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Preparation, Characterization, and Physical Properties of Bis(imidazole)sulfur Difluoride and Bis(4-phenylimidazole)sulfur Difluoride. New Compositions with Unexpected Thermal Stability

Robert G. Syvret

Fluorine Technology Center, Air Products and Chemicals, Inc., 7201 Hamilton Boulevard,
Allentown, Pennsylvania 18195-1501

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Two new bis(imidazole)sulfur difluoride compositions, $(imid)_2SF_2$ (**2**) and $(4\text{-Ph-imid})_2SF_2$ (**4**), have been prepared in high yields from the reactions involving the corresponding TMS precursors and excess SF_4 in anhydrous solvent. Mechanisms are proposed to account for the formation of **2** and **4** preferentially over the corresponding SF_3 derivatives or other isomers containing the SF_2 moiety. These new compositions are stable solids which melt at high temperatures and have been characterized in solution by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and in the solid state by MS (EI), elemental analysis, and single-crystal X-ray diffraction. The crystal structures of **2** and **4** are each based on a pseudo-trigonal-bipyramidal arrangement of two fluorines and two imidazole groups around the central sulfur, with the fluorines occupying axial positions and the imidazole groups in equatorial positions as predicted for these AX_4E compounds by the VSEPR model. Thermal decomposition properties of **2** and **4** have been studied using the Radex−Solo thermal hazards screening system. Compounds **2** and **4** have decomposition onset temperatures similar to those of several common R_2NSF_3 compounds; however, the thermal decomposition of **2** and **4** occurs at much slower rates than that of the R_2NSF_3 compounds and without the rapid release of gaseous byproducts, which is generally characteristic of explosive decomposition events. Therefore, by comparison, compounds **2** and **4** are inherently safer to handle and use.

Introduction

Several new compositions containing the bis(dialkylamino)sulfur difluoride moiety $R_2NSF_2NR'_2$ were first reported[1,2] in 1975 and shown to have potential utility as deoxofluorination agents,[3] for example, for the replacement of a carbon−oxygen bond with a fluorine−carbon bond in the conversion of ROH to RF. However, sustained interest in these new compounds was never realized, and it was subsequently shown many years later that several of these new compounds were notoriously unstable when heated and were in fact quite ineffective as deoxofluorination agents.[4]

The previously known bis(dialkylamino)sulfur difluoride compounds have been prepared by reaction of the corresponding (dialkylamino)sulfur trifluoride, $RR'NSF_3$, with 1 equiv of either the trimethylsilylamine,[1−3] Me_3SiNRR', or a diaminosulfinate,[2,5] $RR'NS(O)NRR'$. Each of the known $R_2NSF_2NR'_2$ compounds exists as expected, with a pseudo-trigonal-bipyramidal (AX_4E) arrangement of ligands around the central sulfur atom, with the two fluorines occupying the axial positions and the two dialkylamino groups and the sulfur lone pair in the equatorial plane. This arrangement was unequivocally confirmed for $(Me_2N)_2SF_2$ with the publication of the first X-ray crystal structure of a fluorosulfurane.[6]

Recently, Mews and co-workers reported the preparation and full characterization of several (azole)(trifluoromethyl)sulfur difluorides, including the X-ray structure determination of the imidazole analogue.[7] In the present work, we describe the preparation and full characterization of two new thermally stable bis(imidazole)sulfur difluoride compounds, including X-ray structural characterization of both compositions. In addition, we have studied the remarkable thermal stability of these compounds using the Radex−Solo thermal screening method and compare the results to common (dialkylamino)sulfur trifluorides.

Experimental Section

Reagents and General Procedures. Solvents CH_2Cl_2, CH_3CN, and hexanes were anhydrous grade (Aldrich), and used as received. Freon-11, $CFCl_3$ (Aldrich), was stored over P_4O_{10} and distilled prior to each use. Reagents (trimethylsilyl)imidazole, 4-phenylimidazole, and $(Me_3Si)_2NH$ and the compounds Me_2NSF_3, Et_2NSF_3, and morpholino-SF_3 were commercial samples (Aldrich) and used as received. SF_4 (Air Products) was pretreated with HF and then stored over dried NaF prior to use. All manipulations were performed under an atmosphere of dry N_2 or Ar using Schlenk techniques or in a glovebox.

