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Syntheses and Structures of Bis(azole)difluorosulfuranes

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Bis(imidazole)sulfur difluoride (**4**), bis(pyrazole)sulfur difluoride (**6**), and bis(1,2,4-triazole)sulfur difluoride (**8**) are formed in the reactions of *N*-(trimethylsilyl)imidazole, *N*-(trimethylsilyl)pyrazole, and 1-(trimethylsilyl)-1,2,4-triazole with SF_4, in high yield. The ring systems in these three molecules occupy equatorial positions in the pseudo-trigonal-bipyramidal coordination sphere of the central sulfur atoms. The angles between the planes of the ring substituents and the FSF axis for **4** and **6** are in the range 23.6−35.3°, and in **8** the triazole rings are almost parallel (deviation 1.7°). The interaction between the heterocyclic substituents and the sulfur centers and their influence on the axial and equatorial bonds is discussed.

(Dialkylamino)sulfur trifluorides, and particularly the diethyl derivative Et_2NSF_3 (DAST),[1] have an important role as selective fluorinating agents in organic chemistry.[2] Bis(dialkylamino)sulfur difluorides $(R_2N)_2SF_2$ can be used in a similar manner;[2] however, caution should be observed when working with these reagents. Earlier studies by Middleton et al.[3] have shown that dialkylamino sulfur trifluorides undergo dismutation reactions to SF_4 and bis(dialkylamino) derivatives, and that the latter, depending upon the substituent, have a tendency to decompose explosively at temperatures a little over 100 °C. Therefore, before using R_2NSF_3 or $(R_2N)_2SF_2$ in synthetic chemistry, it is important not only to choose R on the basis of the yield of the desired product but also to consider how easy the fluorinating agent is to handle.

Due to the practical importance of this class of compounds, further details on stabilities, reactivities, structures, and bonding relationships are of general interest. In the present paper we report the syntheses and structures of bis(imidazole)sulfur difluoride (**4**), bis(pyrazole)sulfur difluoride (**6**), and bis(1,2,4-triazole)sulfur difluoride (**8**).

Experimental Section

The starting materials SF_4,[4] *N*-(trimethylsilyl)imidazole (**3**),[5,6] *N*-(trimethylsilyl)pyrazole (**5**),[5,6] and 1-(trimethylsilyl)-1,2,4-triazole (**7**)[5,6] were prepared according to the literature. IR spectra were recorded on a Nicolet DX-55-FT-IR spectrometer as Nujol or Kel-F mulls, NMR spectra on a Bruker DPX 200 (solvents: $CDCl_3$ for **4** and **6**, CD_3CN for **8**), 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 Mikroanalytische Labor Beller, Göttingen, Germany.

4. A 6.0 g (43 mmol) sample of (trimethylsilyl)imidazole was placed, via a syringe, into a 250 mL two-sided λ-shaped glass vessel with a Teflon valve and magnetic stirrer bar. A 25 mL sample of *n*-pentane and 3.2 g (30 mmol) of sulfur tetrafluoride were then condensed on top under vacuum at −196 °C. The reaction mixture was stirred and allowed to warm to −40 °C. The reaction was complete after 3 h. The resulting product precipitated as a colorless solid. The product was washed by decanting and recondensing the solvent, and finally, the volatiles were pumped off. A 4.2 g sample of of **4** (21.0 mmol, 96%), mp 95 °C (after sublimation under dynamic vacuum at 70 °C), was formed. The product was also recrystallized from dichloromethane/*n*-pentane. Caution: *On one occasion impure **4** decomposed exothermally at room temperature.* To prevent decomposition, **4** should be stored at −30 °C. IR (cm^{-1}): 3158 (m), 3136 (m), 3115 (s), 1646 (vw), 1605 (vw), 1525 (m), 1455 (vs), 1380 (s), 1341 (vw), 1306 (vw) 1271 (w), 1250 (s), 1155 (s), 1104 (m), 1095 (s), 1054 (vs), 974 (vw), 894 (s), 829 (s), 825 (s), 771 (m), 739 (s), 671 (vw), 649 (s), 644 (s), 622 (vs), 605 (vs), 584 (s), 570 (s), 527 (vs); ^{19}F NMR: δ 47.12 (SF_2, ttt, $^4J_{F-H(2)} = 2.15$, $^4J_{F-H(5)} = 1.84$, $^5J_{F-H(3)} = 1.25$ Hz), ^1H NMR: δ 7.54 (C(2)H, tdd, $^3J_{H(2)-H(3)} = 1.84$, $^4J_{H(2)-H(5)} = 1.34$ Hz), 7.20 (C(3)H, dtd, $^4J_{H(3)-H(5)} = 0.90$ Hz), 8.19 (C(5)H, tdd). MS (EI, 70 eV, $T = 230$ °C; *m*/*e* (rel intens, %, fragment)): 204 (0.13, M^+), 185 (0.2, $M - F^+$), 156 (8, $C_3H_3N_2SF_3^+$), 137 (4.7, $C_3H_3N_2SF_2^+$), 89 (32, SF_3^+), 68 (100, $C_3H_4N_2^+$), and further fragments. Analysis for $C_6H_6F_2N_4S$ (204.20): C, 35.5 (calcd 35.29); H, 3.4 (2.96); F, 18.3 (18.61).

