Reactions of (Carbonylimido)sulfur(IV) Derivatives with TAS-Fluoride, $(Me_2N)_3S^+Me_3SiF_2^-$

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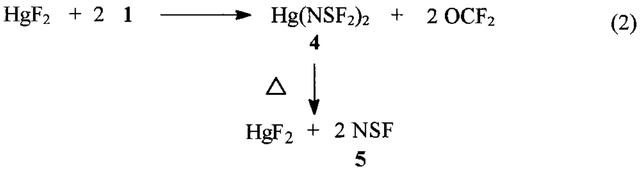
In the reaction of TAS-fluoride, $(Me_2N)_3S^+Me_3SiF_2^-$, with carbonyl sulfur difluoride imides $RC(O)NSF_2$ (R═F, CF_3), C−N bond cleavage is observed, and $TAS^+RC(O)F_2^-$ and NSF are the final products. From TASF and $RC(O)NS(CF_3)F$, the salts $TAS^+RC(O)NS(CF_3)F_2^-$ (R = F (**14**), CF_3 (**15**)), with ψ-pentacoordinate sulfur centers in the anions, are formed. An X-ray structure investigation of **14** shows that the fluorine atoms occupy axial positions and CF_3, NC(O)F, and the sulfur lone pair occupy equatorial positions of the trigonal bipyramid. The −C(O)F group lies in the equatorial plane with the CO bond synperiplanar to the SN bond. According to B3LYP calculations, this structure corresponds to a global minimum and the expected axial orientation of the −C(O)F group represents a transition state. Calculations for the unstable $FC(O)NSF_3^-$ anion show a different geometry. The −C(O)F group deviates 40° from axial orientation, and the equatorially bonded fluorine is, in contrast to the $-CF_3$ group in **14**, syn positioned.

Introduction

Ruff reported that the C−N bond of $FC(O)NSF_2$[1] is cleaved by CsF (excess) to give $Cs^+OCF_3^-$ and $Cs^+NSF_2^-$.[2] The products were characterized by spectroscopic means and by chemical reactions:[2]

$$\underset{\mathbf{1}}{FC(O)NSF_2} + CsF_{XS} \longrightarrow \underset{\mathbf{2}}{Cs^+OCF_3^-} + \underset{\mathbf{3}}{Cs^+NSF_2^-} \qquad (1)$$

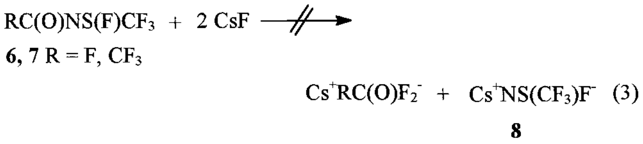


$$HgF_2 + 2\ \mathbf{1} \longrightarrow \underset{\mathbf{4}}{Hg(NSF_2)_2} + 2\,OCF_2 \qquad (2)$$

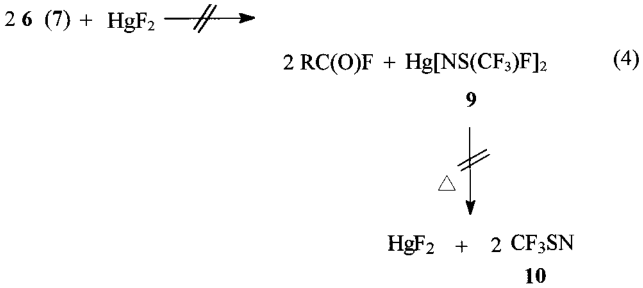
$$\mathbf{4} \xrightarrow{\Delta} HgF_2 + \underset{\mathbf{5}}{2\,NSF}$$

We have shown that **4** is formed at 0 °C from **1** and HgF_2 in a straightforward reaction; OCF_2 is evolved at this temperature.[3,4] **4** is a suitable reagent for the transfer of the NSF_2 group.[5] Additionally, from the thermal decomposition of **4**, the otherwise only tediously accessible NSF (**5**) is obtained in quantitative yields and in high purity.[4] $CF_3C(O)NSF_2$ (**11**)[6] shows behavior toward CsF and HgF_2 similar to that of **1**.[6]

