Inorg. Chem. **1998,** *37,* 6295−6303

Synthesis of Poly- and the First Perfluoroalkyl-$N(SO_2F)_2$ Derivatives: Improved Methods for the Preparation of $XN(SO_2F)_2$ (X = H, Cl) and Single-Crystal Diffraction Studies of $HN(SO_2Cl)_2$, $HN(SO_2F)_2$, and $CF_3CH_2N(SO_2F)_2$[†]

Burkhard Krumm, Ashwani Vij, Robert L. Kirchmeier,* and Jean'ne M. Shreeve*

Department of Chemistry, University of Idaho, Moscow, Idaho 83844-2343

Received January 2, 1998

The preparation of $HN(SO_2F)_2$ was achieved conveniently by fluorination of $HN(SO_2Cl)_2$ with SbF_3. Reactions of $Hg[N(SO_2F)_2]_2$ with fluoroalkyl iodides RI (R = *i*-$C_3F_7CH_2CH_2$ and CF_3CH_2) gave *i*-$C_3F_7CH_2CH_2N(SO_2F)_2$ (**1**) and $CF_3CH_2N(SO_2F)_2$ (**2**). The chlorination of $Hg[N(SO_2F)_2]_2$ provided a high-yield method of synthesizing the well-known $ClN(SO_2F)_2$. N-alkylation of $ClN(SO_2F)_2$ with fluorinated ethenes $CF_2{=}CHal_2$ ($CHal_2 = CF_2$, CFCl, and CCl_2) resulted in the formation of $CF_2ClCF_2N(SO_2F)_2$ (**3**), $CF_2ClCFClN(SO_2F)_2$ (**4a**, major), $CFCl_2CF_2N(SO_2F)_2$ (**4b**, minor), and $CCl_3CF_2N(SO_2F)_2$ (**5**). The synthesis of the first perfluoroalkyl-$N(SO_2F)_2$ derivatives $CF_3N(SO_2F)_2$ (**6**), $C_2F_5N(SO_2F)_2$ (**7**), *n*-$C_3F_7N(SO_2F)_2$ (**8**), and *n*-$C_4F_9N(SO_2F)_2$ (**9**) was accomplished with moderate-to-good yields by reacting $ClN(SO_2F)_2$ with iodoperfluoroalkanes R_FI ($R_F = CF_3$, C_2F_5, *n*-C_3F_7, and *n*-C_4F_9). Similarly, $ClN(SO_2F)_2$ reacted with CF_3CH_2I to give **2**. Photolysis of $ClN(SO_2F)_2$ with iodoperfluoroalkanes R_FI (R_F = *n*-C_3F_7, and *n*-C_4F_9) gave **8** and **9** in low yields. $HN(SO_2F)_2$ belongs to a monoclinic crystal system $P2_1$ (No. 4): $a = 5.1619(5)$ Å, $b = 7.8153(8)$ Å, $c = 6.8028(7)$ Å, $\beta = 100.411(2)°$, $V = 269.92(5)$ Å^3, $Z = 2$. $HN(SO_2Cl)_2$ is monoclinic $P2_1/c$ (No. 14): $a = 7.7331(3)$ Å, $b = 10.0542(2)$ Å, $c = 9.3197(3)$ Å, $\beta = 109.495(1)°$, $V = 683.07(4)$ Å^3, $Z = 4$. $CF_3CH_2N(SO_2F)_2$ is orthorhombic $P2_12_12_1$ (No. 19): $a = 11.1245(1)$ Å, $b = 28.8003(4)$ Å, $c = 7.7120$ Å, $V = 2470.90(4)$ Å^3, $Z = 12$.

Introduction

The chemistry of the strong nitrogen acids $HN(SO_2F)_2$ and $HN(SO_2CF_3)_2$ has been reviewed. These acids and their derivatives have gained much attention because of important applications, for example, as electrolytes, as additives for electrolytes in fuel cells, or as selective electrophilic fluorinating agents.[1]

More recent reports deal with some new $N(SO_2F)_2$ derivatives, such as $R_3EN(SO_2F)_2$ (E = Si,[2,3] Ge,[3] Sn,[3,4] Pb[3]; R = alkyl), $[Ph_3C][N(SO_2F)_2]$,[5] $[Ph_3PH][N(SO_2F)_2]$,[3] and their crystal structures. The crystal structure of $CsN(SO_2F)_2$ was determined independently by two groups.[3,6] Also syntheses of an azido derivative, $N_3N(SO_2F)_2$,[7] and the crystal structure of $S[N(SO_2F)_2]_2$[8] were reported.