6. A 4.8 g (34 mmol) sample of (trimethylsilyl)pyrazole and 2.2 g (20 mmol) of sulfur tetrafluoride were allowed to react in a two-sided λ-shaped glass vessel in a manner analogous to that of **4**. The product **6** also precipitated as a colorless solid. Yield: 3.3 g (16 mmol, 95%). Mp: 39 °C. IR (cm^{-1}): 3175 (m), 3159 (m), 3144 (m), 3120 (m), 1814 (w), 1784 (w) 1772 (vw), 1745 (w), 1623 (m), 1526 (m), 1411 (s) 1364 (s), 1359 (s), 1279 (vs), 1200 (s), 1188 (s), 1147 (vs), 1058 (vs), 1021 (vs), 915 (s), 891 (w), 871 (w), 862 (s), 761 (s), 724 (w), 670 (vw), 667 (w), 609 (w). ^{19}F NMR: δ 56.7 (SF_2, ttt, $^4J_{F-H(2)} = 2.05$, $^5J_{F-H(3)} = 0.9$, $^5J_{F-H(4)} = 1.0$ Hz). ^1H NMR: δ 8.19 (C(2)H, tdd, $^3J_{H(2)-H(3)} = 2.9$, $^4J_{H(2)H(4)} = 0.7$ Hz), 6.57 (C(3)H, ddt, $^4J_{H(3)H(4)} = 1.75$ Hz), 7.82 (C(4)H), dtd). MS (EI, 70 eV, $T = 200$ °C; *m*/*e* (rel intens, %, fragment)): 185 (88.9, $M - F^+$), 166 (1, $M - 2F^+$), 156 (10.5, $C_3H_3N_2SF_3^+$), 147 (1.3), 137 (95.7, $C_3H_3N_2SF_2^+$), 117 (34.6, $C_3H_2N_2$-

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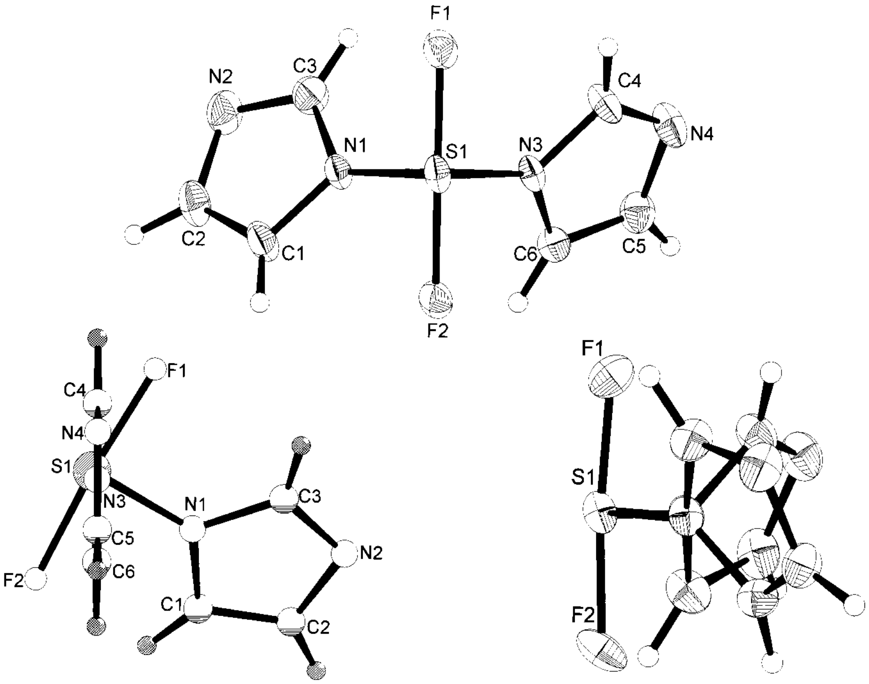

Figure 1. X-ray structure of **4**: (a) deviation of the plane of the imidazole ring from the FSF axis (27° and 29.5°, respectively); (b) influence of the sulfur lone pair on the FSF angle (174.4°).

