaseous and liquid phases, and on molecules isolated in Ne matrix.[4] Since the FS(O)CN molecule has C_1 symmetry, its nine fundamental vibrations transform as 9 a_1 (IR, Ra p). The subsequent wavenumbers discussed are gas phase values and are listed in Table 2. The strong absorption at 2184 cm^{-1} is attributed to ν_1 (ν(CN)), and its $^{12/13}C/^{14/15}N$ isotopic shifts of 51.5/33.2 cm^{-1}, respectively, prove by model calculations that C, N, and S are connected in an S−C−N unit. The SO and SF stretching modes can also be identified unambiguously, because of their characteristic position at 1265 and 752 cm^{-1}, respectively. In FS(O)X compounds these stretching vibrations depend on the electronegativity of X. The following positions are observed: for X = F, 1333/777 cm^{-1} (average of ν_{as} and ν_s);[7] for X = NF_2, 1305/765 cm^{-1};[8] for X = Cl 1293/751 cm^{-1};[9] for X = CF_3 1267/751 cm^{-1}.[9] The last unassigned band above 500 cm^{-1} must belong to ν(SC) at 627 cm^{-1}. Two of the five deformation modes in FS(O)CN belong to the SCN group, which strongly couple with the skeleton modes. They are described by the potential energy distribution presented in Table 4 as the result of a normal coordinate analysis.

Normal Coordinate Analyses. Calculations of a general valence force field of SF_3CN and FS(O)CN are performed using the program NORCOR.[10] The structural parameters of Tables 5 and 6 are adopted as input data along with initial force constants from the ab initio calculations. The final force field is fitted to the observed wavenumbers and isotopic shifts. The results are listed in Table 3 and 4. The vibrational amplitudes calculated from these force fields are included in Tables 5 and 6.

Structure Analyses. The radial distribution functions (RDF) which were calculated by Fourier transform of the molecular intensities with an artificial damping function $\exp(-\gamma s^2)$ (γ = 19 pm^2) are shown in Figures 1 and 2. Preliminary geometric models were derived from the RDF's and refined by least squares fit of the molecular intensities. A diagonal weight function was applied to the intensities, and known scattering amplitudes and phases were used.[11] C_s symmetry was assumed for SF_3CN, and the two similar S−F bond distances were described by the mean value $(S-F)_{mean}$ and the difference between axial and equatorial bond lengths $\Delta SF = (S-F_a) - (S-F_e)$. The difference between the vibrational amplitudes for the two S−F bonds was set to the spectroscopic value. In the least squares analysis for FS(O)CN, vibrational amplitudes for closely spaced nonbonded distances were collected into groups (see Table 6). With these constraints, eight geometric parameters and ten (SF_3CN) or seven (FS(O)CN) vibrational amplitudes a_i were refined simultaneously. The following correlation coefficients had values larger than |0.6| in the analysis for SF_3CN: SC/SCN = 0.67, SF/a(SC) = 0.73, $\Delta SF/a(SF) = -0.78$, SC/a(SF) = −0.89, and $a(F_a\cdots F_e)/a(F_a\cdots C) = 0.79$. No correlations larger than |0.6| occurred in the refinement for FS(O)CN. The results are listed in Tables 5 and 6. Error limits, which are 3 times the standard deviations, account for data correlation.

Discussion

Although both compounds of the present study are S(IV) derivatives, the S−C bond length in the three-coordinated sulfoxide (178.3(3) pm) is appreciably longer than that in the

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Table 3. Force Constants (10^2 N m^{-1}) and Potential Energy Distribution (PED) of SF_3CN[a]

	force constants[b]		PED											
f_K	calcd[c]	exp	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}
f_r	3.95	3.49				0.79					1.03			
f_s	5.32	4.59		0.85										
f_t	4.19	3.97			0.68	0.12	0.11							
f_u	16.51	17.19	0.91		0.12					0.15				
f_α	0.85	1.27					0.27		0.11	0.53				
f_β	0.20	0.30					0.19		0.38	0.57				
f_γ	2.22	2.09					0.13		0.82				1.25	
f_δ	1.93	1.74						0.62		0.50		0.80	0.19	0.33
f_τ	0.001	0.007										0.22		0.75

[a] Key: r, SF_a; s, SF_e, t, SC; u, CN; α, ∠CSF_e; β, ∠SCN; γ, ∠F_aSF_e; δ, ∠CSF_a; τ, torsion about SC bond. [b] Further force constants contributing more than 0.1 to the PED: $f_{u\beta} = -0.72(0.02)$; $f_{u\delta} = 0.84(-0.12)$; $f_{r\gamma} = 0.66(0.19)$; $f_{r'\gamma} = -0.46(-0.24)$; $f_{rr'} = 0.49(0.43)$; $f_{rd} = -0.55(-0.25)$; $f_{\alpha\gamma} = 0.28(0.27)$; $f_{\alpha r} = 0.15(0.28)$; $f_{\beta\gamma} = -0.06(0.01)$; $f_{\beta r} = 0.12(0.05)$ calculated values in parentheses. [c] MP2/6-31G*.