Alkyl and fluoroalkyl derivatives of $HN(SO_2F)_2$ and $HN(SO_2CF_3)_2$ were prepared by the reaction of either the acids or their *N*-chloro derivatives with olefins.[9−11] To the best of our knowledge, the only report of a perfluoroalkyl derivative of $HN(SO_2F)_2$ or $HN(SO_2CF_3)_2$ is the detection of $CF_3N(SO_2CF_3)_2$ as a volatile byproduct formed during the decomposition of $Xe[N(SO_2CF_3)_2]_2$.[12,13]

The present work describes an extension of the chemistry of $ClN(SO_2F)_2$, fluoroalkylation of $Hg[N(SO_2F)_2]_2$, and the synthesis and isolation of the first perfluoroalkyl-$N(SO_2F)_2$ derivatives. In addition to the synthetic studies, we have also carried out single-crystal X-ray diffraction studies on low-melting $HN(SO_2Cl)_2$, $HN(SO_2F)_2$, and $CF_3CH_2N(SO_2F)_2$. Moreover, we report a much improved route for the preparation of $HN(SO_2F)_2$. In addition to the usual methods of characterization, the ^{14}N NMR shifts of these materials were determined. The only previously reported nitrogen NMR data are the ^{15}N shifts for several ^{15}N enriched xenon-containing $N(SO_2F)_2$ species such as $Xe[N(SO_2F)_2]_2$,[14] $[XeN(SO_2F)_2]^+[Sb_3F_{16}^-]$,[15] $FXeN(SO_2F)_2$,[16−18] $HN(SO_2CF_3)_2$, and $[N(SO_2F)_2]_2$.[17] With the exception of $FN(SO_2F)_2$[19] and $ClN(SO_2F)_2$,[20] the IR spectra of

---

[†] Presented at the 15th International Symposium on Fluorine Chemistry, Vancouver, B.C., Canada, 1997; Abstr. Nos. R_FS C-2, P2-177.

(1) Vij, A.; Kirchmeier, R. L.; Shreeve, J. M.; Verma, R. D. *Coord. Chem. Rev.* **1997**, *158*, 413 and references therein.
(2) Trehan, A.; Vij, A.; Walia, M.; Kaur, G.; Verma, R. D.; Trehan, S. *Tetrahedron Lett.* **1993**, *34*, 7335.
(3) Hiemisch, O.; Henschel, D.; Blaschette, A.; Jones, P. G. *Z. Anorg. Allg. Chem.* **1997**, *623*, 324.
(4) Vij, A.; Singh, S.; Verma, R. D. *J. Fluorine Chem.* **1992**, *58*, 43.
(5) Hiemisch, O.; Henschel, D.; Jones, P. G.; Blaschette, A. *Z. Anorg. Allg. Chem.* **1996**, *622*, 829.
(6) Farrugia, L. J.; Holfter, H.; Klapötke, T. M. *J. Fluorine Chem.* **1996**, *78*, 51.
(7) Holfter, H.; Klapötke, T. M.; Schulz, A. *Polyhedron* **1996**, *15*, 1405.
(8) Hass, A.; Klare, Ch.; Betz, P.; Bruckmann, J.; Krüger, C.; Tsay, Y.-H.; Aubke, F. *Inorg. Chem.* **1996**, *35*, 1918.
(9) Varwig, J.; Mews, R.; Glemser, O. *Chem. Ber.* **1974**, *107*, 2468.
(10) Colburn, C. B.; Hill, W. E.; Verma, R. D. *J. Fluorine Chem.* **1981**, *17*, 75.
(11) Vij, A.; Zheng, Y. Y.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1994**, *33*, 3281.
(12) Foropoulos, J., Jr.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720.
(13) Foropoulos, J., Jr.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 4260.
(14) Schumacher, G. A.; Schrobilgen, G. J. *Inorg. Chem.* **1983**, *22*, 2178.
(15) Faggiani, R.; Kennepohl, D. K.; Lock, C. J. L.; Schrobilgen, G. J. *Inorg. Chem.* **1986**, *25*, 563.
(16) DesMarteau, D. D.; LeBlond, R. D.; Hossain, S. F.; Nothe, D. *J. Am. Chem. Soc.* **1981**, *103*, 7734.
(17) Swayer, J. F.; Schrobilgen, G. J.; Sutherland, S. J. *Inorg. Chem.* **1982**, *21*, 4064.
(18) Swayer, J. F.; Schrobilgen, G. J.; Sutherland, S. J. *J. Chem. Soc. Chem. Commun.* **1982**, 210.
(19) Lustig, M.; Bumgardner, C. L.; Johnson, F. A.; Ruff, J. K. *Inorg. Chem.* **1964**, *3*, 1165.

10.1021/ic9800031 CCC: \$15.00

$N(SO_2F)_2$ derivatives in the gas phase have not been reported. All of the IR spectra in this study were recorded in the gas phase, including those for $HN(SO_2F)_2$ and $[N(SO_2F)_2]_2$. Because of the stability of the $N(SO_2F)_2^{\bullet}$ radical vis-à-vis $N(SO_2CF_3)_2^{\bullet}$, we have been successful in carrying out photolytic reactions of $ClN(SO_2F)_2$ with some perfluoroalkyl iodides to generate some *N*-perfluoroalkyl bis(fluorosulfonyl)imide derivatives. $ClN(SO_2CF_3)_2$ is known to decompose under photolytic conditions to form $[CF_3SO_2NSO_2]_2$ and CF_3Cl, but $ClN(SO_2F)_2$ forms $[N(SO_2F)_2]_2$ and Cl_2 exclusively.

