

# Pentacoordinate difluorosulfur(IV) and difluorosulfur(VI) species RR'SF<sub>2</sub> and R<sub>2</sub>S(O)F<sub>2</sub>: some structural relationships

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## Abstract

The syntheses of Az<sub>2</sub>S(O)F<sub>2</sub> (AZ = pyrazole (**7d**), imidazole (**7e**), 1,2,4-triazole (**7f**) from OSF<sub>4</sub> and the corresponding trimethylsilylazoles AzSiMe<sub>3</sub> and the structures of **7d** and **f** as well as those of [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)N]<sub>2</sub>SF<sub>2</sub> (**3b**) and CF<sub>3</sub>S(azole)SF<sub>2</sub> (AZ = 1,2,4-triazole) (**3f**) are reported, the structure of [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>SF<sub>2</sub> (**3a**) was re-determined at –100 °C. The steric influence of the different substituents (F, CF<sub>3</sub>, NR<sub>2</sub>, azolide), of the oxidation state and of the lone pair (LP) in comparison with the doubly bonded oxygen is discussed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Pentacoordination; Trigonal bipyramide; Fluorosulfuranes; X-ray structures

## 1. Introduction

While pentacoordination in phosphorus chemistry has been intensively investigated [1,2], there are only limited reports in sulfur chemistry of this fascinating subject. Since the first preparation of SF<sub>4</sub> [3] and OSF<sub>4</sub> [4,5] a large number of S(IV)-derivatives have been prepared [6,7]. Due to the more difficult preparation of OSF<sub>4</sub>, knowledge about its chemistry is rather restricted. Structure determinations for SF<sub>4</sub> [8], CF<sub>3</sub>SF<sub>3</sub> [9], (CF<sub>3</sub>)<sub>2</sub>SF<sub>2</sub> [10] and Me<sub>2</sub>NSF<sub>3</sub> [11] by GED were reported, X-ray structures of (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub> [12] and more recently of CF<sub>3</sub>(imid)SF<sub>2</sub> [13], AZ<sub>2</sub>SF<sub>2</sub> (AZ = pyrazole, 1,2,4-triazole, imidazole [14,15] and (4-Ph-imid)<sub>2</sub>SF<sub>2</sub> [15]) were determined. These results, together with the additional structures of CF<sub>3</sub>(1,2,4-triaz)SF<sub>2</sub> (**3f**) and [C<sub>6</sub>H<sub>5</sub>(CH<sub>3</sub>)N]<sub>2</sub>SF<sub>2</sub> (**3b**) from the present paper, will allow a discussion on how the geometry at the central S(IV) is influenced by the different substituents. Systems where the sulfur is incorporated in heterocycles will not be considered.

Comparing the structures of SF<sub>4</sub> [8] and OSF<sub>4</sub> [16], Christie and Oberhammer [17] pointed out “evidence for the existence of directional repulsion effects by lone valence electron pairs and π-bonds in trigonal bipyramidal molecules” [17]. They, Seppelt [18,19], Gillespie et al. [20] and we extended this discussion to the electronically related

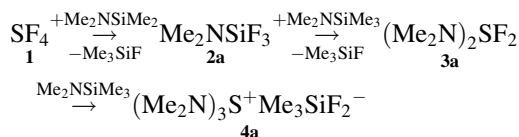
methylene and imino derivatives H<sub>2</sub>C=SF<sub>4</sub> [18,19,21–25] and RN=SF<sub>4</sub> [26–43]. More recently Christie et al. demonstrated that the isoelectronic phosphorus anions PF<sub>4</sub><sup>–</sup> [44] and OPF<sub>4</sub><sup>–</sup> [45] show a similar behavior.

Although in OSF<sub>4</sub>, the angles F<sub>a</sub>SF'<sub>a</sub> and F<sub>e</sub>SF'<sub>e</sub> differ quite markedly from those in SF<sub>4</sub>, for (CF<sub>3</sub>)<sub>2</sub>S(O)F<sub>2</sub> [46] and (CF<sub>3</sub>)<sub>2</sub>-SF<sub>2</sub> [10] identical angles F<sub>a</sub>SF'<sub>a</sub> and F<sub>e</sub>SF'<sub>e</sub> were reported. Further information appears to be necessary in order to discuss the different directional effects of the lone pair (LP) compared to the O=S π-bond on the sulfur bonded substituents. With (pyraz)<sub>2</sub>S(O)F<sub>2</sub> and (1,2,4-triaz)<sub>2</sub>S(O)F<sub>2</sub> in the present paper the first X-ray structures of disubstituted nitrogen derivatives of OSF<sub>4</sub> are reported. They also allow a comparison with the corresponding Az<sub>2</sub>SF<sub>2</sub> derivatives, confirming the different influences of the LP and the O=S π-bond as discussed by Christie and Oberhammer [17] and by Gillespie et al. [20].

## 2. Results and discussion

### 2.1. Syntheses of difluoro derivatives of SF<sub>4</sub> and OSF<sub>4</sub>

Sulfur tetrafluoride reacts with dialkylamino trimethylsilanes with stepwise exchange of the sulfur bonded fluorines [11,47–57]:

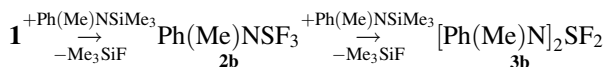


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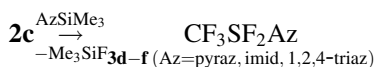
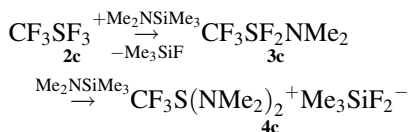
This reaction sequence is quite general, in the same way mono- and disubstituted derivatives are obtained from alkylarylamino trimethylsilanes:



**3b** was isolated as brownish crystals, mp 82 °C, after sublimation at 80 °C under dynamic vacuum.

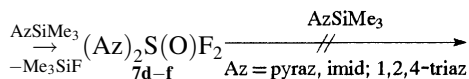
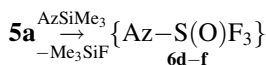
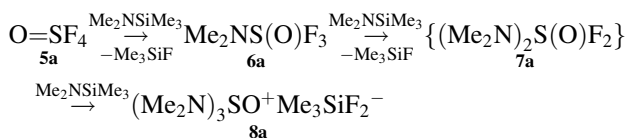
A different pathway is followed in the reaction of SF<sub>4</sub> with trimethylsilylazoles (azole = pyrazole (pyraz), imidazole (imid), 1,2,4-triazole (triaz)). Regardless of the stoichiometry applied only bis(azole)sulfur difluorides Az<sub>2</sub>SF<sub>2</sub> were isolated. Even low temperature NMR investigations gave no hint for the primarily expected azole sulfur trifluorides AZSF<sub>3</sub> [14,15].

With CF<sub>3</sub>SF<sub>3</sub> as starting material similar reaction sequences are followed [58,59]:



Recently, we reported the syntheses of **3d–f** and the X-ray structure of **3e** [13], now we have also succeeded in determining the structure of **3f**. The low melting point of **3d**, however, prevented an X-ray structure determination.

The reactivity of OSF<sub>4</sub> toward dialkylamino trimethylsilanes and trimethylsilylazoles is expected to be similar to that of SF<sub>4</sub>. To date, only a few substitution reactions leading to dialkylamino sulfuroxidetrifluorides R<sub>2</sub>NS(O)F<sub>3</sub> (R<sub>2</sub>N = Me<sub>2</sub>N, Et<sub>2</sub>N, Pip) [60,61] have been reported. Excess of aminosilane gives, regardless of the stoichiometry applied, TAOS fluoride **8a**, no hints for the disubstituted derivative **7a** were found [62].