Table 4. Force Constants (10^2 N m^{-1}) and Potential Energy Distribution (PED) of FS(O)CN[a]

	force constants[b]		PED								
f_K	calcd[c]	exp	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9
f_r	4.08	4.04			0.92	0.14					
f_s	10.57	10.47		1.03							
f_t	2.82	3.10				0.53	0.28				
f_u	15.91	16.33	0.88						0.15		
f_α	1.47	1.59				0.13	0.56		0.18	0.18	
f_β	0.16	0.21							0.21	0.80	
f_γ	1.29	1.52						0.80	0.14		
f_δ	1.52	1.54				0.17		0.11	0.82		
f_τ	0.003	0.002									1.02

[a] Key: r, SF; s, SO, t, SC; u, CN; α, ∠CSO; β, ∠SCN; γ, ∠FSO; δ, ∠CSF; τ, torsion about SC bond. [b] Further force constants contributing more than 0.1 to the PED: $f_{s\tau} = -0.05(0.002)$; $f_{\beta\delta} = 0.12(0.12)$; $f_{\alpha\delta} = 0.36(0.38)$, calculated values in parentheses. [c] MP2/6-31G*.

Table 5. Geometric Parameters and Vibrational Amplitudes for SF_3CN

Geometric Parameters

	GED[a]	HF/3-21G*	HF/6-31G*	MP2/6-31G*
C≡N	115.9(4)	113.6	113.2	118.1
$(S-F)_{mean}$	162.2(2)	161.1	161.1	165.4
ΔSF = $(S-F_a)-(S-F_e)$	10.5(5)	7.7	9.3	8.6
$S-F_e$ [b]	155.2(4)	156.0	155.4	159.7
$S-F_a$ [b]	165.7(3)	163.7	164.7	168.3
S−C	173.6(8)	170.3	173.3	172.9
F_a-S-F_e	86.9(3)	86.4	86.8	87.2
F_a-S-C	86.0(4)	86.4	86.3	86.5
F_a-S-F_a [b]	169.0(6)	168.1	168.7	169.8
F_e-S-C	98.7(8)	105.4	104.6	103.4
S−C≡N	171(4)	177.8	176.8	176.2

Interatomic Distances and Vibrational Amplitudes a_i from GED and Spectroscopic Data[c]

	distance	a(GED)	a(sp)		distance	a(GED)	a(sp)
C≡N	116	3.3(5)	3.6	$F_e\cdots C$	250	8.1(14)	8.2
$S-F_e$	155	4.7(5)	4.3	S···N	2.89	5.9(6)	5.0
$S-F_a$	166	5.5(5)[d]	5.1	$F_a\cdots N$	3.23	10.3(10)	11.6
S−C	174	5.1(7)	4.6	$F_a\cdots F_a$	3.30	6.5(10)	6.0
$F_a\cdots F_e$	221	6.3(6)	6.6	$F_e\cdots N$	3.56	12.5(22)	11.2
$F_a\cdots C$	231	5.6(10)	7.7				

[a] r_a distances in pm and $\angle_\alpha$ angles in degree, error limits are 3σ values. [b] Dependent parameter. [c] Values in pm, error limits are 3σ values. [d] Difference between $a(S-F_e)$ and $a(S-F_a)$ fixed to spectroscopic value.

Table 6. Geometric Parameters and Vibrational Amplitudes for FS(O)CN

Geometric Parameters

	GED[a]	HF/3-21G*	HF/6-31G*	MP2/6-31G*
C≡N	115.0(3)	113.9	113.4	118.5
S=O	143.2(2)	143.3	142.6	146.3
S−F	159.8(3)	158.2	158.3	164.3
S−C	178.3(3)	174.6	177.2	178.1
F−S=O	104.9(4)	107.6	108.3	109.6
C−S=O	105.3(5)	107.6	106.4	106.4
F−S−C	93.9(4)	92.4	92.5	91.0
S−N≡C	176(4)	176.4	174.2	172.6

Interatomic Distances and Vibrational Amplitudes a_i from GED and Spectroscopic Data[b]

	distance	a(GED)	a(sp)		distance	a(GED)	a(sp)
C≡N	115	3.3(4)	3.6	O···F	2.40	5.5(10)	6.7
S=O	143	3.7(3)	3.6	F···C	2.48		7.1
S−F	160	4.7(2)	4.5	O···C	2.57		7.3
S−C	178	4.5(4)	4.9	S···N	2.93	6.2(5)	5.7
				F···N	3.45	10.6(17)	12.4
				O···N	3.60		10.7

[a] r_a distances in pm and $\angle_\alpha$ angles in degree, error limits are 3σ values. [b] Values in pm, error limits are 3σ values.

four-coordinate sulfurane (173.6(8) pm). This trend is also reflected in the respective force constants of 3.10 and 3.97 × 10^2 N m^{-1} in FS(O)CN and SF_3CN, respectively. In both S(IV) compounds the S−C bonds are longer than those in S(II) cyanides (e.g., 170.1(3) pm in $S(CN)_2$[2] or 168.4(3) pm in CH_3SCN[12] or 169.3 pm in ClSCN[13]).