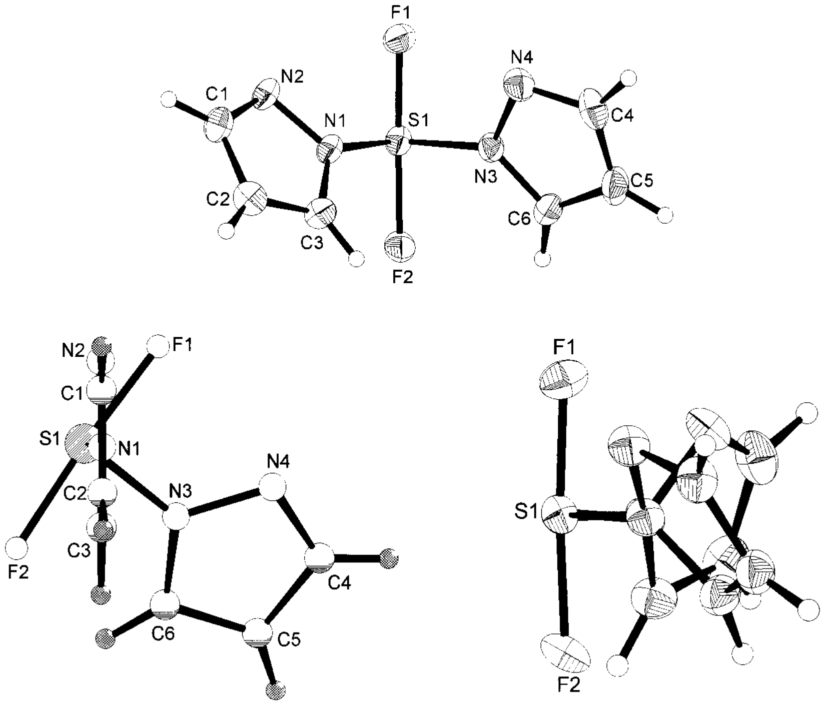

Figure 2. X-ray structure of **6**: (a) deviation of the plane of the pyrazole ring from the FSF axis (23.6° and 35.3°, respectively); (b) influence of the sulfur lone pair on the FSF angle (175.9°).

SF), 106 (100, $C_6H_6N_2^+$), and further fragments. Analysis for $C_6H_6F_2N_4S$ (204.20): C, 36.4 (calcd 35.29); H, 3.1 (2.96); F, 17.1 (18.61).

8. A 5.5 g (39 mmol) sample of 1-(trimethylsilyl)-1,2,4-triazole and 4.25 g (39 mmol) of sulfur tetrafluoride were allowed to react in 25 mL of *n*-pentane in a manner analogous to that of **4**. The product **8** was purified by sublimation in dynamic vacuum at 85 °C. Yield: 3.61 g (17.5 mmol, 89%). Mp: 114 °C. IR (cm^{-1}): 3162 (m), 3102 (w), 1856 (w), 1770 (vw), 1561 (vw), 1513 (s), 1509 (m,s), 1455 (m), 1332 (m), 1319 (s), 1279 (s) 1198 (s), 1136 (s), 1081 (s), 1035 (w, sh), 963 (s), 933 (s), 892 (s), 720 (m), 670 (vs), 623 (vs). ^{19}F NMR: δ 54.06 (SF_2, tt, $^4J_{F-H(2)} = 1.94$, $^5J_{F-H(4)} = 1.27$ Hz). ^1H NMR: δ 8.96 (C(2)H, t), 8.17 (C(4)H, t). MS (EI, $T = 50$ °C; *m*/*e* (rel intens, %, fragment)): 138 (30, $[(C_2H_2N_3SF_2)^+]$, 111 (40, $[(CHN_2SF_2)^+]$, 69 (100, $[(C_2H_3N_3)^+]$, and further fragments. Analysis for $C_4H_4F_2N_6S$ (206.17): C, 23.5 (calcd 23.30); H, 2.0 (1.94); F, 18.3 (18.45).