Instrumentation and Analysis. ^1H, $^{13}C\{^1H\}$, and ^{19}F NMR spectra were recorded on a Bruker ACP-300 operating at 300.13, 75.47, and 282.41 MHz, respectively, and referenced with respect to external neat TMS (^1H and ^{13}C) and $CFCl_3$ (^{19}F). A positive chemical shift denotes a resonance to low field of the reference. Mass spectra (solids, probe) were recorded on a VG ZAB-EQ double-focusing magnetic sector mass spectrometer. Elemental analyses were performed by Oneida Research Services and Schwarzkopf Microanalytical Laboratory. Melting and

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(3) Middleton, W. J. U.S. Patent 3,888,924, 1975.
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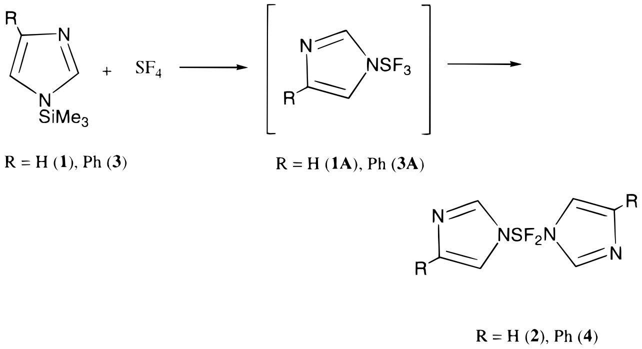
boiling points are uncorrected. Thermal analyses were performed using a Radex−Solo thermal hazards screening system instrument (SYSTAG, Switzerland). X-ray crystallographic data for **2** and **4** were collected using a P4 Siemens diffractometer, equipped with a Siemens SMART 1K charge-coupled device (CCD) area detector (using the program SMART) and a rotating anode using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Details of crystallographic determination and structure refinement are available as Supporting Information.

Preparation of Bis(imidazole)sulfur Difluoride (2). Method A: From 1-(Trimethylsilyl)imidazole and Sulfur Tetrafluoride. A solution of 1-(trimethylsilyl)imidazole (**1**) (4.95 g, 35.3 mmol) in $CFCl_3$ (25 mL) was added dropwise over a 15 min period to a stirred solution of SF_4 (6.5 g, 60 mmol) in $CFCl_3$ (25 mL) at −78 °C. The resulting solution was stirred for an additional hour at −78 °C and subsequently warmed to −63 °C. The −63 °C solution was evacuated under dynamic vacuum (∼0.1 Pa) for 30 min and then warmed to −12 °C at which temperature it was further evacuated for an additional 45 min. The flask and contents were then warmed to room temperature and evacuated until all volatiles had been removed. The resulting pale-yellow free-flowing solid was transferred to the dry nitrogen atmosphere of a glovebox where all subsequent manipulations on the solid were conducted. Analysis of the pale-yellow solid was consistent with bis(imidazole)sulfur difluoride (**2**), pale-yellow, crystalline solid (3.5 g, 17.2 mmol, 98%), mp 93.5−95.0 °C. Anal. Calcd for $C_6H_6F_2N_4S$: C, 35.29; H, 2.96; F, 18.61; N, 27.44; S, 15.70. Found: C, 34.90; H, 2.93; F, 17.78; N, 27.51; S, 15.29. ^{1}H NMR (in $CDCl_3$ at 24 °C): δ 8.06 (m, $J = 0.95$ Hz; 2 H, imid-H_2), 7.42 (m, $J = 1.84$ Hz; 2 H, imid-H_5), 7.06 (m, $J = 0.80$ Hz; 2 H, imid-H_4); $^{13}C\{^1H\}$ NMR (in $CDCl_3$ at 24 °C): δ 137.86 (t, $J_{CF} = 9.8$ Hz; 2 C, imid-C_2), 130.34 (s, 2 C, imid-C_4), 119.01 (t, $J_{CF} = 7.6$ Hz; 2 C, imid-C_5). ^{19}F NMR (in $CDCl_3$ at 24 °C): δ 47.81 (br s, 2 F). EI-MS (70 eV): *m/e* (ion, %) 204 (M^+, 2.4), 185 ($[M - F]^+$, 16), 137 ($[imid]^+$, 100). Dark-yellow crystals of **2** suitable for X-ray crystallography were obtained by recrystallization from CH_2Cl_2/hexanes (4:1) at −25 °C.

Preparation of Bis(imidazole)sulfur Difluoride (2). Method B: Directly from Imidazole and Sulfur Tetrafluoride. A solution of imidazole (3.64 g, 53.5 mmol) in CH_2Cl_2 (50 mL) was added dropwise over a 60 min period to a stirred slurry containing SF_4 (15.2 g, 141 mmol) and dry NaF (5.5 g, 131 mmol) in CH_2Cl_2 (30 mL) at −78 °C. After the addition was complete, the slurry was stirred for an additional 45 min at −78 °C and then allowed to warm to room temperature overnight. After the specified time, the off-white slurry was transferred to a glovebox and filtered; filtration afforded a pale-yellow solution which, upon evaporation to dryness, afforded the expected product **2** (1.90 g, 9.3 mmol, 35%).