We will first discuss the bonding properties in SF_3CN. $S-CH_3$ bond lengths in SF_3CH_3 (179.0(13) pm[14]) and in SF_5CH_3 (179.3(8) pm[15]), as well as $S-CF_3$ bond lengths in SF_3-

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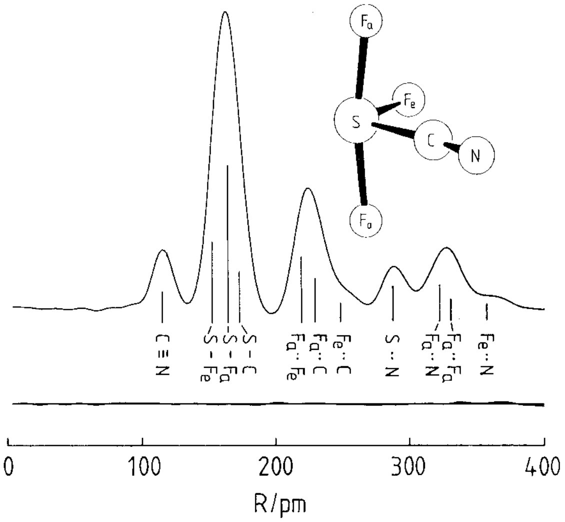

Figure 1. Experimental radial distribution function and difference curve, RDF(exp) − RDF(calc), for SF_3CN. The positions of interatomic distances are shown by vertical bars.

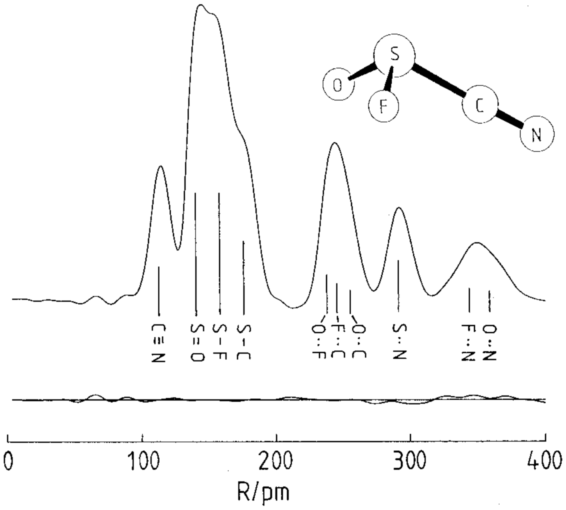

Figure 2. Experimental radial distribution function and difference curve, RDF(exp) − RDF(calc), for FS(O)CN. The positions of interatomic distances are shown by vertical bars.

CF_3 (188.7(8) pm[16]) and SF_5CF_3 (188.7(8) pm[17]), demonstrate that S−C bond lengths in these compounds do not depend on the oxidation state of sulfur. The strong difference between $S-CH_3$ and $S-CF_3$ bond distances has been rationalized by polar effects $S^{+\delta}-C^{+\delta}$ which lead to lengthening of these bonds in the CF_3 derivatives.[17,18] On the other hand, the S−C bond in the cyanide SF_3CN (173.6(8) pm) is ca. 3 pm shorter than this bond in SF_5CN. When comparing $S-CH_3$, $S-CF_3$, and S−CN bonds in these compounds, three possible effects have to be considered. (i) First, values for single-bond radii of C(sp^3) and C(sp) atoms are different. Values of 77 and 69 pm have been proposed for these radii, i.e., a difference of 8 pm.[19] (ii) Second, different polar contributions are responsible for the large difference between $S-CH_3$ and $S-CF_3$ bonds of nearly 10 pm. (iii) Third, possible mesomeric contributions $S^+{=}C{=}N^-$ must be considered. Since no sulfur lone pair is available in SF_5CN, and no lp(S) → π^*(C≡N) interaction can occur, the difference between $S-CH_3$ and S−CN bond lengths in the S(VI) derivatives is due to effects i and ii only.