By analogy to eqs 1 and 2, the products expected from CsF (HgF_2) and $FC(O)NS(F)CF_3$[7] are $Cs^+NS(CF_3)F^-$ (**8**) and $Hg[NS(CF_3)F]_2$ (**9**), respectively:



$$\underset{\mathbf{6},\,\mathbf{7}\ R\,=\,F,\,CF_3}{RC(O)NS(F)CF_3} + 2\,CsF \not\longrightarrow Cs^+RC(O)F_2^- + \underset{\mathbf{8}}{Cs^+NS(CF_3)F^-} \qquad (3)$$



$$2\ \mathbf{6}\ (\mathbf{7}) + HgF_2 \not\longrightarrow 2\,RC(O)F + \underset{\mathbf{9}}{Hg[NS(CF_3)F]_2} \qquad (4)$$

$$\mathbf{9} \overset{\Delta}{\not\longrightarrow} HgF_2 + \underset{\mathbf{10}}{2\,CF_3SN}$$

We performed these reactions several times with the aim of finding an easy route to "CF_3SN" (**10**), but in reactions 3 and 4, almost no formation of OCF_2 was observed. The metal fluorides reacted with **6** and **7** to give colorless solids, which on some occasions decomposed violently on heating.[8] With TASF, a fluoride ion donor readily soluble in aprotic organic solvents, e.g., CH_3CN, we expected to follow the progress of the reaction by NMR spectroscopy.

Experimental Section

General Informations. The starting materials TASF,[9] $FC(O)NSF_2$ (**1**),[1] $F_3CC(O)NSF_2$ (**12**),[6] $FC(O)NS(CF_3)F$ (**6**),[7] and $F_3CC(O)NS(CF_3)F$ (**7**)[10] were prepared according to the literature. IR spectra were recorded on a Nicolet DX-55-FT-IR spectrometer using either 10 cm gas cells or Nujol or Kel-F mulls, and NMR spectra were obtained on a Bruker WP80SY spectrometer. All operations were carried out in a dry nitrogen or argon atmosphere because of the moisture sensitivity of the products;

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volatile materials were transferred via a glass vacuum line. Elemental analyses were performed by the Mikroanalytisches Labor Beller, Göttingen, Germany.

Reaction of TASF with $FC(O)NSF_2$ (1). A 5 mL portion of CH_3CN and 0.47 g (3.6 mmol) of **1** were condensed onto 0.84 g (3.05 mmol) of TASF at −196 °C via a vacuum line, and the reaction mixture was warmed to −40 °C and stirred at this temperature for 15 min. All volatiles were removed at −10 °C, leaving 0.76 g of $TAS^+CF_3O^-$ (quantitative yield) as a colorless residue, mp 190−192 °C. IR and NMR data are in agreement with literature reports.[11] The volatile products Me_3SiF and NSF and a minor amount of COF_2 (from the decomposition of excess $FC(O)NSF_2$) were identified by IR spectroscopy.

Reaction of TASF with $F_3CC(O)NSF_2$ (12). In an NMR experiment, 0.16 g (0.58 mmol) of TASF was reacted with 0.4 g (0.2 mmol) of **12** at −40 °C in CD_3CN. Under these conditions, **12** was quantitatively converted to $TAS^+CF_3CF_2O^-$ ($\delta = -31.2$ (s, CF_2), −82.3 (s, CF_3))[12] and $TAS^+NSF_2^-$ (δ = 162.2).[13] The data are in good agreement with literature reports.

Preparation of $TAS^+FC(O)NS(CF_3)F_2^-$ (14). From 0.92 g (3.3 mmol) of TASF and 0.82 g (4.5 mmol) of **6** after 40 min reaction time at −40 °C was obtained 1.2 g (quantitative yield) of colorless **14** in the reaction vessel after removal of all volatiles. IR (anion only): 1761 w, 1724 vs, 1219 vs, 1129 vs, 843 s, 772 s, 520 cm^{-1} vs. ^{19}F NMR (CD_3CN, −40 °C, excess TASF): δ 19.0 (SF_2, s, br), −4.7 (FC(O), s, br), −69.7 (CF_3, s). ^{19}F NMR (CD_3CN, −10 °C, excess TASF): δ 18.8 (SF_2, d, q), −4.7 (FC(O), s, br), −69.9 (t, CF_3); $^4J(SF_2{-}FC(O))$ = 7.3, $^3J(SF_2{-}CF_3)$ = 18.1 Hz. Anal. Found (calcd) for $C_8H_{18}F_6N_4OS_2$ (M_r = 364.36): C, 27.6 (26.4); H, 5.01 (4.98); F, 29.9 (31.2). Single crystals suitable for X-ray investigations were obtained by recrystallization from CH_3CN/ether at −40 °C.