Preparation of 1-(Trimethylsilyl)-4-phenylimidazole (3). Into a 100 mL three-neck round-bottom flask fitted with a dropping funnel, nitrogen inlet tube, and gas exit tube were loaded 4-phenylimidazole (5.08 g, 35.2 mmol) and 75 mL of anhydrous CH_3CN under nitrogen. Hexamethyldisilazane (4.40 g, 27.3 mmol) was added over 5 min, and the resulting slurry was stirred for 1 h at room temperature, after which time it became homogeneous and clear. This solution was then gently refluxed for 20 h under nitrogen. After the specified time, the flask and contents were cooled slightly, the flask was fitted with a fractional distillation head, and then heating was continued. The first liquid fraction was collected at 80 °C (101.3 kPa). When the last amount of the first liquid fraction had been collected, the system was put under vacuum (26 Pa), and heating was continued. A second liquid fraction was collected at 147−150 °C (26 Pa) and shown by analysis to be consistent with the desired product **3** (6.71 g, 31.0 mmol, 88%), light-yellow liquid, bp 148 °C (26 Pa). Anal. Calcd for $C_{12}H_{16}N_2Si$: C, 66.62; H, 7.45; N, 12.95; Si, 12.98. Found: C, 66.02; H, 7.52; N, 12.86; Si, 12.03. ^{1}H NMR (in $CDCl_3$ at 24 °C): δ 7.68 (s, 1 H, imid-H_2), 7.39 (s, 1 H, imid-H_5), 7.96 (dm, $J_{HH} = 8.3$, 1.4 Hz; 2 H, Ph-H_2), 7.45 (tm, $J_{HH} = 7.6$, 1.5 Hz; 2 H, Ph-H_3), 7.30 (tt, $J_{HH} = 7.4$, 1.5 Hz; 1 H, Ph-H_4), 0.52 (s*, 9 H, $^2J_{HSi} = 6.9$ Hz; $SiMe_3$). $^{13}C\{^1H\}$ NMR (in $CDCl_3$ at 24 °C): δ 143.91 (s, 1 C, imid-C_2), 116.12 (s, 1 C, imid-C_5), 140.63 (s, 1 C, imid-C_4), 134.92 (s, 1 C, Ph-C_1), 128.80 (s, 2 C, Ph-$C_{2,6}$), 126.72 (s, 1 C, Ph-C_4), 125.16 (s, 2 C, Ph-$C_{3,5}$), −0.52 ppm (s*, 3 C, $^1J_{HSi} = 28.8$ Hz; $SiMe_3$). [s* denotes a singlet resonance with ^{29}Si satellites.] EI-MS (70 eV): *m/e* (ion, %) 216 (M^+, 24), 143 ($[M - SiMe_3]^+$, 5), 116 (21), 73 ($[SiMe_3]^+$, 100).