8′. ^{19}F NMR: δ 50.96 (SF_2 qu (dt) d, $^4J_{F-H(5),F-H(3')/H(5')} = 1.97$ Hz, $^5J_{F-H(3)} = 1.09$ Hz). ^1H NMR: δ 8.93 (C(5)H, t, 1H), 8.79 (C(3)′H/C(5)′H, t, 2H, 8.13 (C(3)H, br s, 1H).

Results and Discussion

There are currently a considerable number of aminosulfur trifluorides[7] and bis(amino)sulfur difluorides[8] described in the

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(7) *Gmelin Handbook of Inorganic and Organometallic Chemistry, Sulfur−Nitrogen-Compounds Part 8*; Springer: Berlin, 1991; p 373.

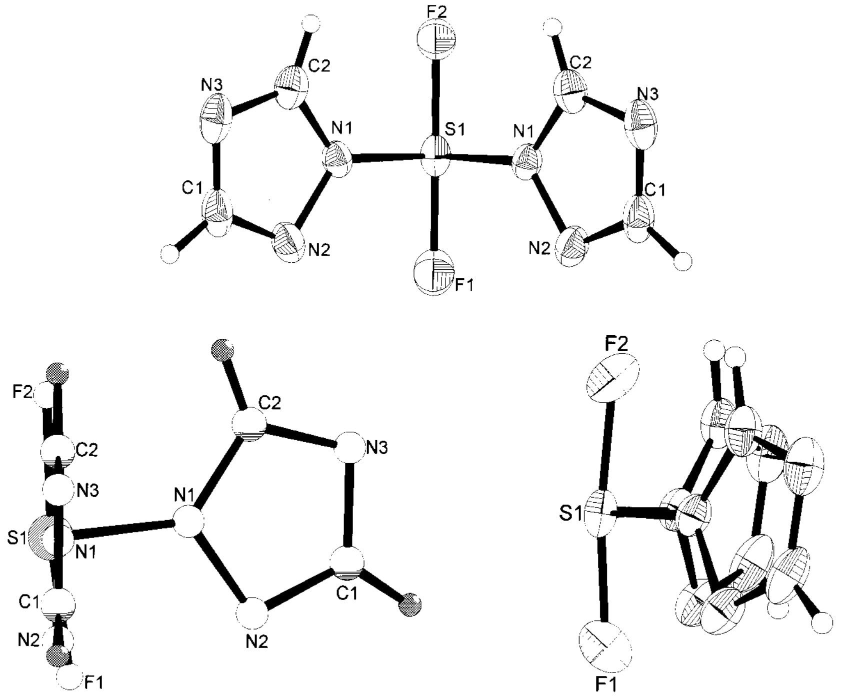


Figure 3. X-ray structure of **8**: (a) deviation of the plane of the triazole ring from the FSF axis (1.7° and 1.7°, respectively); (b) influence of the sulfur lone pair on the FSF angle (172.6°).

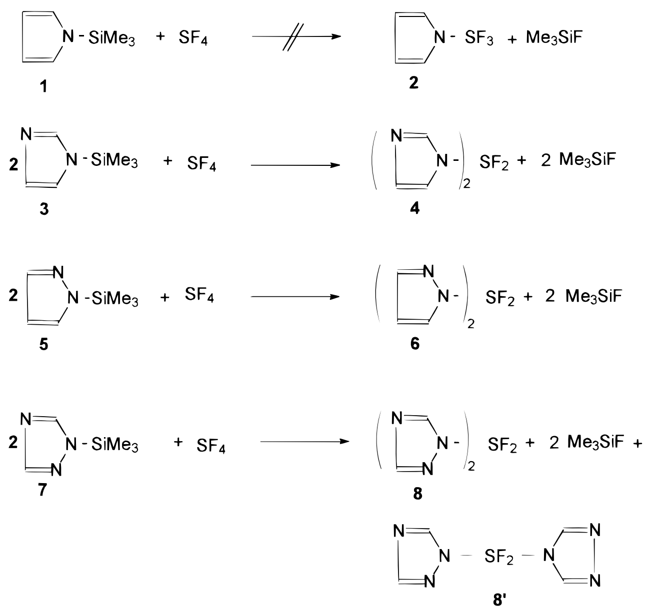
Table 1. Selected Bond Distances (pm) and Bond Angles (deg) for **4**, **6**, and **8**