On the other hand, in the reactions with trimethylsilylazoles the disubstituted bis(azole)sulfuroxidetrifluorides were the only products to be isolated. PF<sub>5</sub>, isoelectronic with OSF<sub>4</sub>, and its organo derivatives R<sub>n</sub>PF<sub>5-n</sub> were allowed to react with a variety of lithiated and silylated azoles by Schmutzler and coworkers. Due to the higher Lewis acidity of the phosphoranes a different chemical behavior is observed [63–66].

Table 1  
<sup>19</sup>F and <sup>1</sup>H chemical shifts for bis(azole) sulfur difluorides<sup>a</sup> and sulfuroxidetrifluorides

	δ(SF)	H(2)	H(3)	H(4)	H(5)
	56.7	8.19	6.57	7.82	–
	88.85	8.42	6.68	7.95	–
	47.12	7.54	7.20	–	8.19
	95.13	7.80	7.16	–	8.37
	54.06	8.96 <sup>b</sup>	–	8.17 <sup>c</sup>	–
	91.60	9.14 <sup>d</sup>	–	9.14 <sup>e</sup>	–

<sup>a</sup> From [14].

<sup>b</sup> <sup>4</sup>J = 1.94 Hz.

<sup>c</sup> <sup>5</sup>J = 1.27 Hz.

<sup>d</sup> <sup>4</sup>J = 3.00 Hz.

<sup>e</sup> <sup>5</sup>J = 2.52 Hz.

**7d–f** are colorless solids, they were characterized by IR, NMR, mass spectroscopy and X-ray crystallography (**7d** and **f**). Due to its low thermal stability **7e** was characterized only by NMR spectroscopy. In Table 1, the <sup>1</sup>H and <sup>19</sup>F NMR data for **7d–f** are compared with those of the corresponding S(IV) derivatives. Chemical shifts for fluorine bonded to sulfur are found at about 90 ppm, while for the S(IV) derivatives chemical shifts at about 50 ppm are observed. A similar shielding is found for the protons at the azole rings when comparing the S(VI) and S(IV) <sup>1</sup>H NMR data. All resonances are shifted upfield except that for H(3) in the imidazole ring of **7e**.

## 2.2. X-ray structure investigation of (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub> (**3a**) [Ph(Me)N]<sub>2</sub>SF<sub>2</sub> (**3b**), CF<sub>3</sub>(1,2,4-triaz)SF<sub>2</sub> (**3f**), (pyraz)<sub>2</sub>S(O)F<sub>2</sub> (**7d**) and (1,2,4-triaz)<sub>2</sub>S(O)F<sub>2</sub> (**7f**)

Single crystals suitable for X-ray structure investigations of **3b**, **7d** and **7f** were isolated after slow diffusion of pentane into CH<sub>2</sub>Cl<sub>2</sub> solutions of the appropriate compounds at

–30 °C. Single crystals of **3a** and **f** were obtained by vacuum sublimation. In Table 2, crystal data and details of the structure refinement for **3a**, **b**, **f** and **7f** are given.

### 2.2.1. Structures of $(Me_2N)_2SF_2$ (**3a**) and $[Ph(Me)N]_2SF_2$ (**3b**)

Cowley et al. reported the molecular structure of **3a**, the first X-ray structure of a fluorosulfurane [12]. They discussed in detail the bonding situation at the central sulfur, the conformation of the  $Me_2N$  groups, the interaction of the LP at the nitrogens with that on the sulfur and their interaction with the hypervalent axial SF bonds [12]. In disagreement with VSEPR rules, one particularly remarkable result was that the SF bonds were found to be bent towards the sulfur LP. Cowley et al. stated, “the possibility that the small bending of the S–F bonds toward the LP of the sulfur atom is due partially or wholly to weak attractive intermolecular forces cannot be dismissed” [12]. An answer to this question might be obtained from variation of the nitrogen-bonded substituents. Since the effects of different substituents on bond distances and angles were expected to be small, X-ray data for different molecules should be collected under identical conditions. To minimize thermal effects we routinely investigate our structures at –100 °C. Therefore, we re-determined the structure of **3a** at this temperature. Fig. 1

shows the X-ray structures of **3a** and **b** with selected bond distances and bond angles, in Fig. 2, intermolecular hydrogen bonding to the hypervalent axial SF bonds is indicated. Compared to the results of Cowley et al. (obtained at –35 °C), under these conditions, the SF and SN bonds are found to be slightly longer, the FSF bonds are bent to the LP by 4.6 instead 5.3°, the sum of the angles at the  $Me_2N$ -groups in our determination is 340.9°, these groups are slightly more pyramidal than in the earlier investigation (342.3°).

In **3b**, one of the methyl groups at each nitrogen is exchanged by a phenyl group, The geometries at the central sulfur and at the nitrogens are almost not affected. The nitrogen bonded phenyl groups are in an equatorial *syn*-position (angles S1N1C10 113.6(4)°, S1N2C20 112.9(4)°), the non-equivalence of the phenyl groups results from different torsion angles between the aryl and the NSN planes (ring 1/NSN 40.4(2)°; ring 2/NSN 65.6(2)°). This difference has a small influence on the CNC angles (C2N2C20 114.8(4)°, C1N1C10 116.9(4)°). N1 is slightly less pyramidal (sum of the angles 349.5°) than N2 (346.9°). Compared to **3a** (340.9°), this increase of the  $sp^2$  character should lead to a decrease of the SN bond distance. On the other hand, the decrease of the anomeric interaction  $n_N - \sigma_{SF}^*$  should increase the SN distance. The net effect is, as documented by the structure determinations of **3a** and **b**, that this bond