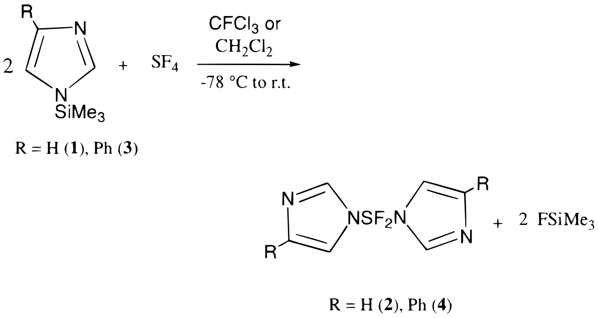
Scheme 1



Preparation of Bis(4-phenylimidazole)sulfur Difluoride (4). A solution of 1-(trimethylsilyl)-4-phenylimidazole (**3**) (5.201 g, 24.0 mmol) in $CFCl_3$ (35 mL) was added dropwise over a 15 min period to a stirred solution of SF_4 (5.4 g, 50 mmol) in $CFCl_3$ (40 mL) at −78 °C. The resulting solution was stirred for an additional 2 h at −78 °C and subsequently warmed to 0 °C, at which temperature it was pumped on in a vacuum (∼0.1 Pa) for 60 min. The flask and contents were then warmed to room temperature and pumped on until all volatiles had been removed. The resulting free-flowing white solid was transferred to the dry nitrogen atmosphere of a glovebox, where all subsequent manipulations on the solid were conducted. Analysis of the free-flowing white solid was consistent with the proposed structure of bis(4-phenylimidazole)sulfur difluoride (**4**), white solid (3.21 g, 9.0 mmol, 75%), mp 133−134 °C. Anal. Calcd for $C_{18}H_{14}F_2N_4S$: C, 60.66; H, 3.96; F, 10.66; N, 15.72; S, 9.00. Found: C, 60.48; H, 4.03; F, 10.77; N, 15.70; S, 8.63. ^{1}H NMR (in $CDCl_3$ at 24 °C): δ 8.22 (m), 7.76 (m), 7.32 (m). $^{13}C\{^1H\}$ (in $CDCl_3$ at 24 °C): δ 143.23 ppm (s, 2 C, Ph-C_1), 138.24 (t, $J_{CF} = 10.1$ Hz; 2 C, imid-C_2), 131.87 (s, 2 C, Ph-C_1), 128.78 (s, 4 C, Ph-$C_{3,5}$), 128.37 (s, 2 C, Ph-C_4), 125.30 (s, 4 C, Ph-$C_{2,6}$), 113.65 (t, $J_{CF} = 8.0$ Hz; 2 C, imid-C_5). ^{19}F NMR (in $CDCl_3$ at 24 °C): δ 47.22 (br s, 2 F). EI-MS (70 eV): *m/e* (ion, %) 213 ($[M - Ph - imid]^+$, 2.0), 144 ($(M - Ph - imid - SF_2]^+$, 100). White crystals of **4** suitable for X-ray crystallography were obtained by recrystallization from CH_2Cl_2/hexanes (10:1) at −25 °C.

Results and Discussion

Formation and Characterization of $(imid)_2SF_2$ (2) and $(4\text{-Ph-imid})_2SF_2$ (4). Compounds **2** and **4** were prepared in high yield from the corresponding trimethylsilyl derivatives according to eq 1. It is interesting to note that although the stoichiometry of eq 1 requires two (trimethylsilyl)imidazoles (TMS-imid) per SF_4 for production of either **2** or **4**, in actual fact all reactions were run with at least a 200% molar excess of SF_4. Even in experiments where reactions were run in an autoclave to ensure an excess of SF_4 in solution, none of the most probable imid-SF_3 intermediates, compound **1A** or **3A** in Scheme 1, were ever isolated.



(1)

Presumably, the SF_3 moiety in either **1A** or **3A** is more susceptible to nucleophilic attack by a second TMS-imid than is SF_4. Furthermore, once compounds **2** and **4** are formed, they are completely resistant to further attack by SF_4, which is consistent with the observations made on several bis(dialkylamino)sulfur difluoride species in a previous report.[2]

Compounds **2** and **4** were characterized in solution by ^1H, ^{13}C, and ^{19}F NMR spectroscopy and as solids by elemental analysis, MS (EI, solids, probe), and X-ray crystallography (see below). The NMR parameters of **2** and **4** are consistent with each existing in solution as monomeric units, with a pseudo-trigonal-bipyramidal arrangement of two equivalent fluorine atoms and two equivalent imidazole groups around the central sulfur atom. As a result, in the ^{13}C NMR spectrum of **2** and **4** the resonances corresponding to the C_2 and C_5 imidazole ring carbons appear as triplets (compound **2**, $\delta(^{13}C_2) = 137.86$, $^3J_{CF} = 9.8$ Hz and $\delta(^{13}C_5) = 119.01$, $^3J_{CF} = 7.6$ Hz; compound **4**, $\delta(^{13}C_2) = 138.24$, $^3J_{CF} = 10.1$ Hz and $\delta(^{13}C_5) = 113.65$, $^3J_{CF} = 8.0$ Hz), representing the three-bond coupling of each carbon with two magnetically equivalent fluorine atoms. Furthermore, the two fluorine atoms are represented by singlets in the ^{19}F NMR spectra of **2** and **4** (compound **2**, $\delta(^{19}F) = 47.81$; compound **4**, $\delta(^{19}F) = 47.22$), which supports their magnetic equivalence in these compounds.