	(imidazole)$_2$SF$_2$ (**4**)	(pyrazole)$_2$SF$_2$ (**6**)	(1,2,4-triazole)$_2$SF$_2$ (**8**)
S(1)−F (1)	169.30(12)	167.02(12)	165.1(3)
S(1)−F(2)	170.75(13)	170.80(12)	168.2(3)
S(1)−N (1)	170.2(2)	170.1(2)	171.4(2)
S(1)−N(3)/(1a)	169.9(2)	170.1(2)	171.4(2)
F(1)−S(1)−F(2)	174.41(7)	175.88(2)	172.6(2)
N(1)−S(1)−N(3)/(1a)	101.91(8)	102.78(8)	104.3(2)

literature. Saturated cyclic and acyclic N-bonded groups have been exclusively used, and one also finds derivatives in which the nitrogen is incorporated into unsaturated heterocycles.[9] Reports of pyrrole-, imidazole-, pyrazole-, and triazolesulfur trifluorides or -sulfur difluorides in which the nitrogen is part of a planar, aromatic system were unreported in the literature at the outset of our work. Amino sulfur trifluorides are generally accessible through reaction of SF$_4$ with N-silylated amines;[10] excess amine and higher reaction temperatures lead to exchange of the second sulfur-bonded fluorine atom with formation of (R$_2$N)$_2$SF$_2$.[11,12]

Recently, we demonstrated that (trifluoromethyl)(azole)sulfur difluorides CF$_3$SF$_2$Az (Az = pyrazole, imidazole, 1,2,4-triazole) are accessible through reaction of CF$_3$SF$_3$ with the appropriate silylated azole derivative.[13] The corresponding azolesulfur trifluorides should be formed in an analogous fashion by reaction with SF$_4$.

N-silylated pyrrole (**1**) does not react with SF$_4$ at room temperature; however, the reaction with the corresponding pyrazole, imidazole, triazole, and tetrazole derivatives occurs at −30 °C:



(The 1,2,3-triazole and tetrazole derivatives decompose explosively on workup, and for this reason no further investigations were undertaken on these compounds.) Despite variation of the reaction conditions (stoichiometry, temperature, coordination of the silylated heterocycles to transition metals and ensuing reaction with SF$_4$), we were unable to detect the expected products of the first step, namely, pyrazole-, imidazole-, or 1,2,4-triazolesulfur trifluorides.

According to the previously referred to investigations by Middleton et al.,[3] dismutation of the aminosulfur trifluorides

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(8) *Gmelin Handbook of Inorganic and Organometallic Chemistry, Sulfur−Nitrogen-Compounds Part 8*; Springer: Berlin, 1991; p 397.

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(12) Heilemann, W.; Mews, R.; Oberhammer, H. *J. Fluorine Chem.* **1988**, *39*, 261.

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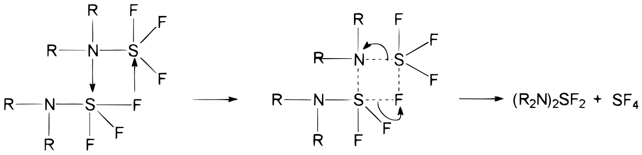
(14) Gombler, W.; Seel, F. H. *J. Fluorine Chem.* **1974**, *4*, 333.

Table 2. Crystal Data and Structure Refinement for **4**, **6**, and **8**[a]

	(imidazole)$_2$SF$_2$ (**4**)	(pyrazole)$_2$SF$_2$ (**6**)	(1,2,4-triazole)$_2$SF$_2$ (**8**)
empirical formula	$C_6H_6F_2N_4S$	$C_6H_6F_2N_4S$	$C_4H_4F_2N_6S$
M	204.21	204.21	206.19
T/K	173(2)	173(2)	173(2)
wavelength (Å)	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	orthorhombic	orthorhombic
space group	*Pn*	$P2_12_12_1$	*Pcam*
a (Å)	6.023(2)	7.070(1)	7.490(1)
b (Å)	10.084(4)	9.802(2)	5.712(1)
c (Å)	6.774(3)	11.639(2)	17.248(3)
β (deg)	99.50(3)		
V (Å^3)	405.8(3)	806.6(2)	737.9(2)
Z	2	4	4
D_c (mg m^{-3})	1.671	1.682	1.856
μ(Mo $K\alpha$) (mm^{-1})	0.387	0.390	0.434
cryst size (mm)	0.5 × 0.4 × 0.1	0.8 × 0.4 × 0.2	0.8 × 0.2 × 0.05
θ range (deg)	3.66−27.54	2.72−27.50	3.76−27.51
index range	$-7 \leq h \leq 7, -13 \leq k \leq 13, -8 \leq l \leq 8$	$-9 \leq h \leq 9, -12 \leq k \leq 12, -15 \leq l \leq 15$	$-1 \leq h \leq 9, -7 \leq k \leq 7, -19 \leq l \leq 0$
no. of reflns collected	3713	4632	1898
no. of indep reflns	1860 [R(int) = 0.0679]	1848 [R(int) = 0.0544]	856 [R(int) = 0.0896]
params	119	119	66
R1, wR$_2$ [$I > 2\sigma(I)$]	0.0311, 0.0709	0.0356, 0.0862	0.0659, 0.1618
R1, wR$_2$ (all data)	0.0327, 0.0720	0.0369, 0.0867	0.0798, 0.1704
absolute structure param	0.001(6)	0.00(8)	
largest diff peak (hole/e Å^{-3})	0.621/−0.382	0.357/−0.759	0.937/−0.603