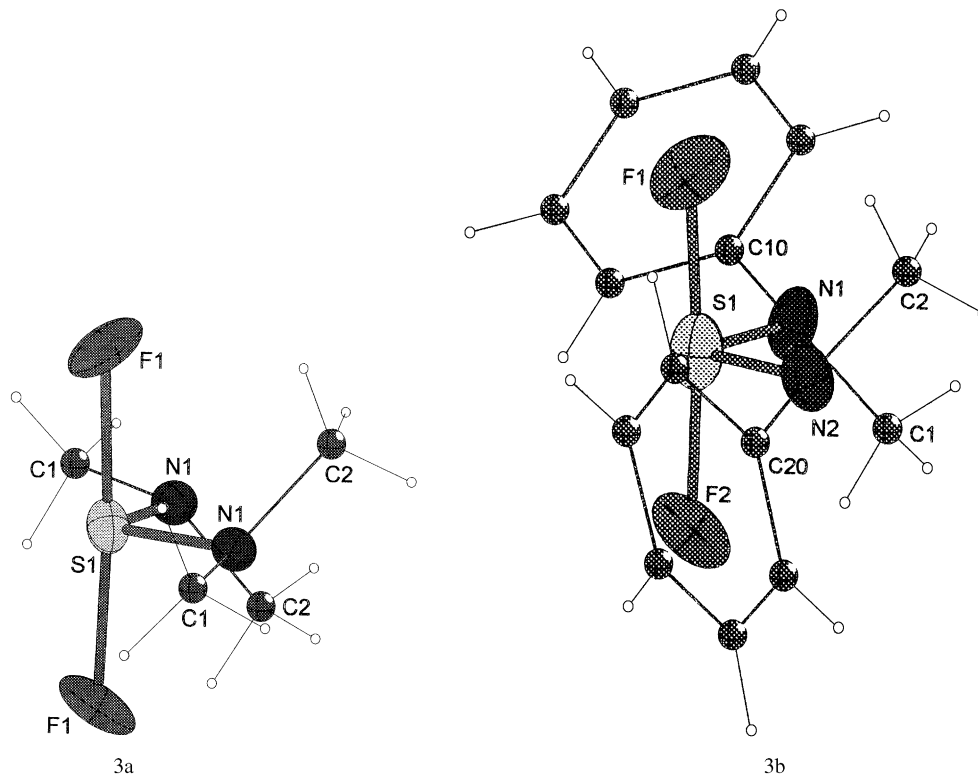


Fig. 1. Molecular structures of  $[(CH_3)_2N]_2SF_2$  (**3a**) and  $[CH_3(C_6H_5)N]_2SF_2$  (**3b**) with selected bond distances and bond angles: (**3a**) S(1)N(1) 165.8(2), S(1)F(1) 177.5(2), N(1)C(1) 147.8(4), C(2) 146.0(4), N(1) N(1)S(1)N(1)#1 102.3(2), N(1)S(1)F(1) 93.9(1), N(1)#1S(1)F(1) 89.0(1), F(1)S(1)F(1)#1 184.6(2), C(2)N(1)C(1) 112.8(2), C(2)N(1)S(1) 118.0(2), C(1)N(1)S(1) 110.1(2); (**3b**) S(1)N(1) 166.5(4), S(1)N(2) 165.2(4), S(1)F(1) 175.7(3), S(1)F(2) 175.3(3), N(1)C(1) 145.9(7), N(1)C(10) 144.5(7), N(2)C(2) 147.1(6), N(2)C(20) 145.4(6), N(1)S(1)N(2) 99.7(2), N(1)S(1)F(1) 89.2, N(1)S(1)F(2) 93.4(2), N(2)S(1)F(1) 93.4(2), N(2)S(1)F(2) 89.0(2), F(1)S(1)F(2) 184.2(2) S(1)N(1)C(1) 119.0(4), S(1)N(1)C(10) 113.6(3), C(1)N(1)C(10) 116.9(4), S(1)N(2)C(2) 112.9(3), S(1)N(2)C(20) 119.2(3), C(2)N(2)C(20) 114.8(4).

Table 2  
Crystal data and structure refinement for **3a**, **3b**, **3f**, and **7f**<sup>a</sup>

	<b>3a</b>	<b>3b</b>	<b>3f</b>	<b>7f</b>
Empirical formula	C <sub>4</sub> H <sub>12</sub> F <sub>2</sub> N <sub>2</sub> S	C <sub>14</sub> H <sub>16</sub> F <sub>2</sub> N <sub>2</sub> S	C <sub>3</sub> H <sub>2</sub> F <sub>5</sub> N <sub>3</sub> S	C <sub>4</sub> F <sub>2</sub> N <sub>6</sub> OS
Formula weight	158.22	282.35	207.14	222.19
Temperature	173(2)	173(2)	173(2)	173(2)
Wavelength	71.073	71.073	71.073	71.073
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group	<i>C2/c</i>	<i>Pna2(1)</i>	<i>Pbca</i>	<i>P2<sub>1</sub>/c</i>
<i>a</i> (pm)	1092.6(2)	1115.2(2)	586.70(10)	929.98(18)
<i>b</i> (pm)	563.40(10)	1011.5(2)	1342.9(3)	1051.4(3)
<i>c</i> (pm)	1214.5(2)	1240.0(2)	1676.5(3)	838.82(19)
$\beta$ (°)	92.73(3)	90	90	101.768(16)
Volume (nm <sup>3</sup> )	0.7468(2)	1.3988(4)	1.3209(4)	0.8030(3)
<i>Z</i>	4	4	8	4
Density (calculated) (Mg/m <sup>3</sup> )	1.407	1.341	2.083	1.838
Absorption coefficient (mm <sup>-1</sup> )	0.390	0.242	0.535	0.415
<i>F</i> (0 0 0)	336	592	816	448
Crystal size (mm <sup>3</sup> )	0.50 × 0.40 × 0.40	0.60 × 0.50 × 0.50	0.50 × 0.40 × 0.40	0.90 × 0.50 × 0.30
Theta range for data	3.36–27.55°	2.60–27.49°	3.89–26.12°	2.96–26.50°
Index ranges	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 7, 15 ≤ <i>l</i> ≤ 5	0 ≤ <i>h</i> ≤ 14, 0 ≤ <i>k</i> ≤ 13, 16 ≤ <i>l</i> ≤ 0	−7 ≤ <i>h</i> ≤ 7, −15 ≤ <i>k</i> ≤ 15, −20 ≤ <i>l</i> ≤ 20	−11 ≤ <i>h</i> ≤ 11, −13 ≤ <i>k</i> ≤ 13, −1 ≤ <i>l</i> ≤ 10
Reflections collected	964	1616	13542	3945
Independent reflections	855 [ <i>R</i> (int.) = 0.0210]	1587 [ <i>R</i> (int.) = 0.0196]	1267 [ <i>R</i> (int.) = 0.0784]	1663 [ <i>R</i> (int.) = 0.0861]
Completeness to $\theta = 27.37^\circ$ (%)	99.9	94.4	96.3	99.9
Maximum and minimum transmission	0.8597, 0.8290	0.8887, 0.8685	0.8143, 0.7756	0.8855, 0.7063
Data/restraints/parameters	855/0/46	1587/1/177	1267/0/110	1663/0/129
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.041	0.875	1.173	1.006
Final <i>R</i> indices [ <i>I</i> > 2 $\sum(I)$ ]	<i>R</i> 1 = 0.0550, <i>wR</i> 2 = 0.1591	<i>R</i> 1 = 0.0527, <i>wR</i> 2 = 0.1168	<i>R</i> 1 = 0.0340, <i>wR</i> 2 = 0.877	<i>R</i> 1 = 0.0574, <i>wR</i> 2 = 0.1295
<i>R</i> indices (all data)	<i>R</i> 1 = 0.0705, <i>wR</i> 2 = 0.1672	<i>R</i> 1 = 0.0884, <i>wR</i> 2 = 0.1274	<i>R</i> 1 = 0.0398, <i>wR</i> 2 = 0.1077	<i>R</i> 1 = 0.0959, <i>wR</i> 2 = 0.1478
Absolute structure parameter	–	−0.04(18)	–	–
Extinction coefficient	0.005(5)	0.002(2)	None	0.005(3)
Largest differential peak and hole (Å <sup>-3</sup> )	0.666, −0.605	0.358, −0.433	0.361, −0.314	0.516, −0.611

<sup>a</sup> Refinement method full-matrix least squares on *F*<sup>2</sup> $\omega$  − 2 $\theta$  scans; Siemens P4 diffractometer; refinement based on *F*<sup>2</sup>; *R*<sub>1</sub> =  $\sum ||F_0| - F_c| / \sum |F_0|$ ; *wR*<sub>2</sub> =  $(\sum [w(F_0^2 - F_c^2)] / \sum [w(F_0^2)^2])^{1/2}$ , programs and SHELX-97 [14] and DIAMOND [15].