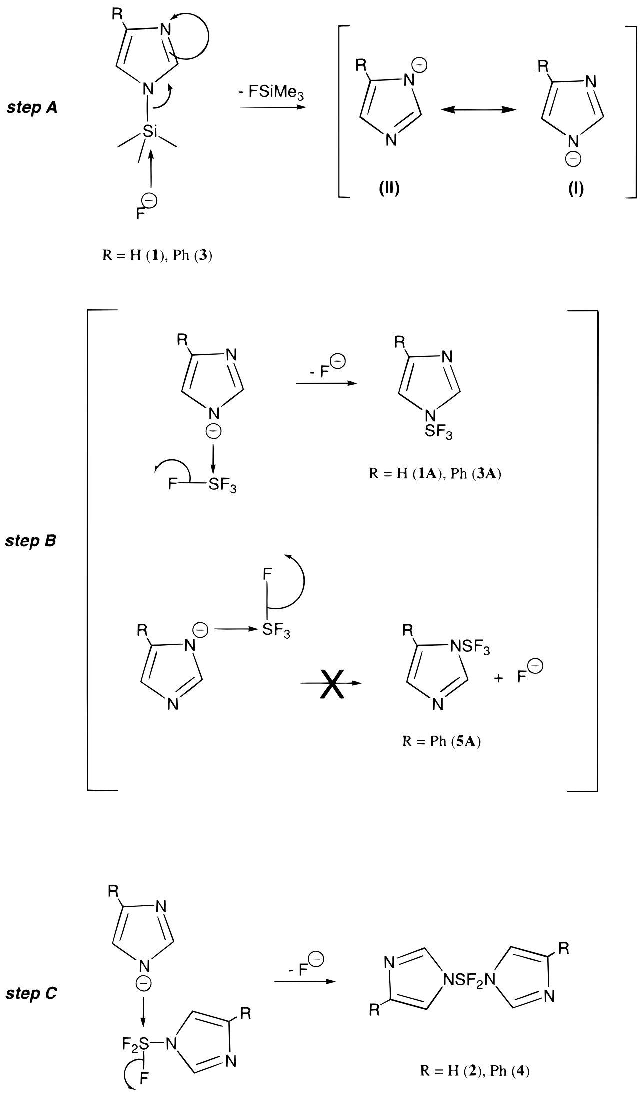
An alternative method of preparing **2** involves the direct reaction between imidazole and SF_4 in the presence of dry NaF as an HF scavenger. Although this method has the advantage of not requiring the TMS-imid precursor, it produces much lower yields of **2**.

The formation of **2** and **4** is thought to occur according to the mechanism given in Scheme 2. Step A in Scheme 2 depicts the attack of fluoride ion on the silicon atom of TMS-imid (**1** or **3**), which results in formation of the imidazolate anion and $FSiMe_3$. Although the equilibrium between the two forms of the imidazolate anion (**I** $\Leftrightarrow$ **II**) should result in an equivalence of the two imidazole nitrogens, in actuality, at least when R = Ph, the imidazolate anion form with Ph in the 4-position (**I**) is favored over the other anion form (**II**) with Ph in the 5-position, presumably because of steric crowding in the latter isomer. Thus, whereas nucleophilic attack by anion **I** on SF_4 leads to intermediate **3A** and ultimately to compound **4** according to step B, a similar attack by anion **II** does not occur since this would result in formation of the sterically crowded intermediate **5A** and compound **6**. In step C, nucleophilic attack by imidazolate anion on the intermediate **1A** or **3A** produces the observed product compound **2** or **4**.

In the recent work of Mews and co-workers[7] they present a "plausible" mechanism for the formation of (imid)SF_2CF_3 from TMS-imid which involves intramolecular elimination of $FSiMe_3$. While this mechanism provides a satisfactory explanation of their observations in the case of unsubstituted imidazole, it cannot account for the observations in the present work, at least in the formation of **4**. If the reaction between SF_4 and **3** occurred according to the proposed mechanism of Mews and co-workers,[7] one would expect the 5-phenyl-substituted derivative **6** to be formed via intermediate **5A** as indicated in Scheme 3, and not compound **4** as observed in this work.

Structure of (imid)$_2$SF$_2$ (2) and (4-Ph-imid)$_2$SF$_2$ (4). X-ray quality crystals of **2** and **4** were obtained from CH_2Cl_2/hexanes solutions, 4:1 and 10:1 (v/v), respectively, at −25 °C. Crystal data, details of measurement, and structure refinement parameters for **2** and **4** are given in Table 1. ORTEP plots (50% probability ellipsoids) of **2** and **4** are given in Figures 1 and 2, respectively.