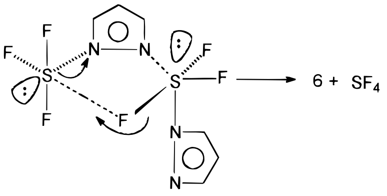
[a] Details in common: $\omega-2\theta$ scans; Siemens P4 diffractometer; refinement based on F^2; $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. Programs used: SHELX-97[26] and Diamond.[27]

occurs at around 90 °C; the authors suggest the following mechanism:



NMR studies by Seel and Gombler [14] suggest that SF_4 and CF_3-SF_3 dimerize or oligomerize via fluoride ion bridges, with the axial fluorine substituents attacking the equatorial positions of the neighboring molecules. Proof for this assignment of the NMR spectra came from the gas-phase structure determination of $F_2C(SF_3)_2$.[15] Interactions of the sort described above are also observed between the SF_3 groups in the gas phase.

With the imidazole, pyrazole, and triazole groups there are equatorially bonded substituents available, which can interact with the equatorial positions of neighboring molecules, as has been demonstrated by the solid-state structure of pyrazole−SF_2−CF_3.[13] Since, on the other hand, an axially bonded fluorine atom can interact with an equatorial site of an attacking molecule, it is easy to explain the facile dismutation via unsymmetric bridging (in agreement with the suggestion of Middleton[3]) as, for example, the pyrazole derivative shows. But this might not be the only possible pathway.



4, **6**, and **8** are colorless, hydrolysis-sensitive crystalline compounds, mp 95, 39, and 114 °C, respectively. The bis(azole)sulfur difluorides **4**, **6**, and **8** were characterized by elemental analysis, IR and ^{1}H and ^{19}F NMR spectroscopies, and X-ray structure analysis. The chemical shifts of the sulfur-bonded fluorines are in the range 47−57 ppm, which is characteristic for axially bonded fluorine substituents in diaminodifluorosulfuranes.[7] The equivalence of the two axial fluorines shows that the rotation of the azole rings is not restricted under measurement conditions (room temperature). F−H couplings are observed for all protons on the azole groups (see Experimental Section).

The observation of two signals of equal intensity in the ^{1}H NMR spectrum of **8** verifies that the 1,2,4-triazole rings are bonded to the sulfur center at position 1. This isomer has also been characterized by single-crystal X-ray diffraction. The ^{19}F NMR spectrum shows an additional multiplet, the ^{1}H NMR spectrum three further multiplets of considerably less intensity (6−8%). These signals have been assigned to the unsymmetrical 1,4-bis(1,2,4-triazole)sulfur difluoride (**8′**).

Structural Studies on Bis(imidazole)sulfur Difluoride (4), Bis(pyrazole)sulfur Difluoride (6), and Bis(1,2,4-triazole)-sulfur Difluoride (8)

Single crystals suitable for X-ray structure analysis were obtained by crystallization from dichloromethane/*n*-pentane at −20 °C. The molecular structures of **4**, **6**, and **8** are presented in Figures 1−3. Table 1 shows selected bond lengths and angles. To elucidate the conformation, we have presented two further projections of the three molecules: (a) shows the deviation of the azole planes from the FSF axis and (b) the influence of the sulfur lone pair on the FSF angle. Details of the structure determinations for compounds **4**, **6**, and **8** are given in Table 2.