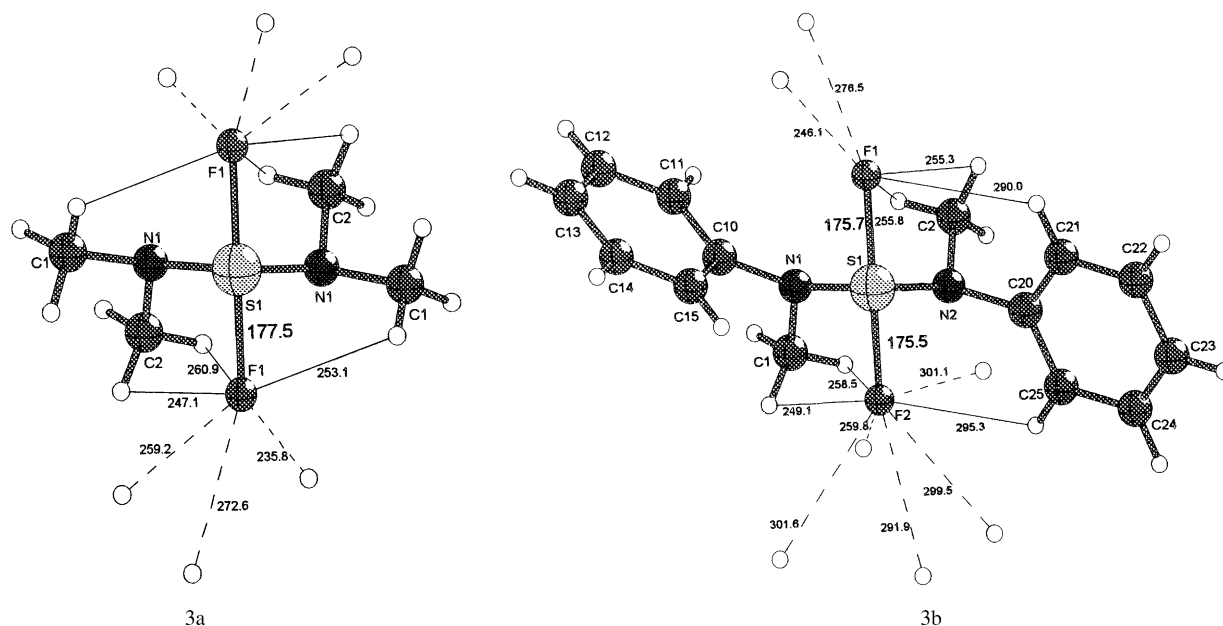


Fig. 2. Intermolecular hydrogen bonding to the axial fluorines in **3a** and **3b**.

distance remains unchanged. The longer SF bond (by 2 pm) in **3a** compared to **3b** is explained by the stronger anomeric interaction in **3a**.

The decrease of the NSN angle from 102.3° in **3a** to 99.7° in **3b** might have steric reasons.

Fig. 2 shows the intramolecular and intermolecular H···F interactions in **3a** and **b**. While intramolecular interactions should bend the SF bonds away from the LP, intermolecular interactions might have the opposite effect, as discussed by Cowley et al. [12]. In the dimethyl derivative **3a**, the strongest H···F interaction is intermolecular, while for **3b**, Fig. 2 supports that intramolecular interactions are strongest. The decrease of the bending of the axial SF bonds

towards the LP by 0.5 to 4.1(2)° in **3b** compared to **3a** is almost insignificant. Since the bending toward the one pair seems to be independent of the substituents bonded at nitrogen, this bending should be an intrinsic property of bis(amino)sulfur difluorides.

Quantum chemical calculations (RHF/6-311 + G\*, B3LYP/6-311 + G\*) confirm the experimentally determined geometry (Table 3). With both methods an  $F_aSF'_a$  angle larger than 180° is obtained (182.0 and 184.7°, respectively). The RHF calculated distances and the  $N_eSN'_e$  angle are in excellent agreement with the experiment. The angle  $N_eSN'_e$  obtained by the DFT method is slightly too small, the bond distances, as usual, too large.

Table 3

Experimental and calculated (RHF/16-311 + G\*, B3LYP/6-311 + G\*) structures of S(IV) difluorides RR'SF<sub>2</sub>

R=R'	SF <sub>a</sub>	SF <sub>e</sub>	SR <sub>e</sub>	F <sub>a</sub> SF' <sub>a</sub>	R <sub>e</sub> SR' <sub>e</sub>	Method
F	164.6	154.5	–	173.1	101.6	Experimental
	164.3	153.4	–	170.9	102.3	RHF
	170.6	159.5	–	174.5	101.4	B3LYP
Me <sub>2</sub> N	177.5	–	165.8	184.6	102.3	Experimental
	174.9	–	166.3	182.0	102.0	RHF
	182.7	–	170.4	184.7	98.9	B3LYP
Triaz	165.1/168.2	–	171.4/171.4	172.6	104.3	Experimental
Triaz(C <sub>2</sub> )	166.9	–	168.8	171.2	106.2	RHF
	173.4	–	173.8	176.1	102.9	B3LYP
Triaz(C <sub>s</sub> )	161.4/174.8	–	168.3/168.0	173.0	105.6	RHF
	167.2/179.7	–	174.3/174.6	174.6	104.5	B3LYP
Pyraz	167.0/170.8	–	170.1/170.1	175.9	102.8	Experimental
Pyraz(C <sub>2</sub> )	168.2	–	168.3	172.7	104.7	RHF
	174.1	–	173.7	174.5	102.8	B3LYP
Pyraz(C <sub>s</sub> )	160.9/176.5	–	168.3	175.1	107.0	RHF
	167.3/181.0	–	174.4	176.2	105.1	B3LYP

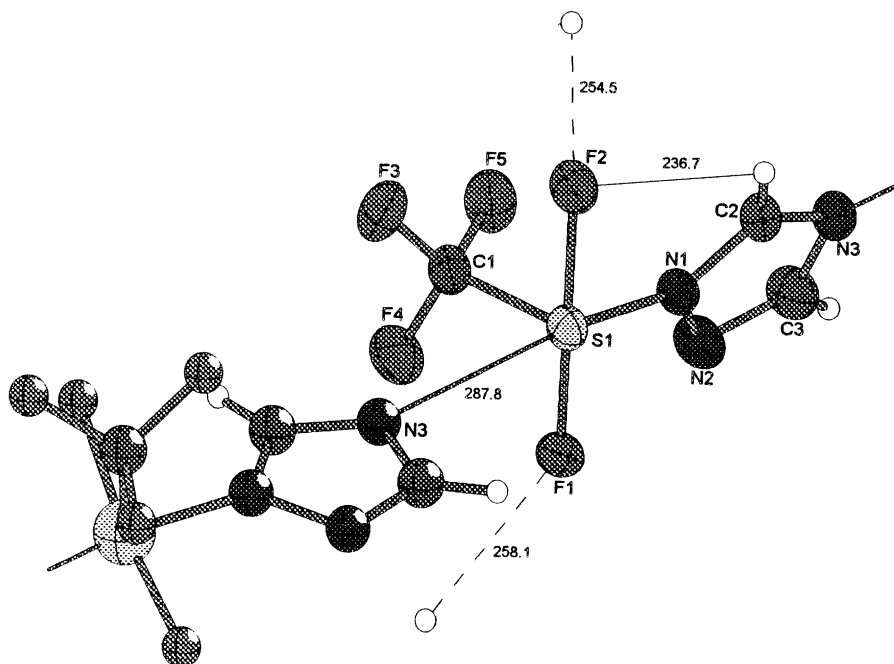


Fig. 3. Molecular structure of  $\text{CF}_3(1,2,4\text{-triazole})\text{SF}_2$  (**3f**) with selected bond distances and bond angles and intermolecular  $\text{S}\cdots\text{N}$  and  $\text{F}\cdots\text{H}$  contacts in **3f**: S(1)F(1) 165.5(2), S(1)F(2) 173.1(2), S(1)N(1) 171.4(2), S(1)C(1) 190.8(3), CF (a.v.) 131.1; N(1)N(2) 137.0(3), N(1)C(2) 136.0(3), C(2)N(3) 130.8(4), N(2)C(3) 130.6(4), C(3)N(3) 136.9(4); F(1)S(1)F(2) 171.8(2), F(1)S(1)N(1) 89.2, F(1)S(1)C(1) 89.9(1), F(2)S(1)N(1) 86.0(1), F(2)S(1)C(1) 84.6(1), C(1)S(1)N(1) 100.9(1).