Scheme 2



The structures of compounds **2** and **4** are based on a pseudo-trigonal -bipyramidal arrangement of ligands around the central sulfur atom, with two fluorine atoms occupying axial positions and two imidazole groups and the sulfur "lone pair" in the three equatorial plane positions. The local structure around sulfur is therefore C_{2v} and is in complete agreement with the expectations for AX_4E geometry derived from VSEPR rules[8] as well as the observed geometries in the related X-ray crystal structures of $(Me_2N)_2SF_2$[6] and (imid)SF_2CF_3.[7] The planar imidazole rings in **2** are arranged around sulfur much like the blade "pitch" of a propeller, forming angles between the two ring planes and the axial F−S−F plane of 25.0° and 31.9°, respectively. In the structure of **4** the planar imidazole rings are also "pitched" with respect to one another; however, they are also nearly axially aligned with the F−S−F plane, in part because of the influence of the phenyl rings. The angles between the planar imidazole and phenyl rings are about 7.6° in each case, while the angles between the two imidazole ring planes and the F−S−F axial plane are 3.4° and 20.2°, respectively.

Selected bond distances and bond angles for **2**, **4**, and the closely related (imid)SF_2CF_3 are given in Table 2. While the S−F bond distances in **2** and **4** are nearly the same, the slight

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(8) Gillespie, R. J. *Molecular Geometry*; Van Nostrand Reinhold: London, 1972.

Scheme 3

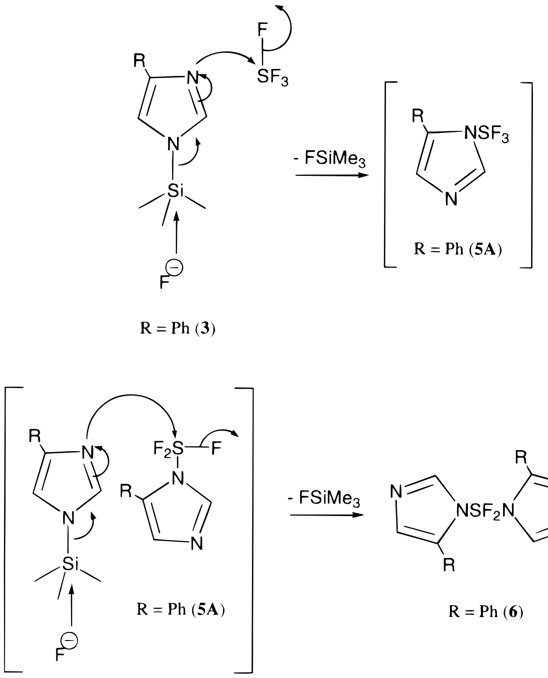

Table 1. Crystal Data and Details of Measurement and Structure Refinement for Compounds **2** and **4**

parameter	(imid)$_2SF_2$, **2**	(4-Ph-imid)$_2SF_2$, **4**
formula	$C_6H_6F_2N_4S$	$C_{18}H_{14}F_2N_4S$
fw (g mol^{-1})	204.21	356.39
temp (K)	160(2)	160(2)
λ (Å)	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	*Pn*	$P2_1/c$
a (Å)	6.010(3)	14.343(6)
b (Å)	10.064(5)	5.935(2)
c (Å)	6.767(3)	19.378(8)
β (deg)	99.450(10)	101.719(6)
V (Å^3)	403.7(3)	1615.2(11)
Z	2	4
ρ_{calcd} (g cm^{-3})	1.680	1.466
μ (mm^{-1})	0.389	0.230
R1[a]	0.0334	0.0693
wR2[b]	0.0648	0.1635

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

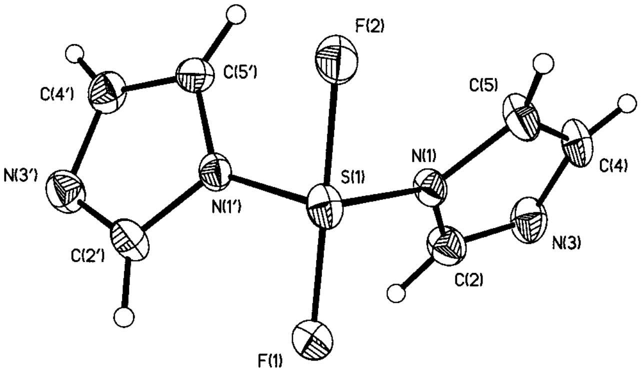

Figure 1. Structure of **2**. Thermal ellipsoids are shown at the 50% probability level.