Preparation of $TAS^+F_3CC(O)NS(CF_3)F_2^-$ (15). Similar to the previous reaction, from 0.27 g (0.98 mmol) of TASF and 0.28 g (1.2 mmol) of **7** within 30 min reaction time at −40 °C was obtained 0.40 g (quantitative yield) of colorless **15**. IR (anion only): 1850 vw, 1750 vw, 1640 vs, 1204 vs, 1132 vs, 885 s, 811 m, 779 s, 563 vs, 548 vs, 439 cm^{-1} s. ^{19}F NMR (CD_3CN, −40 °C, excess TASF): δ 16.1 (q, SF_2), −68.6 (t, SCF_3), −72.9 (s, CCF_3); $^3J(SF_2{-}CF_3)$ = 17.6 Hz. ^{19}F NMR (CD_3CN, −40 °C, without excess TASF): δ −72.6 (s), −68.2 (s); the SF signal was not observed under these conditions.

Quantum Chemical Calculations. The structures of isomers **E** and **F** (Chart 1; see below) and that of the unstable $FC(O)NSF_3^-$ anion were optimized using density functional theory (B3LYP/6-31G*). In Table 3, the geometric parameters of the most stable isomer, **E**, are compared with experimental results from X-ray diffraction and with GED and computational results for the parent neutral molecule $FC(O)NS(CF_3)F$. The vibrational frequencies for **E** and **F** were also calculated with the B3LYP method using the Gaussian 98 program.[14] Calculated bond distances and angles for $FC(O)NSF_3^-$ are given in the caption of Figure 2.

Results and Discussion

From the reactions of TASF with **1** and with $CF_3C(O)NSF_2$ (**12**), only NSF (**5**) and $TAS^+OCF_3^-$ (**11**) and $TAS^+CF_3C(O)F_2^-$ (**13**) are isolated:

$$\mathrm{TASF} + \mathbf{1} \xrightarrow[-40°\mathrm{C}]{\mathrm{CH_3CN}} \underset{\mathbf{11}}{\mathrm{TAS^+OCF_3^-}} + \mathbf{5} \qquad (5)$$

$$\mathrm{TASF} + \underset{\mathbf{12}}{\mathrm{CF_3C(O)NSF_2}} \xrightarrow[-40°\mathrm{C}]{\mathrm{CH_3CN}} \underset{\mathbf{13}}{\mathrm{TAS^+CF_3C(O)F_2^-}} + \mathbf{5} \qquad (6)$$

Even at −40 °C in CH_3CN, the reactions are too rapid for the observation of intermediates by NMR spectroscopy. It is not possible to decide where the primary attack of the fluoride ion occurs. The isolated final products **11**, **13**, and **5** show that fluorocarbonyl derivatives are better fluoride ion acceptors than **5**. The formation of $Hg(NSF_2)_2$ (**4**) and OCF_2 in reaction 2 is due to the high affinity of mercury for nitrogen. Structure investigations of **4** show that this is a covalent, not an ionic, compound.[3]

From the reaction of **6** with TASF, the thermally stable salt **14** is formed (eq 7). In a similar manner, salt **15** is obtained from the corresponding trifluoroacetyl derivative **7** (eq 8). At least in these two examples, primary attack of a fluoride ion on carbonylsulfur(IV) imides occurs at the sulfur centers. In earlier investigations, we showed that exchange of a fluorine by a CF_3 group will enhance the acceptor properties of a sulfur center;[15] similar behavior was shown for carbon centers, e.g., of OCF_2 and $OC(CF_3)_2$.[12] On going from $FC(O)NSF_2$ (**1**) to $FC(O)NS(CF_3)F$ (**6**), whereby the sulfur-bonded fluorine is exchanged by a trifluoromethyl group, the regioselectivity of the primary attack of F^- could be shifted from carbon to sulfur because of the enhancement in the acceptor properties of the sulfur. In $F_3CC(O)NS(CF_3)F$ (**7**), where the S- and the C-bonded fluorines are exchanged by CF_3 groups, attack of F^- also exclusively at the sulfur, not at the >C=O group, is observed. It is reasonable that, in the reactions with **1** and with **11**, primary attack of F^- also occurs at the sulfur. The different stabilities of the anions $FC(O)NSF_3^-$ and $FC(O)NS(CF_3)F_2^-$ must be due to the exchange of the equatorial fluorine by the trifluoromethyl substituent.