As discussed by Cowley et al. [12], the LPs at the pyramidal nitrogens at the amino groups in **3a** (and also in **3b**) deviate from an alignment parallel to the  $\text{F}\cdots\text{F}$  axis by approximately  $30^\circ$ . The interactions of these LPs with  $\sigma_{\text{SF}}^*$  are responsible for the short SN and the long SF bonds. The bending of the axial fluorines toward the LP is interpreted as a result of electrostatic interaction between the nitrogen LPs and the axial fluorines.

#### 2.2.2. Structure of $\text{CF}_3(1,2,4\text{-triazole})\text{SF}_2$ (**3f**)

In Fig. 3, the molecular structure of **3f** with selected bond distances and angles and the intermolecular  $\text{S}\cdots\text{N}$  and

$\text{F}\cdots\text{H}$  contacts are shown. The geometry around the central sulfur is very similar to that of **3e**; exchange of the imidazole by the triazole substituent results in a small elongation of the SN bond, similar to  $(\text{imid})_2\text{SF}_2$  and  $(1,2,4\text{-triazole})_2\text{SF}_2$ , while the averaged SF bond distances in **3e** and **f** are almost not affected. The different axial SF bond lengths in both compounds result from differences in hydrogen bonding in the solid state. Also in both compounds, the “pyridine” nitrogens interact equatorially with adjacent sulfur centers ( $\text{S}\cdots\text{N} = 287.8$  pm in **3f**, 285.9 in **3e**; sum of the van der Waals radii of S and N 335 pm). The equatorial CSN angle  $100.9(1)^\circ$  (**3f**) and  $100.1(2)^\circ$  (**3e**), respectively) are in the

Table 4  
Bond angles and lengths for difluorosulfur(IV) compounds

R=	R' =	SF <sub>a</sub>	SF <sub>c</sub>	SR <sub>c</sub>	F <sub>a</sub> SF' <sub>a</sub>	R <sub>c</sub> SR' <sub>c</sub>	Reference
F	F	164.6(3)	154.5(3)	–	173.1(5)	101.6(5)	[8]
F	CF <sub>3</sub>	165.5(5)	156.5(8)	188.7(7)	169.4(13)	98.4(32)	[9]
CF <sub>3</sub>	CF <sub>3</sub>	168.1(3)	–	188.8(4)	173.9(8)	97.3(8)	[10]
F	NMe <sub>2</sub>	167.0(7)	156.3	163.9(13)	174.0(12)	104.6(10)	[11]
NMe <sub>2</sub>	NMe <sub>2</sub>	177.0(2)	–	164.8(2)	185.3(2)	102.3(1)	[12]
<b>3a</b> Nme <sub>2</sub>	NMe <sub>2</sub>	177.5(2)	–	165.8(2)	184.6(2)	102.3(2)	This work
<b>3b</b> NPhMe	NPhMe	175.6(3)	–	165.9	184.1(2)	99.7(2)	This work
Pyraz	Pyraz	168.9 <sup>a</sup>	–	170.1	175.88(2)	102.78(8)	[14]
Imidaz	Imidaz	170.0 <sup>a</sup>	–	170.1	174.4(7)	101.91(8)	[14,15]
Triaz	Triaz	166.6 <sup>a</sup>	–	171.4	172.6(2)	104.3(2)	[14]
<b>3d</b> CF <sub>3</sub>	Imid	169.9	–	169.9(3)	171.8(1)	100.1(2)	[13]
<b>3f</b> CF <sub>3</sub>	Triaz	169.3	–	190.1(4) 171.4(2)1 190.8(3)	171.8(1)	100.9(1)	This work

<sup>a</sup> Averaged bond lengths.

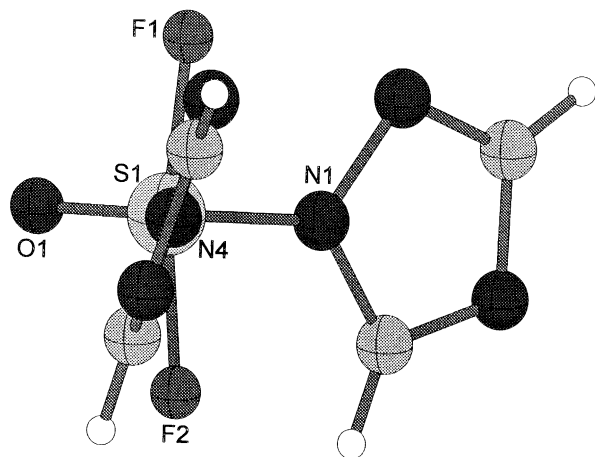


Fig. 4. Molecular structure of (1,2,4-triazole)<sub>2</sub>S(O)F<sub>2</sub> (**7f**) showing the deviation of the azole planes from the FSF axis and the influence of the SO bond on the FSF angle: S(1)F(1) 161.5(2), S(1)F(2) 160.3(2), S(1)O(1)-141.8(3), S(1)N(1) 168.6(3), S(1)N(4)168.6(3), F(1)S(1)F(2) 167.5(1), F(1)S(1)O(1) 95.5(2), F(2)S(1)O(1) 97.0(2), N(1)S(1)N(4) 116.2(2), N(1)-S(1)O(1) 122.1(2)N(4)S(1)O(1) 121.7(2), F(1)S(1)N(1)86.8(1), F(1)S(1)-N(4) 86.9(1), F(2)S(1)N(1) 86.6(1), F(2)S(1)N(4) 86.5(1).

expected range (Table 4), it seems that this angle is not influenced by intermolecular S...N interactions. In agreement with the VSEPR rules [77–79], the axial SF bonds are bent away from the LP (FSF angle 171.8°), the planar triazole ring is almost axially oriented, the plane of the ring and the F<sub>a</sub>...F<sub>a</sub> axis form an angle of 27.8°.

### 2.2.3. Structures of (pyrazole)<sub>2</sub>S(O)F<sub>2</sub> (**7d**) and (1,2,4-triazole)<sub>2</sub>S(O)F<sub>2</sub> (**7f**)

The molecular structure of **7f** is presented in Fig. 4. It shows the deviation of the azole planes from the F<sub>a</sub>...F<sub>a</sub> axis and the influence of the SO bond on the FSF angle. The equatorially bonded azole rings are oriented axially, their planes deviate from an axial alignment parallel to the F<sub>a</sub>...F<sub>a</sub> axis by 3.8° (N1) and 17.6° (N4), respectively. For **7d**, only a preliminary structure determination from an incomplete data set was obtained [67] (see Table 5). In Fig. 5, the molecular structure is also given for **7d**. The pyrazole rings deviate appreciably more from the F...F axis (deviation by 21.5° (N1) and 33.2° (N3), respectively) than the triazole rings in **7f**.

As expected from the orbital contraction due to the higher oxidation state SN (**7d**: 166.85 pm, **7f**: 168.7 pm) and SF bond distances (**7d**: 162.2 pm, **7f**: 160.9 pm) are shorter

Table 5  
Bond angles and lengths for difluorosulfur(VI) compounds

R=R'	SF <sub>a</sub>	SR <sub>e</sub>	F <sub>a</sub> SF' <sub>a</sub>	R <sub>e</sub> SR' <sub>e</sub>	Reference
F	159.6(3)	153.9(3)	164.6(2)	112.8(4)	[16]
CF <sub>3</sub>	164.1(4)	189.1(5)	173.1(6)	97.8(8)	[46]
<b>7d</b> pyraz	161.8 <sup>b</sup>	166.8 <sup>b</sup>	169.6(2)	115.3(2)	This work <sup>a</sup>
<b>7f</b> triaz	160.9 <sup>b</sup>	168.7 <sup>b</sup>	167.5(1)	116.1(1)	This work

<sup>a</sup> Preliminary results from an incomplete data set (41% of the data collected) [67].