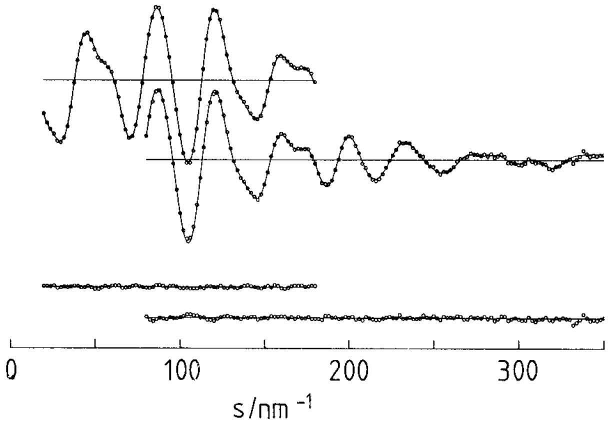

Figure 3. Averaged molecular intensities for the long (above) and short (below) camera distances for SF_3CN and differences between experimental and calculated values.

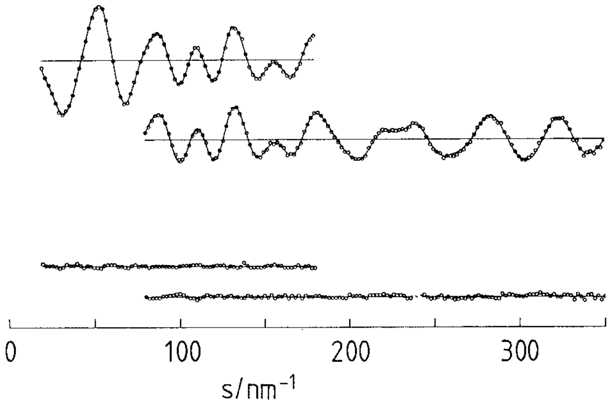

Figure 4. Averaged molecular intensities for the long (above) and short (below) camera distances for FS(O)CN and differences between experimental and calculated values.

When we take the difference in covalent radii (8 pm) into account, the experimental value of 176.5(5) pm in SF_5CN implies lenthening due to polar repulsion which is about half as much as that in $S-CF_3$ bonds. The shortening of the S−CN bond lengths between SF_5CN and SF_3CN of 2.9(10) pm can now be attributed to the mesomeric contribution $S^+{=}C{=}N^-$ in the S(IV) compound. This explanation is supported by the simultaneous lengthening of the C≡N bond by 0.7 pm.

The $S-CF_3$ bonds in the three- and four-coordinate S(IV) compounds $FS(O)CF_3$ (188.9(5) pm[16]) and SF_3CF_3 (188.7(7) pm) are equal. On the other hand, the S−CN bond in FS(O)CN is 4.7(9) pm longer than that in SF_3CN. This difference corresponds to the estimated mesomeric contribution in the latter compound within the experimental uncertainties. Thus, no such lp(S) → π^*(C≡N) interaction occurs in the three-coordinate S(IV) compound, although a lone pair is available at the sulfur atom. This conclusion is supported also by the short C≡N bond in FS(O)CN (115.0(3) pm).

Tables 5 and 6 compare the experimental geometric parameters with those obtained by three different ab initio methods. C≡N bond lengths are predicted slightly too short in the HF approximations and too long with the MP2 method. Whereas the HF calculations reproduce the S=O and S−F distances very well, the MP2 approximation results in bond lengths which are 3−4 pm too long. On the other hand, the S−C bond lengths and their difference between the two sulfur(IV) cyanides are reproduced perfectly with the MP2 method and are underestimated in the HF/3-21G* calculation. Thus, different types of

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bonds are reproduced well with these different calculational methods. The experimental bond angles are reproduced by all three ab initio methods to within about ±3°. The largest discrepancy occurs for the equatorial angle F_e−S−C in SF_3CN, where calculated values are 4−7° larger than the experimental angle.

Experimental Section

Samples of SF_3CN and FS(O)CN were prepared according to the reported procedure by the metathesis between SF_4 and $(CH_3)_3SiCN$ at −30 °C or by the treatment of SF_3CN with SeO_2, respectively.[4] The compounds were transported from Hannover to Tübingen at liquid nitrogen temperature. To ensure proper vapor pressure and constant gas flow of SF_3CN and FS(O)CN through the nozzle into the Gasdiffractograph KD-G2,[20] the samples were kept at −45 and −25 °C, respectively. The electron diffraction intensities were recorded at 25 and 50 cm camera distances, with an accelerating voltage of ca. 60 kV. Exposure times were 5−8 s for the long camera distances and 20−30 s for the short camera distances. The electron wavelength was calibrated in each experiment with ZnO powder diffraction. The photographic plates were analyzed with the usual methods,[21] and averaged molecular intensities in the s-ranges 20−180 and 80−350 nm^{-1} are shown in Figures 3 and 4.

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