$$\mathrm{TASF} + \mathbf{6} \longrightarrow \underset{\mathbf{14}}{\mathrm{TAS^+\,FC(O)NS(CF_3)F_2^-}} + \mathrm{Me_3SiF} \qquad (7)$$

$$\mathrm{TASF} + \mathbf{7} \longrightarrow \underset{\mathbf{15}}{\mathrm{TAS^+\,F_3C(O)NS(CF_3)F_2^-}} + \mathrm{Me_3SiF} \qquad (8)$$

No structures of ψ-trigonal bipyramidal sulfur(IV) amide ions have been described in the literature. In amidosulfur trifluorides R_2NSF_3 (R = CH_3),[16] bis(amido)sulfur difluorides $(RR'N)_2SF_2$ (R = R′ = CH_3;[17] R = CH_3, R′ = Ph[18]), $(Az)_2SF_2$ (Az = pyrazole, imidazole, 1,2,4-triazole),[19,20] and $AzS(CF_3)F_2$[21] (Az = pyrazole), the equatorial R_2N groups are almost coplanar with the FSF axis. Also, in imidosulfur tetrafluorides $RN{=}SF_4$ (R = CH_3,[22] F[23]), the substituent R is found to be axially

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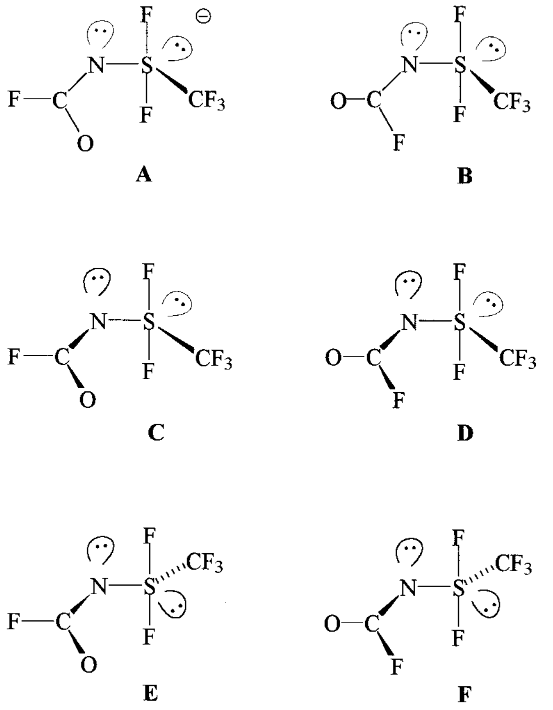
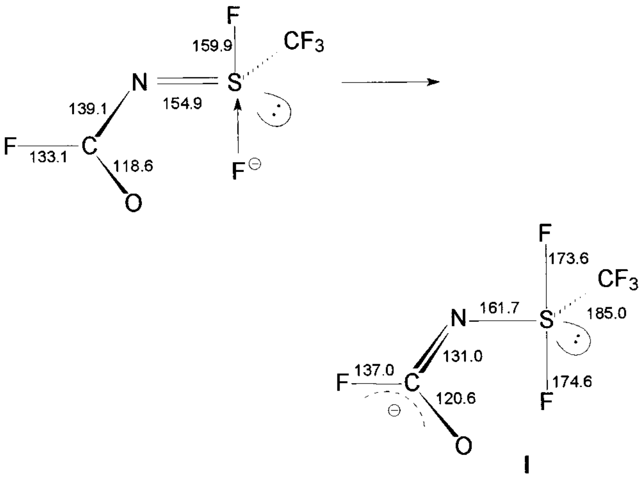
Chart 1



Scheme 1



oriented. Preliminary X-ray investigations on the sulfur(VI) amide $NCNS(O)F_3^-$ [24] also show that the CN group of the equatorially bonded bent NCN substituent is situated axially.