At first glance the structures are as expected; however, on closer inspection they show a variety of unusual and interesting details. The central sulfur has pseudo-trigonal-bipyramidal geometry, and the electronegative fluorine atoms occupy the axial positions. The planes of the imidazole, pyrazole, and triazole rings deviate from an axial alignment parallel to the

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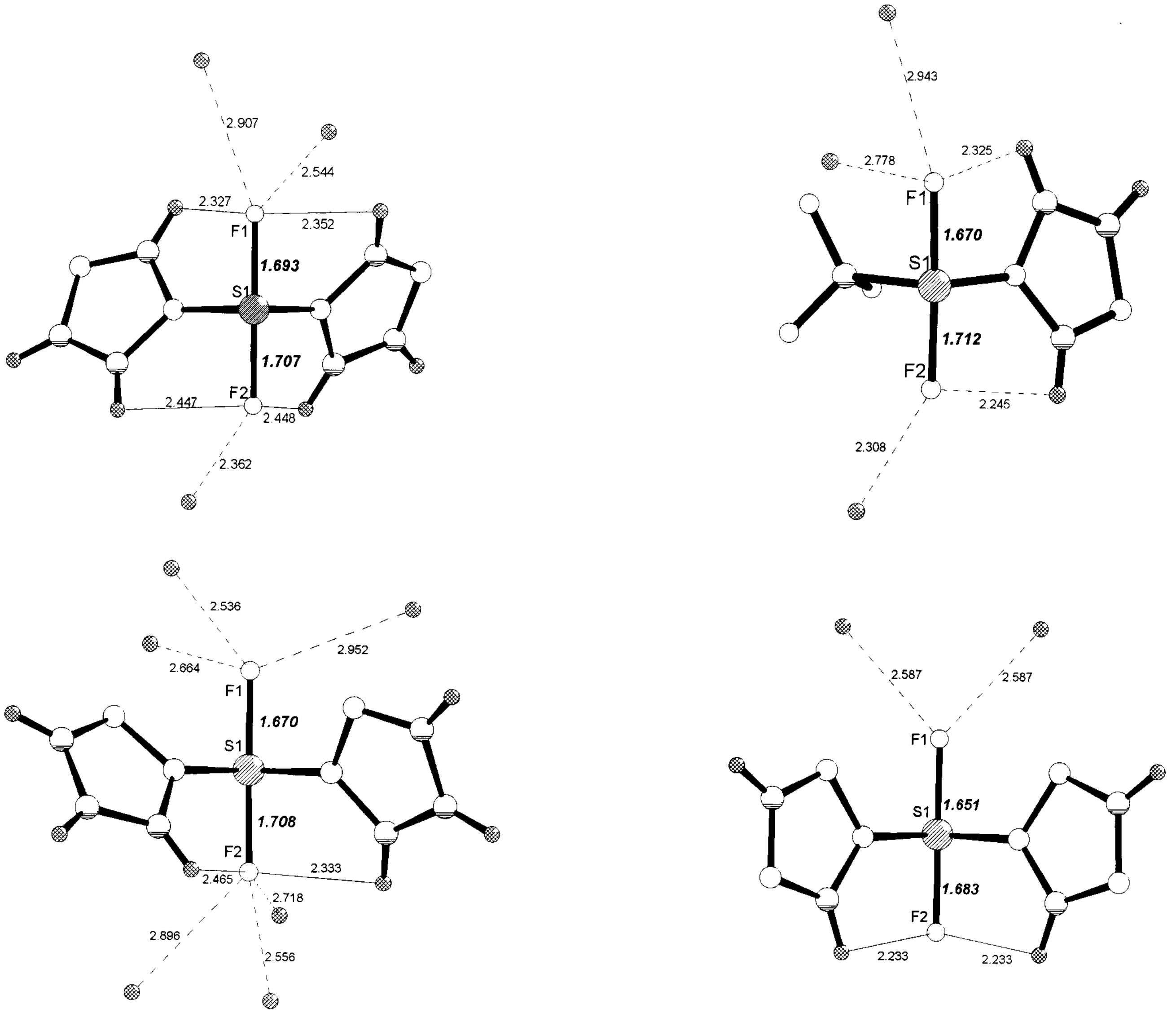

Figure 4. Hydrogen bonding in **4** (a), CF_3-SF_2-imidazole (b), **6** (c), and **8** (d). Intra- and intermolecular distances up to 300 pm are considered.