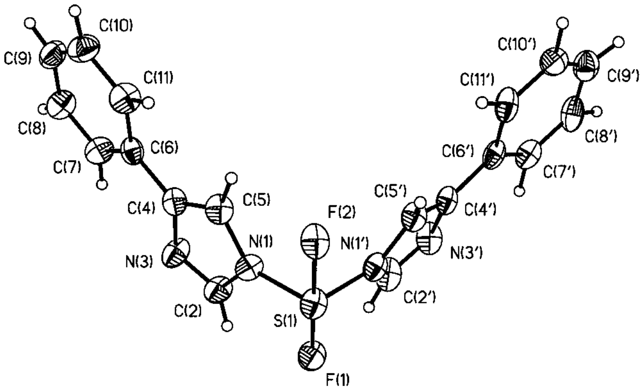

Figure 2. Structure of **4**. Thermal ellipsoids are shown at the 50% probability level.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**, **4**, and (imid)SF_2CF_3[7]

bond or angle	compound **2**	compound **4**	(imid)SF_2CF_3[7]
S−F(1)	1.693(2)	1.685(3)	1.681(2)
S−F(2)	1.709(2)	1.704(3)	1.717(2)
S−N(1)	1.700(2)	1.706(4)	1.699(3)
S−N(1′)	1.690(3)	1.705(4)	
S−C(4)			1.901(4)
F(1)−S−F(2)	173.86(12)	174.79(17)	171.82(11)
F(1)−S−N(1)	88.71(11)	88.44(17)	88.93(11)
F(1)−S−N(1′)	88.01(11)	88.96(18)	
F(2)−S−N(1′)	87.81(12)	88.01(18)	
F(2)−S−N(1)	87.74(12)	88.12(17)	87.89(12)
N(1)−S−N(1′)	101.74(13)	103.2(2)	
N(1)−S−C(4)			100.12(15)

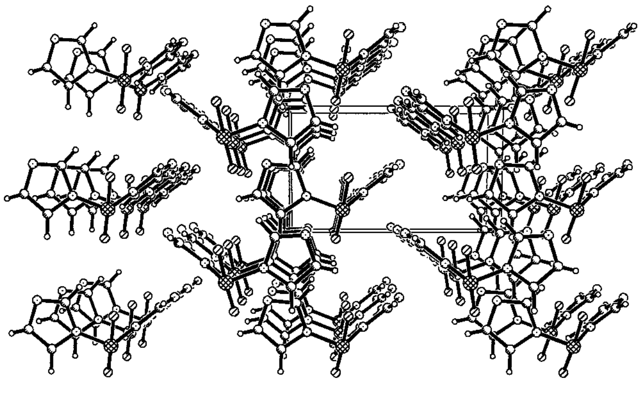

Figure 3. View of the unit cell of **2** showing the packing along the *c* axis.

differences are consistent with the different local environments around each bond, and are dominated presumably by intramolecular hydrogen bonding. For instance, in compound **2**, the shortest intramolecular H−F distance for F(1) is 2.417 Å, while for F(2), the shortest intramolecular H−F contact is 2.306 Å. Both are within the sum of the van der Waals radii for H−F (2.55 Å) and are to be considered significant. In compound **4**, the discrepancy is even greater as the shortest intramolecular H−F distances for F(1) and F(2) are 2.110 and 2.331 Å, respectively. A similar effect presumably accounts for the nonequivalent S−F bond distances in (imid)SF_2CF_3.[7]

There are significant intermolecular S−N contacts in the structure of **2** (2.94 Å) which are within the sum of the van der Waals radii for S and N (3.55 Å) and which undoubtedly influence the crystal packing in this structure. A similar short contact can also be found in the structure of (imid)SF_2CF_3 (2.859 Å).[7] A view of the unit cell of **2** along the *c* axis is given in Figure 3. It is interesting to note the uniformity in packing, with each row of molecular units aligned in a similar orientation. Compare this to the packing of the unit cell in the structure of **4**, viewed along the *b* axis in Figure 4, where there is also an alternating arrangement of molecular units in adjacent rows.

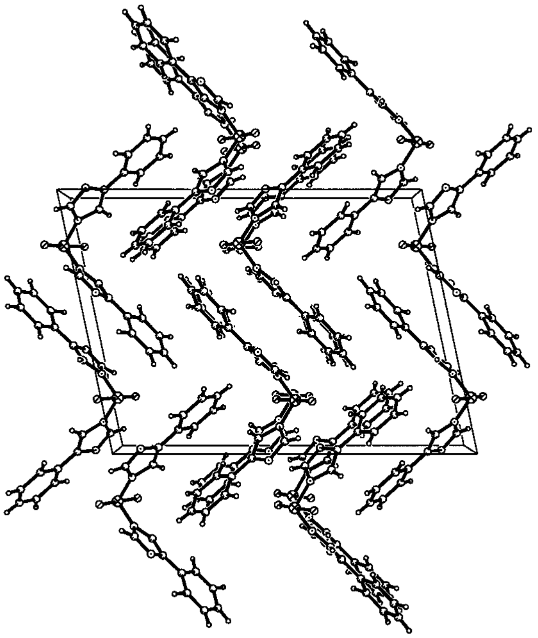

Figure 4. View of the unit cell of **4** showing the packing along the *b* axis.