Structural investigations on (trifluoromethyl)sulfur(IV) acylamide ions are extremely interesting because of their large conformational variety. A priori there are six different conformations (**A**−**F**, Chart 1) possible if the fluorines occupy axial positions and the NC(O)F and CF_3 groups and the sulfur lone pairs occupy equatorial positions.

In **A** and **B**, the nitrogen-bonded −C(O)F group is axially oriented; in **A** the CO bond is synperiplanar and in **B** it is antiperiplanar with respect to the NS bond. Electron diffraction studies on sulfur (fluorocarbonyl)imides FC(O)N═SRR′ (R = R′ = F;[25] R = F, R′ = CF_3[26]) show a preference of the oxygen for the syn position. Because of this *syn*-(**C**, **E**) $\rightleftharpoons$ *anti*-(**D**, **F**) isomerism and a possible lone pair/CF_3 permutation at the sulfur center, four different possible isomers might exist when the −C(O)F group lies in the equatorial plane.

IR spectroscopy is a good probe for the detection of isomers. In the IR spectrum of **14**, besides a very strong band at 1724 cm^{-1}, a much weaker band at 1761 cm^{-1} suggests the presence of two different species, but these data cannot be assigned to specific isomers **A**−**F**. In the spectrum of **15**, only one strong band at 1640 cm^{-1} is dominant; two very weak bands at 1750 and 1850 cm^{-1} do not fully exclude the possibility of the presence of other isomers.

Table 1 gives selected NMR data for the anions of **14** and **15**, and ^{19}F chemical shifts and coupling constants for $C_2F_5N(CF_3)SF_2^-$ are included for comparison. Compared to the case of the corresponding neutral precursors **6** (δ(SF) −49.0; $^3J(CF_3-SF) = 2.2$ Hz), **7** (δ(SF) −47.1; $^3J(CF_3-SF) = 0.7$ Hz), and $C_2F_5NSFCF_3$ (δ(SF) −17.7; $^3J(CF_3-SF)$ not observed),[10] the change in the bonding situation of the sulfur-bonded fluorines (transformation of 2c-2e bonds at ψ-tetracoordinate centers to 3c-4e bonds at ψ-pentacoordinate centers) leads to the expected low-field shift of the axially bonded fluorines. The influence of the nitrogen-bonded substituents in the anions on δ(SF) parallels that in the neutral species. Another indication of ψ-pentacoordination with axially bonded fluorines and equatorial CF_3 groups is a $^3J(CF_3-SF)$ value of approximately 18 Hz. For the neutral species CF_3SF_3 (21.7 Hz),[27] $(CF_3)_2SF_2$ (19.5 Hz),[28] azole-SF_2CF_3 (19.6−19.9 Hz) (azole = triazole, pyrazole, imidazole),[21] and $Me_2NSF_2CF_3$ (12.4 Hz),[29] this coupling constant is found in the same range.

Equivalence of the axial fluorine substituents is not an indication for the isomers **C**−**F**. NMR investigations of TAS salts are best performed in polar aprotic organic solvents; especially suitable is CD_3CN. Because of the relatively high melting point of this solvent (−40 °C), the observation of only one isomer with equivalent axial fluorines might be due to rapid exchange by rotation around the NS bond; even **A** and **B** cannot be excluded. Differentiation among the isomers **A**−**F** seems to be possible only by X-ray structure investigations.

Structural Studies of $TAS^+FC(O)NS(CF_3)F_2^-$ (14). Single crystals suitable for X-ray structure analysis were obtained by crystallization from acetonitrile/ether at −30 °C. **14** crystallizes in the space group *Pc* with 4 molecules in the asymmetric unit. The structure of **14** is presented in Figure 1. Crystal data and details of the structure determination of **14** are given in Table 2, and Table 3 lists averaged bond lengths and angles for the anion of salt **14** and for the parent neutral derivative FC(O)NS(CF_3)F (**6**) (determined by GED[26]) as well as for ab initio calculated structures of both species.