F−S−F axis by 27.0°/29.5°, 23.6°/35.3°, and 1.7°/1.7°, respectively. All SN bond distances in **4** and **6** (170 pm) are virtually identical within the standard deviations; for **8** SN was determined to be 171.4(2) pm. These bonds are considerably longer than in $(Me_2N)_2SF_2$ (164.8 pm),[16] an indication of the lower SN multibonding character in **4**, **6**, and **8**. While in $(Me_2N)_2$-SF_2 and also in $(PhMeN)_2SF_2$[17] both SF distances are equally long (177.0)/177.0(2) and 175.5(3)/175.6(3) pm, respectively), in **4**, **6**, and **8** they are different because of their different chemical environment. In each case the shorter bonds are found for the SF syn to the next neighboring ring N atom. In the imidazolyl derivative **4** this difference is 1.4 pm; in **6** and **8**, with direct N-neighbors, this difference is 3 pm more pronounced. For CF_3SF_2-imidazole[13] two different SF bond distances were also determined (168.1(2) and 171.7(2) pm, respectively), but there the SF bond syn to the N atom in the β position is longer. Therefore, stereoelectronic reasons are not responsible for these differences. They are probably due to intramolecular and intermolecular hydrogen bonding, as shown by Figure 4. For **4** with a relatively small difference in the axial SF distances, this argument is not very obvious, but for **6**, **8**, and CF_3SF_2-pyr[13] the longer SF bonds are related to distinctly shorter hydrogen bridges.

The average SF bond lengths in **4**, **6**, and **8** (165−171 pm) are considerably shorter than in the bis(dimethylamino) derivative (177 pm) as a result of less electron transfer from the N-substituents to the central sulfur atoms. In the dimethylamino derivative the Me_2N groups cause an unusual bending of the FSF angle in the direction of the lone pair of electrons. In **4**, **6**, and **8** the SF bonds are bent toward the N-substituents due to the steric influence of the sulfur lone pair as predicted by VSEPR rules;[18] this can be seen in Figures 1b−3b. The FSF angle in **4** is 174.4°, in **6** 175.9°, and in **8** 172.6°.

Cowley et al.[16] reported a detailed study of the conformation of the R_2N group and the mutual influences of the axial (hypervalent) FSF bond and the equatorial SN bond in $(Me_2N)_2$-SF_2, the only amino fluoro sulfurane for which an X-ray structure determination was available, by comparison with theoretical studies by Chen and Hoffmann on the model

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(16) Cowley, A. H.; Riley, P. E.; Szobota, J. S.; Walker, M. L. *J. Am. Chem. Soc.* **1979**, *101*, 5620.

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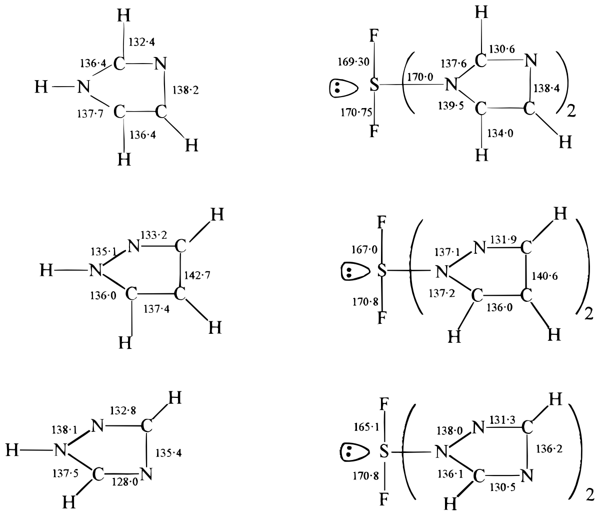
sulfurane $H_2N{-}SH_3$.[19] From the theoretical studies it has been possible to determine two factors which can define the conformation of the nitrogen substituents: (a) dative π-interactions of the occupied nitrogen orbitals (ligand π-orbitals) favor, applied to our examples, the axial alignment of the substituents; (b) the repulsion of the occupied orbitals on the sulfur by those of the substituents will lead to an orthogonal arrangement of these orbitals and thus to an equatorial alignment of the ring planes. The structure determinations of **4**, **6**, and **8** (as well as $(Me_2N)_2SF_2$) suggest that factor (a) is the more dominant. The structure determinations give no indication of disorder of the pyrazole, imidazole, or triazole substituents; a syn arrangement of the heterocycles was observed in all cases.

The change in the bond lengths on going from the free imidazole to the sulfurane-bonded imidazole is represented in the following illustration. The cited structures for the free azoles are all gas-phase structures;[20−22] in the solid state the bond lengths are distorted due to hydrogen bonding between individual azole molecules.[23−25]



To explain the change in the bond distances within the azole rings by electron transfer from the HOMO of the substituent to the sulfur center is too simple. Theoretical investigations of this problem are in progress.

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Supporting Information Available: Tables of experimental details for the crystal structure determinations, atomic coordinates, bond lengths, bond angles, torsion angles, and anisotropic parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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