<sup>b</sup> Average bond distances.

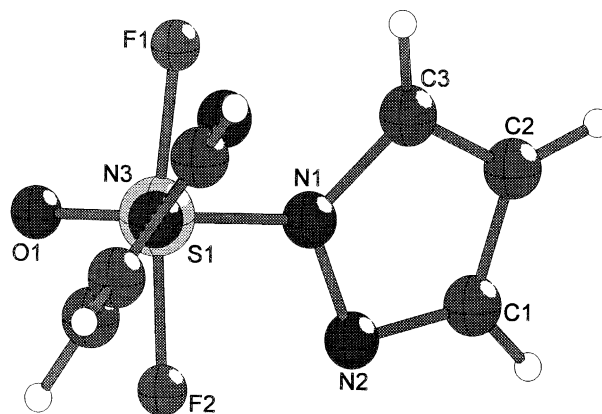


Fig. 5. Molecular structure of (pyrazole)<sub>2</sub>S(O)F<sub>2</sub> (**7d**) showing the deviation of the azole planes from the FSF axis and the influence of the SO bond on the FSF angle: S(1)F(1) 161.2(3), S(1)F(2) 162.4(2), S(1)O(1) 141.8(3), S(1)N(1) 166.9(3), S(1)N(3) 166.8(5), F(1)S(1)F(2) 169.6(1), F(1)S(1)O(1) 95.9(2), F(2)S(1)O(1) 94.5(2), N(1)S(1)N(3) 115.3(2), N(1)S(1)O(1) 122.9(2), N(3)S(1)O(1) 121.8(2), F(1)S(1)N(1) 86.3(1), F(1)S(1)N(3) 87.8(2), F(2)S(1)N(1) 88.3(1), F(2)S(1)N(3) 86.4(1).

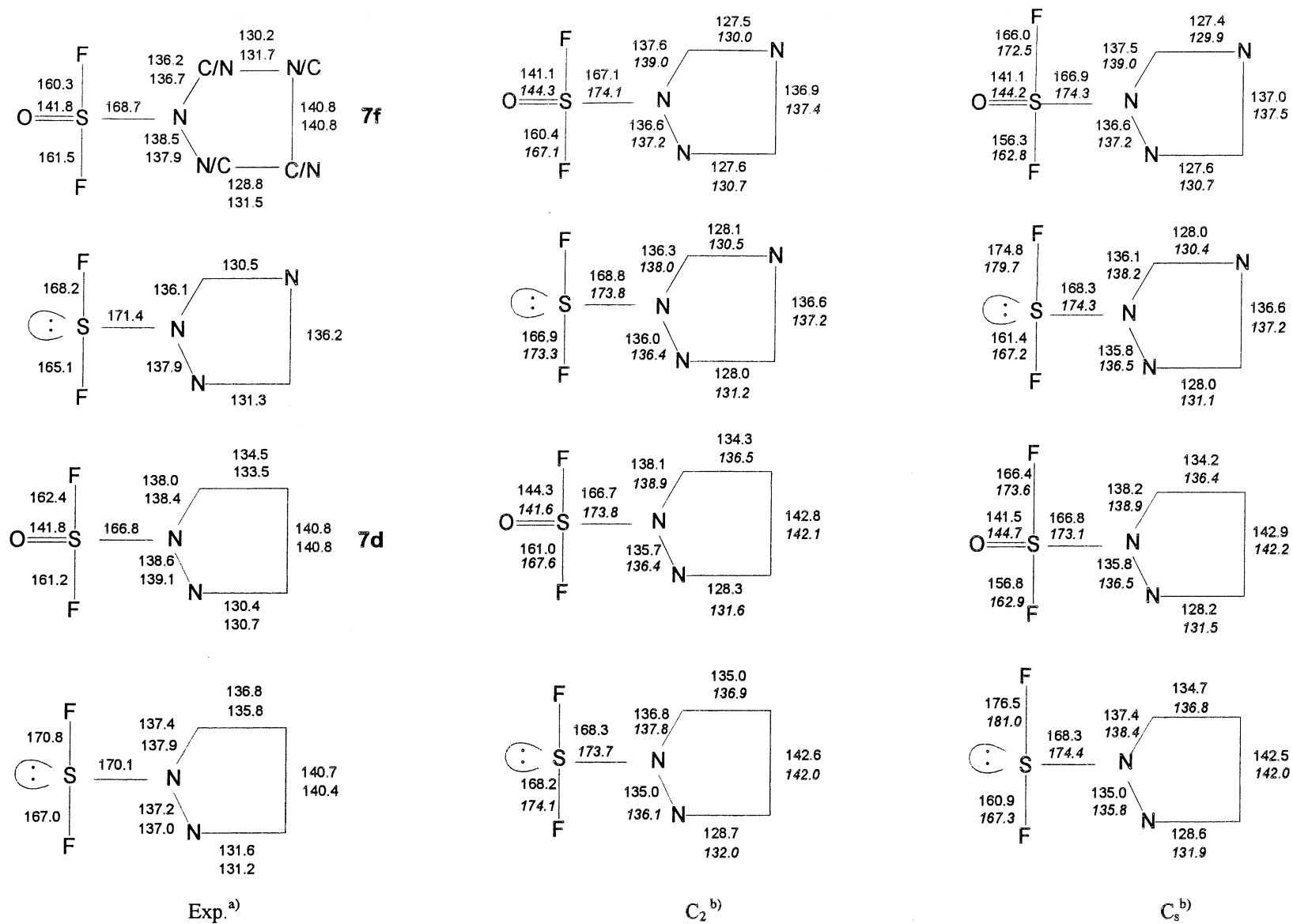
than those in the corresponding S(IV) derivatives (170.1/171.4 pm and 168.9/166.0 pm, respectively).

According to quantum chemical calculations (RHF/6-311 + G\*; B3LYP/6-311 + G\*), the energy difference is only 0.4–1.3 kcal between the two different axial arrangements of the azole groups, either *syn*-(C<sub>s</sub>-symmetry) or *anti*-(C<sub>2</sub>-symmetry). The C<sub>2</sub> structure is the more stable in all S(IV) and S(VI) derivatives, except for (triaz)<sub>2</sub>SF<sub>2</sub> (RHF, ΔE = 0.1 kcal). The main structural differences between the two possible isomers are found for the axial SF bonds, according to the calculations they differ by approximately 10 pm for C<sub>s</sub>-symmetry, but are equal for C<sub>2</sub>-symmetry. The bond angles and the SN distances around the central sulfurs, for **7d** and also for the corresponding (1,2,4-triazole)<sub>2</sub>SF<sub>2</sub> the bond distances within the azole rings, are almost not affected (Fig. 6). Therefore, for our discussion of the structural influence of the SO bond compared to the LP possible disordering of the azole rings is insignificant.

The almost identical axial SF bond distances in **7f** suggest C<sub>2</sub>-symmetry, the X-ray data show CN disordering in the triazole rings. For **7d** and the corresponding (pyrazole)<sub>2</sub>SF<sub>2</sub> the C<sub>s</sub> isomers seems to be dominant.