The anion of **14** adopts conformation **E**; bond angles and distances of the B3LYP/ 6-31G* calculated structure are in good agreement with the experimental data. The largest deviation is in the SF distances (4 pm). The B3LYP method usually predicts SF bonds too long in S(IV) and S(VI) compounds. According to these calculations, **F** also represents a stable minimum, only 0.98 kJ/mol higher in energy than **E**. The bond distances of **E** and **F** are almost identical, with the exception of NC (for **F**, this bond length is calculated to be 0.4 pm shorter), CO (−1.0

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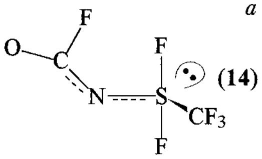
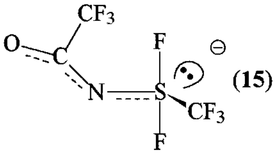
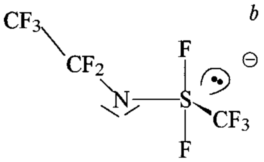
Table 1. ^{19}F NMR Data for ψ-Pentacoordinated (Trifluoromethyl)difluorosulfur(IV) Imide Anions

	 (14) [a]	 (15)	 [b]
$\delta(SF)_{ax}$	18.8	16.1	32.6
SCF_3	-69.5	-68.6	-71.8
-C(O)F	-4.7		
-C(O)CF_3		-72.9	(CF_2)-72.2
$^3J(CF_3\text{-}SF_2)$	18.1 Hz	17.6 Hz	18.0 Hz

[a] ^4J(F−F) = 7.3 Hz. [b] Reference 10; $^4J(CF_2{-}SF)$ = 18.0 Hz, $^3J(CF_2{-}CF_3)$ = 2.2 Hz.

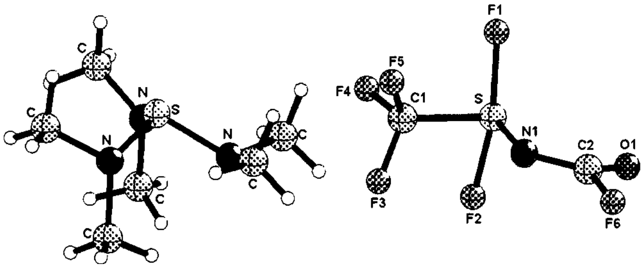


Figure 1. X-ray structure of one ion pair of **14**.

Table 2. Crystal Data and Structure Refinement Details for TAS$^+$FC(O)NS(F_2)CF_3^- (**14**)[a]

empirical formula	$C_6H_{18}F_6N_4OS_2$
M_r	364.38
T/K	173(2)
wavelength/Å	0.71073
crystal system	monoclinic
space group	*Pc*
a/Å	22.844(2)
b/Å	8.6680(10)
c/Å	16.216(2)
β/deg	100.110(10)
V/Å^3	3161.1(6)
Z	8
D_c/Mg m^{-3}	1.531
μ(Mo Kα)/mm^{-1}	0.402
F(000)	1504
crystal size/mm^3	0.5 × 0.3 × 0.3
θ range/deg	2.52−25.00
index ranges	$-29 \le h \le 29$, $-1 \le k \le 11$, $-21 \le l \le 1$
no. of reflns collected	6604
no. of indep reflns	5501 [R(int) = 0.0820]
refinement	full-matrix least-squares on F^2
no. of data/restraints/params	5501/32[b]/758
goodness-of-fit on F^2	1.055
R1, wR2 [$I > 2\sigma(I)$]	0.0838, 0.2088
R1, wR2 (all data)	0.1393, 0.2540
absolute struct param	−0.1(2)
largest diff peak, hole/e Å^{-3}	1.008, −0.682 min

[a] $\omega-2\theta$ scans; Siemens P4 diffractometer; refinement based on F^2; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$. Programs used: SHELX-97[33] and DIAMOND.[34] [b] The anisotropic components of five carbon atoms were restrained to isotropic behavior.

pm), and CF (+3.5 pm). The remarkable lengthening of the CF bond is easily understood from the stronger $n_N-\sigma^*_{CF}$ interaction with the fluorine in the syn position. Decrease of the $n_N-\sigma^*_{CO}$ interaction leads to strengthening of this bond and to a shift of ν_{CO} from 1800 cm^{-1} in **E** to 1864 cm^{-1} in **F**; experimentally we observed 1724 and 1761 cm^{-1}, respectively. This supports the assumption that **F** could be the second isomer suggested by IR spectroscopy. It might be present in the bulk material. If it was present in the crystal investigated, O/F disorder would result in the anion of **14**. From our investigations, we consider this to be quite unlikely.