The F−S−F three-center bond angle is distorted from linearity by approximately 6°, 5°, and 8°, respectively, in **2**, **4**, and (imid)SF_2CF_3. In each case, the F−S−F bond is bent back toward the equatorial substituents and away from the sulfur lone pair of electrons as would be predicted by VSEPR.[8] The opposite of this is noted in the structure of $(Me_2N)_2SF_2$,[6] where the F−S−F bond is actually bent about 5° (from linear) toward the sulfur lone pair of electrons.

In compound **4**, a slightly shortened S−F(1) distance of 1.685(3) Å results in a concomitant expansion of the N−S−N equatorial bond angle (103.2°), which is to be expected on the basis of VSEPR[8] rules since a compression of axial bonds will normally lead to an expansion of the equatorial bond angle to minimize bonded pair to bonded pair interactions. The converse effect is observed in compound **2**, where a slightly longer S−F(1) distance of 1.693(2) Å accompanies the reduced N−S−N bond angle of 101.74°.

Thermal Properties of (imid)$_2$SF$_2$ (2) and (4-Ph-imid)$_2$SF$_2$ (4). Many of the known (dialkylamino)sulfur trifluorides and bis(dialkylamino)sulfur difluorides are widely regarded as being notoriously unsafe in their common use as deoxofluorination agents, primarily because of their propensity to undergo catastrophic decomposition reactions when heated. In fact, a study[4] of the thermal properties of some of the more popular of these compositions measured by differential thermal analysis (DTA) concluded that even the most stable of all compositions, 4-morpholinosulfur trifluoride, will detonate at 175 °C. Furthermore, in the same work, some of the more unstable bis(dialkylamino)sulfur difluoride derivatives were shown to be detonators at much lower temperatures than their sulfur trifluoride analogues; for example, bis(diethylamino)sulfur difluoride detonated at 108 °C, while (diethylamino)sulfur trifluoride detonated at 147 °C.

Table 3. Thermal Properties of **2**, **4**, and Three Common R_2NSF_3 Compounds As Measured by Radex−Solo[9]

compound	onset of decomp (°C)	max rate of temp increase (°C min^{-1})	max rate of pressure increase (MPa min^{-1})
2	69	21	5
4	101	25	5
Me_2NSF_3	123	114	113
Et_2NSF_3	97	174	108
$O(CH_2)_4NSF_3$	130	71	71

In the present work the Radex−Solo thermal hazards screening method[9] was used which is generally considered a more sensitive thermal analytical method than DTA because it employs a larger sample size and measures the rates of pressure generation and temperature increase as a function of temperature during the thermal decomposition event. Using the Radex method, the data summarized in Table 3 were collected on **2**, **4**, Me_2NSF_3, Et_2NSF_3, and $O(CH_2)_4NSF_3$. There are three noteworthy features represented in the data of Table 3 which need to be addressed. First, the onset temperature at which the thermal decomposition events begin is in general lower for **2** and **4** than for the R_2NSF_3 compounds. This fact is consistent with the observations made in the previous work.[4] Second, the rate at which thermal decomposition occurs, once initiated, is considerably greater for the R_2NSF_3 compounds than for either **2** or **4**, as reflected in the higher rate of maximum temperature increase for the R_2NSF_3 compounds. This result is quite surprising given that "detonations" were observed during the thermal decomposition of all bis(dialkylamino)sulfur difluoride compounds as measured by DTA.[4] Third, and most surprising yet, is the observed rate of pressure generation which accompanies the thermal decomposition event. As noted in Table 3, the maximum rate of pressure generation during the decomposition event is 5 MPa, whereas the same rate for each of the R_2NSF_3 compounds is more than an order of magnitude greater. Again, it is unclear why **2** and **4** do not display the catastrophic decomposition observed in the previous work.[4]

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Supporting Information Available: A description of the Radex−Solo thermal hazards screening method, Radex thermal decomposition plots measured on **2**, **4**, Me_2NSF_3, Et_2NSF_3, and $O(CH_2)_4NSF_3$, and tables listing crystallographic data including bond lengths and angles, atomic positional parameters, and acquisition parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Details of the Radex−Solo thermal hazards screening system are included in the Supporting Information.