### 2.2.4. Comparison of the steric influence of the lone pair and the S=O bond in RR'SF<sub>2</sub> and RR'S(O)F<sub>2</sub>

As mentioned earlier, the different influences of the sulfur LP and the S=O bond on the geometry of the trigonal bipyramidal molecules SF<sub>4</sub> and OSF<sub>4</sub> were discussed by Christe and Oberhammer [17] and later, in more detail, by Gillespie et al. [20]. It is expected that the LP will have a greater effect on the larger, and therefore, more easily deformed equatorial-equatorial bond angle than on the smaller, less easily deformed equatorial-axial bond angles. This prediction implies that the LP is not axially



a) The two bond distances given belong to the two different rings in the molecules; b) RHF and B3LYP (in italics) calculated distances.

Fig. 6. Experimental and calculated (RHF/6-311 + G\* and B3LYP/6-311 + G\*) structures of (azole)<sub>2</sub>SF<sub>2</sub> and (azole)<sub>2</sub>S(O)F<sub>2</sub> (az = 1,2,4-triazole, pyrazole).



Table 6  
Experimental and calculated (RHF/6-311 + G\*, B3LYP/6-311 + G\*) structures of selected S(VI) oxide difluorides RR'(O)F<sub>2</sub>

R=R'=	SF <sub>a</sub>	SF <sub>e</sub>	SR <sub>e</sub>	F <sub>a</sub> SF' <sub>a</sub>	R <sub>e</sub> SR' <sub>e</sub>	Method
F	159.6	153.9	–	164.6	112.8	Experimental
	158.5	152.7	–	165.3	111.6	RHF
	164.9	160.0	–	166.1	112.6	B3LYP
Me <sub>2</sub> N	168.2	–	163.2	171.7	117.4	B3LYP
	177.4	–	169.4	170.1	118.3	
<b>7d</b> pyraz	161.2/162.4	–	166.8/166.9	169.6	115.3	Experimental
Pyraz(C <sub>2</sub> )	161.0	–	166.7	170.6	114.1	RHF
	167.6	–	173.8	167.3	113.9	B3LYP
Pyraz(C <sub>s</sub> )	166.4/156.8	–	166.8	169.8	115.3	RHF
	173.6/162.9	–	173.1	168.3	115.1	B3LYP
<b>7f</b> triaz	160.3	–	168.7	167.5	116.1	Experimental
	161.5	–	168.8	–	–	–
Triaz(C <sub>2</sub> )	160.4	–	167.1	168.7	114.2	RHF
	167.1	–	174.1	166.9	114.1	B3LYP
Triaz(C <sub>s</sub> )	166.0/156.3	–	166.9/166.9	168.6	114.7	RHF
	172.5/162.8	–	174.3/174.1	166.4	114.8	B3LYP

symmetrical, but is more spread in the equatorial than in the axial plane [20].

The data in Table 4 nicely confirm this point of view. Independent of the substituents R, R' in RR'SF<sub>2</sub>, the axial–equatorial bond angles are pushed together by less than 5° (the axial–axial bond angles range from 170 to 185°), while the R<sub>e</sub>SR'<sub>e</sub> angle is compressed by 15–20° to 100–105°.

The observed trend is also confirmed by quantum chemical calculations (Table 3).

In contrast to the LP the S=O bond is more cylindrical, compared to the LP the SO bond has relatively less charge density in the equatorial plane and more in the axial plane. This is in agreement with ab initio calculations performed by Oberhammer and Boggs [68], who calculated populations of  $\pi_{\text{eq}} = 0.17$  a.u. and  $\pi_{\text{ax}} = 0.12$  a.u. for OSF<sub>4</sub>. Compared to SF<sub>4</sub> for OSF<sub>4</sub> a decrease of the axial–equatorial and an increase of the equatorial–equatorial angle is expected.

Table 5 confirms this trend for OSF<sub>4</sub> and the azole derivatives, the experimental results are supported by theoretical calculations (Table 6).

For (CF<sub>3</sub>)<sub>2</sub>S(O)F<sub>2</sub>, the experimentally determined equatorial angle is much smaller and the axial angle larger than in the other compounds. According to Oberhammer [69], the experimental angles are not confirmed by quantum chemical calculation (HF/3-21G\* and B3LYP/6-31G\*) which predict equatorial angles of 123.5 and 126.0° and axial angles of 158.0 and 156.5°. Both computational methods predict a staggered orientation of the CF<sub>3</sub> groups with respect to the S=O bond which implies eclipsed orientation of one C–F bond of each CF<sub>3</sub> group with respect to the opposite S–C bond.

Repulsion between these two fluorine atoms in the equatorial plane leads to the very large CSC bond angle. In the experimental gas electron diffraction analysis [46], a molecular model with CF<sub>3</sub> groups eclipsing the S=O bond was

used and in this result in incorrect bond angles. The experimental trends for the S–C and S–F bond lengths, i.e. the very similar S–C bond lengths in the S(IV) and S(VI) compound and the shorter S–F bonds in the S(VI) derivative are confirmed by the quantum chemical calculations [69].

### 3. Conclusions

The experimental data show, that SF<sub>4</sub> and its derivatives on one side and OSF<sub>4</sub> and its derivatives on the other side form two distinctively different sets of structures. In R<sub>2</sub>SF<sub>2</sub> derivatives,  $\sphericalangle$  F<sub>a</sub>SF'<sub>a</sub> is 170–175° and  $\sphericalangle$  R<sub>e</sub>SR'<sub>e</sub> is 100–105°, while for R<sub>2</sub>S(O)F<sub>2</sub>  $\sphericalangle$  F<sub>a</sub>SF'<sub>a</sub> is found in the range 165–170° and  $\sphericalangle$  R<sub>e</sub>SR'<sub>e</sub> 113–116°. The structural data reported for (CF<sub>3</sub>)<sub>2</sub>S(O)F<sub>2</sub> are probably based on an incorrect model, a re-determination seems to be necessary [69]. The steric influence of the LP compared to the S=O bond is in agreement with the VSEPR model [77–79], the sum of the angle compressions for  $\sphericalangle$  F<sub>a</sub>SF'<sub>a</sub> and  $\sphericalangle$  R<sub>e</sub>SR'<sub>e</sub> are larger for R<sub>2</sub>SF<sub>2</sub> than for R<sub>2</sub>S(O)F<sub>2</sub>. The experimental data, supported by quantum chemical calculations, show the different directional effects of the LP and the S=O bond on the axial and equatorial angles F<sub>a</sub>SF'<sub>a</sub> and R<sub>e</sub>SR'<sub>e</sub>. As pointed out by Christe and Oberhammer [17] and by Gillespie et al. [20], the cylindrical SO bond has a similar effect on both angles, while the LP “is spread more in the equatorial plane” [20],  $\sphericalangle$  R<sub>e</sub>SR'<sub>e</sub> is compressed more and  $\sphericalangle$  F<sub>a</sub>SF'<sub>a</sub> less in R<sub>2</sub>SF<sub>2</sub> than in R<sub>2</sub>S(O)F<sub>2</sub>.

In bis(dimethylamino)sulfur difluoride (Me<sub>2</sub>N)<sub>2</sub>SF<sub>2</sub> and bis(methylphenylamino) sulfurdifluoride [Me(Ph)N]<sub>2</sub>SF<sub>2</sub> the bending of the axial substituents toward the LP is an intrinsic property of these compounds, confirmed by experimental data and quantum chemical calculations (Table 3).

For the future, these interesting findings deserve a more detailed theoretical investigation.