Table 3. Averaged Experimental and Calculated Geometric Data (Distances/pm; Angles/deg) for the Anion of **14**, FC(O)NS(CF_3)F_2^-, and the Parent Neutral Molecule, FC(O)NS(CF_3)F[a]

	FC(O)NS(CF_3)F_2^-		FC(O)NS(CF_3)F	
parameter	X-ray	B3LYP/6-31G*	GED[b]	B3LYP/6-31G*
SF1	174.6(6)	178.5	159.9(4)	166.0
SF2	173.6(6)	178.5		
SN1	161.7(7)	164.7	154.9(5)	157.3
SC1	185.0(10)	187.3	185.2(6)	187.4
ClF3	130.1(10)	133.4	132.1(2)	132.8
ClF4	132.4(10)	135.3		
ClF5	130.0(11)	1.334		
N1C2	131.0(10)	134.0	139.1(8)	139.5
C2F6	137.0(9)	138.6	133.1(2)	133.8
C2O1	120.6(9)	121.9	118.6(5)	120.2
F1SF2	169.2(3)	166.4		
F1SC1	86.0(4)	85.4	90.3(14)	91.8
F2SC1	85.7(4)	85.4		
N1SF1	93.5(3)	95.4	108.8(33)	111.4
N1SF2	94.5(3)	95.4		
N1SC1	97.0(4)	96.2	97.4(12)	97.5
C2N1S	111.5(6)	111.0	112.4(11)	111.9
O1C2N1	134.0(8)	134.1	129.9(12)	129.6
O1C2F6	116.0(7)	117.3	121.9(16)	121.8
N1C2F6	109.9(7)	108.6	108.2(12)	108.6
F3C1F4	108.3(8)	107.9	109.7(4)	110.1
F3C1F5	107.5(9)	107.4		
F4C1F5	107.9(8)	107.9		
F3C1S	114.0(6)	113.0	110.6(4)	111.4
F4C1S	106.0(7)	107.5	106.4(4)	107.3
F5C1S	112.9(7)	113.0	110.6(4)	111.4
SN1C2O1	3(1)	0.0		
SN1C2F6	178.5(5)	180.0	166.3[c]	166.3
C1SN1C2	172.9(6)	180.0	158(8)	168.3
F1SN1C2	98.4(6)	94.1	−110.9	−96.7
F2SN1C2	−89.0(6)	−94.1		
N1SC1F4	175.3(7)	180.0	169(5)	172.1
N1SC1F5	−57.5(8)	−61.1		
N1SC1F3	65.4(8)	61.1		
F1SC1F3	158.5(8)	156.1		
F2SC1F3	−28.5(7)	−33.9		
F1SC1F4	−82.4(7)	−85.0		
F2SC1F4	90.7(7)	85.0		
F1SC1F5	35.5(7)	33.9		
F2SC1F5	−151.4(7)	−156.1		

[a] Reference 26. [b] γ_a values with 3σ uncertainties. [c] Not refined.

Although comparison of structures **6** and **14**, determined by different methods in different phases, is problematic, a discussion of their differences might prove useful. Addition of F$^-$ to

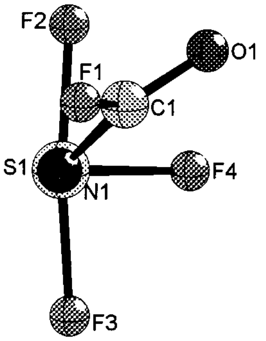


Figure 2. B3LYP/6-31G* calculated structure of FC(O)NSF$_3^-$. Distances (pm): SN 159.1, NC 134.2, CO 120.9, CF 139.3, SF(2) 176.05, SF(3) 176.4, SF(4) 166.1. Angles (deg): SNC 123.3, NCO 134.9, NCF 107.8, NSF(2) 95.6, NSF(3) 92.1, NSF(4) 111.6, OCNS −17.2, CNSF(2) −41.6, CNSF(3) 131.95, CNSF(4) 45.8.

the parent sulfur(IV) (fluoroformyl)imide causes some dramatic changes in the bond distances, whereas the bond angles are almost unaffected. The largest change in the angles is observed for NSF from 110.0(38)° in **6** (with a ψ-tetrahedral center) to 93.5(3)° in **14** (for N$_{eq}$SF$_{ax}$).

From the change in the bond distances, the anion of **14** is best described by resonance structure **I**. Addition of F$^-$ to **6** weakens the NS (change in bond distance +6.8 pm), CO (2.0 pm), CF (of the −C(O)F group, 3.9 pm), and SF bonds (14−15 pm).The CN bond is strengthened (−8.1 pm), while the SCF$_3$ unit is almost unaffected. The SN bond acquires more single-bond character and the CN bond more double-bond character. The dramatic change in the SF bond distances is readily explained by the different bonding situations in **6** and **14**. The 2c-2e bond in neutral **6** is converted to 3c-4e bonds in anionic **14**. In SF$_4$[30] and CF$_3$SF$_3$,[31] the axial SF bonds are 10 pm longer than the SF$_{eq}$ bonds; for the SF$_5^-$ anion, the apical 2c-2e bond (155.9 pm) is reported to be 16 pm shorter than the equatorial 3c-4e bonds (171.9 pm).[32] The SF bond distances in **14** are not the longest determined for SF$_{ax}$ in ψ-pentacoordinate S(IV) compounds; for (Me$_2$N)$_2$SF$_2$, the axial sulfur−fluorine bonds are reported to be 177 pm.[17]

Figure 2 shows the B3LYP/6-31G* calculated structure of the unstable anion FC(O)NSF$_3^-$. In comparison to **14**, the main differences are the different positions of the equatorial CF$_3$ and F substituents relative to the −NC(O)F group and the rotation of this group to a position between equatorial and axial. With the classifications given in Chart 1, this structure is intermediate between **A** and **C**. The different positions of the CF$_3$/F groups are due to a strong anomeric interaction between the n$_N$ and σ^*_{SF} orbitals; this interaction is also documented by a decrease of 5.5 pm in the SN bond of FC(O)NSF$_3^-$. The effect on the other bonds is less pronounced. The syn orientation of the oxygen relative to F(2) and F(4) leads to steric interactions; a position intermediate between axial and equatorial seems to be the sterically least hindered. Even in this position the O···F(2) distance is only 286 pm, less than the sum of the van der Waals radii (300 pm). To diminish steric strain, the COF group is twisted around the CN bond by 17°. The shortest nonbonded distance of the carbon to a sulfur-bonded fluorine is that involving F(2) at 277 pm, well below of the sum of r_{vdW}(F) and r_{vdW}(O) (315 pm). This close proximity could be the reason for an easy transfer of F(2) from sulfur to carbon and decomposition to give OCF$_2$ and NSF$_2^-$.

Conclusions

Pentacoordinate nitrogen−sulfur(IV) (R$_2$NSF$_3$,[16] (R$_2$N)$_2$SF$_2$,[17−20] RNSF$_3^-$,[15,36] RNS(CF$_3$)F$_2^-$ [15,36]) and sulfur(VI) species (RNSF$_4$,[22,23,35] R$_2$NS(O)F$_3$,[37] (R$_2$N)$_2$S(O)F$_2$,[18] RNS(O)F$_3^-$,[15,36] R$_2$NSF$_4^+$ [38]) are expected to show a fascinating stereochemical diversity. Of special interest are the interactions of the amido and imido groups with the sulfur centers and the natures of the sulfur−nitrogen bonds. To date, structure determinations have been reported only for R$_2$NSF$_3$,[16] (R$_2$N)$_2$SF$_2$,[17−20] and RNSF$_4$ (R = CH$_3$,[22] F[23]). In the present study, we unexpectedly found for the anion FC(O)NS(CF$_3$)F$_2^-$ an equatorial orientation of the equatorially bonded −C(O)F group. According to theoretical calculations for FC(O)NSF$_3^-$, exchange of the equatorial CF$_3$ group by fluorine results in a rearrangement of the equatorial substituents (lone pair/CF$_3$ and F, respectively) and rotation of the −C(O)F group to a position intermediate between equatorial and axial. Calculations for CF$_3$NSF$_3^-$ and CF$_3$NS(CF$_3$)$_2$F$_2^-$ show the nitrogen-bonded CF$_3$ group in CF$_3$NSF$_3^-$ axially oriented and that in CF$_3$NS(CF$_3$)$_2$F$_2^-$ equatorially oriented.[39] The positions of the nitrogen-bonded substituents seem to be very sensitive to steric and electronic influences. The evaluation of these influences will be the subject of further investigations.

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Supporting Information Available: An X-ray crystallographic file, in CIF format, for **14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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