## 4. Experimental

The starting materials SF<sub>4</sub> [70], OSF<sub>4</sub> [71,72], CF<sub>3</sub>SF<sub>3</sub> [73], *N*-trimethylsilyl-imidazole [74,75], *N*-trimethylsilyl-pyrazole [74,75], *N*-trimethylsilyl-1,2,4-triazole [74,75], *N*-trimethylsilyl-methylaniline [76] were prepared according to literature methods. Recently we described the preparation of CF<sub>3</sub>SF<sub>2</sub> (1,2,4-triaz) [13]. [(CH<sub>3</sub>)<sub>2</sub>N]<sub>2</sub>SF<sub>2</sub> (**3a**) was prepared by the literature method [12], [CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)N]<sub>2</sub>SF<sub>2</sub> (**3b**) from CH<sub>3</sub>(C<sub>6</sub>H<sub>5</sub>)NSi(CH<sub>3</sub>)<sub>3</sub> and SF<sub>4</sub> by a similar procedure. IR spectra were recorded on a Nicolet DX-55 FT-IR spectrometer as Nujol- or the Kel-F-mulls, NMR-spectra on a Bruker DPX 200 (solvent: CD<sub>3</sub>CN), and mass spectra (EI, 70 eV) on a Finnigan MAT 8200 spectrometer. All operations were carried out in a nitrogen atmosphere due to the moisture sensitivity of the products. Elemental analyses were performed by the Mikroanalytisches Labor Beller, Göttingen.

### 4.1. Compound 7d

A 4.95 (35.3 mmol) sample of trimethylsilyl-pyrazole was placed via a syringe into a 250 ml λ-shaped glass vessel with a Teflon valve and magnetic stirring bar. A 25 ml of *n*-pentane as a solvent and 2.5 g (20.16 mmol) OSF<sub>4</sub> were then condensed into the vessel under vacuum at −196 °C. The reaction mixture was allowed to warm to −40 °C under stirring kept at that temperature for 2 h. Product **7d** precipitates as colorless solid, it is washed several times with the reaction solution by decanting the solution from one side of the λ-vessel into the other. Finally, all volatiles were removed under vacuum. A 2.85 g sample of **7d** (13.0 mmol, 73%), mp 106 °C (after sublimation under dynamic vacuum at 60 °C), was formed. The product was re-crystallized from dichloromethane/pentane at −30 °C. To prevent decomposition, **7d** should be stored at −20 °C. IR (cm<sup>−1</sup>): 3172 (w), 3130 (m), 1643 (vw), 1544 (vw), 1537 (w), 1421 (m), 1418 (m, sh), 1371 (m, sh), 1339 (w), 1301 (m, sh), 1286 (s), 1260 (s, sh), 1256 (s), 1203 (w), 1155 (m), 1065 (s), 1048 (w, sh), 1035 (m, sh), 1029 (m), 974 (vw), 913 (m), 881 (vw), 753 (s), 723 (vs), 668 (m, sh), 648 (s), 628 (m), 613 (m), 598 (m), 573 (m), 567 (m), 520 (vs); <sup>19</sup>F NMR: δ 88.85 (m), <sup>1</sup>H NMR: δ 8.42 (C(2)H) (m); 6.68 (C(3)H) (m), 7.95 (C(9)H) (m). MS (EI; 70 eV; *T* = 60 °C; *m/e* (rel. int., %, fragment)): 201 (2; (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)<sub>2</sub>SOF<sup>+</sup>), 153 (100; (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)SOF<sub>2</sub><sup>+</sup>), 134 (3; (C<sub>3</sub>H<sub>3</sub>N<sub>2</sub>)SOF<sup>+</sup>), 67 (11; C<sub>3</sub>H<sub>3</sub>N<sub>2</sub><sup>+</sup>), and further fragments.

### 4.2. Compound 7c

Similar to **7d** from 2.26 g (16.1 mmol) trimethylsilyl-imidazole and 2.00 g (16.13 mmol) OSF<sub>4</sub> in 10 ml *n*-pentane after 1 h at −60 °C 1.75 g (7.95 mmol, 99%) **7c** were obtained as a yellow powder, mp 97 °C (decomposition). The

compound can be stored at −20 °C, at room temperature, **7e** quickly decomposes. IR (cm<sup>−1</sup>): 3170 (m), 3141 (m), 3121 (m), 1657 (vw), 1650 (vw), 1547 (w), 1537 (m), 1426 (m), 1362 (m, sh), 1353 (w, sh), 1277 (m, sh), 1258 (s), 1243 (s, sh), 1238 (s, sh), 1152 (s), 1101 (m), 1092 (s), 1074 (s), 1057 (s), 1001 (w, sh), 970 (m), 960 (w), 887 (m), 835 (m), 827 (m), 780 (m), 750 (s), 722 (vs), 655 (s), 637 (vs), 617 (vs), 598 (s, sh), 584 (vs), 577 (s), 519 (vs); <sup>19</sup>F NMR δ 95.13 (m); <sup>1</sup>H NMR: 7.80 (C(2)H) (m), 7.16 (C(3)H) (m), 8.37 (C(5)H) (m).

### 4.3. Compound 7f

A 3.74 g (26.5 mmol) trimethylsilyl-1,2,4-triazole and 3.00 g (24.2 mmol) OSF<sub>4</sub> in 20 ml *n*-pentane gave after 5 h at −40 °C 2.75 g (12.4 mmol, 93%) **7f** as colorless 97 °C (after sublimation under vacuum at 80 °C). IR (cm<sup>−1</sup>): 3134 (vs), 1781 (vw), 1536 (s), 1512 (vw), 1404 (m), 1334 (m), 1328 (m), 1294 (vs), 1279 (vs), 1282 (s, sh), 1209 (vs), 1198 (s), 1128 (vs), 1121 (s), 1104 (vs), 1086 (s, sh), 979 (vw), 964 (m), 952 (vs), 935 (m, sh), 889 (m), 767 (vs), 670 (vs), 658 (vs), 639 (s), 619 (vs), 585 (s), 586 (m), 528 (vs); <sup>19</sup>F NMR: δ 91.60 (m), <sup>1</sup>H NMR: 9.14 (C(2)H), t, <sup>4</sup>*J*<sub>F-H(2)</sub> = 3.00 Hz), 8.29 (C(4)H), <sup>5</sup>*J*<sub>F-H(4)</sub> = 2.52 Hz). MS (EI; 70 eV; *T* = 60 °C; *m/e* (rel. int., %, fragment)): 203 (3; (C<sub>2</sub>H<sub>2</sub>N<sub>3</sub>)<sub>2</sub>SOF<sup>+</sup>), 154 (58; ((C<sub>2</sub>H<sub>2</sub>N<sub>3</sub>)SOF<sub>2</sub>)<sup>+</sup>), 128 (4; (NCNSONCN)<sup>+</sup>), 127 (100; ((C<sub>2</sub>H<sub>3</sub>N)SOF<sub>2</sub>)<sup>+</sup>) and further fragments.

## 5. Crystallographic analysis

The single crystal X-ray structure determinations (Table 2) were carried out a diffractometer using Mo Kα (0.71073 Å) radiation with a graphite monochromator. Refinement based on  $F^2$ ;  $R1 = \sum ||F_0| - |F_c||$ ;  $wR2 = (\sum [w(F_0^2 - F_c^2)]^2) / \sum [w(F_0^2)]^{1/2}$ . Programs used: SHELX-97 [80] and DIAMOND [81]. The structures were solved by direct methods (SHELXS) [80]. Subsequent least squares refinement (SHELXL 97-2) [80] located the positions of the remaining atoms in the electron density maps. All non-H atoms were refined anisotropically.<sup>1</sup>

The crystals were mounted using KEL-F oil on a thin glass fiber.

## 6. Computational methods

All ab initio calculations were performed with the GAUSSIAN'98 program [82].

<sup>1</sup>Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 165192 (**3a**), CCDC 165193 (**3b**), CCDC 16519 (3f), CCDC 165194 (**7f**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336043 or e-mail: deposit@ccdc.cam.ac.uk).

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