Results and Discussion

Previously, the synthesis of the starting material, $HN(SO_2F)_2$, was best achieved by fluorination of $HN(SO_2Cl)_2$[21] with AsF_3.[22] However, separation problems due to the presence of HSO_3F made the isolation of $HN(SO_2F)_2$ difficult and resulted in only about 52% isolated yields. A modification to the procedure for separating HSO_3Cl from $HN(SO_2Cl)_2$ and subsequent fluorination and removal of traces (<5%) of HSO_3F using KCl monitored by ^{19}F NMR spectroscopy resulted in pure $HN(SO_2F)_2$ in yields as high as ~92%.[23]

Fluorination of $HN(SO_2Cl)_2$ with SbF_3 has been reported recently, but no detailed procedure is listed.[3] We found that SbF_3 was superior to AsF_3 for the fluorination of $HN(SO_2Cl)_2$. It replaced the relatively expensive AsF_3, which also has higher toxicity. Another important aspect is the fact that we never observed the formation of HSO_3F as a byproduct. SbF_3 was utilized in slight excess at room temperature as shown in Scheme 1. $HN(SO_2F)_2$ was isolated in good yields.

Scheme 1

$$3\ HN(SO_2Cl)_2 + 2\ SbF_3 \xrightarrow[-\ 2\ SbCl_3]{25\ ^\circ C/4\ h} 3\ HN(SO_2F)_2$$

The mercury salt $Hg[N(SO_2F)_2]_2$[24] proved to be a useful intermediate. For example, $ClN(SO_2F)_2$ was prepared from $Hg[N(SO_2F)_2]_2$ (Scheme 2) in higher yield than that from the silver salt $AgN(SO_2F)_2$, which gave only moderate yields of $ClN(SO_2F)_2$.[20]

Scheme 2

$$Hg[N(SO_2F)_2]_2 + 2\ Cl_2 \xrightarrow[-\ HgCl_2]{25\ ^\circ C/5\ d} 2\ ClN(SO_2F)_2$$

Alkylation of $Hg[N(SO_2F)_2]_2$ with polyfluoroalkyl iodides (Scheme 3) at elevated temperatures led to the respective polyfluoroalkyl-$N(SO_2F)_2$ derivatives **1** and **2**. The less reactive polyfluoroalkyl iodides required more vigorous conditions than those described for the reactions of the nonfluorinated iodides CH_3I and C_2H_5I with $AgN(SO_2F)_2$ (2 h/25 °C).[25]

Scheme 3

$$Hg[N(SO_2F)_2]_2 + 2\ i\text{-}C_3F_7CH_2CH_2I \xrightarrow[-\ HgI_2]{70\ ^\circ C/12\ h} 2\ i\text{-}C_3F_7CH_2CH_2N(SO_2F)_2 \quad \mathbf{(1)}$$

$$Hg[N(SO_2F)_2]_2 + 2\ CF_3CH_2I \xrightarrow[-\ HgI_2]{120\ ^\circ C/48\ h} 2\ CF_3CH_2N(SO_2F)_2 \quad \mathbf{(2)}$$

The reaction of perhalogenated ethenes with $ClN(SO_2F)_2$ gave the perhalogenoalkyl-$N(SO_2F)_2$ derivatives **3**, **4a**/**4b**, and **5** (Scheme 4). Interestingly for the reaction with $CF_2{=}CFCl$, we observed the formation of two isomers. The main product was found to be isomer **4b**, formed by attack of the $N(SO_2F)_2$ moiety on the CFCl carbon atom. Because of the slightly lower vapor pressure of **4b**, it was possible to separate **4b** from **4a** by low-temperature vacuum distillation as described in the Experimental Section.

Scheme 4

$$ClN(SO_2F)_2 + CF_2{=}CF_2 \xrightarrow{25\ ^\circ C/3\ d} CF_2ClCF_2N(SO_2F)_2 \quad \mathbf{(3)}$$

$$ClN(SO_2F)_2 + CF_2{=}CFCl \xrightarrow{25\ ^\circ C/3\ d} \underset{1\ /\ 2.5}{CFCl_2CF_2N(SO_2F)_2\ /\ CF_2ClCFClN(SO_2F)_2} \quad \mathbf{(4a/4b)}$$

$$ClN(SO_2F)_2 + CF_2{=}CCl_2 \xrightarrow{25\ ^\circ C/3\ d} CCl_3CF_2N(SO_2F)_2 \quad \mathbf{(5)}$$

The reaction of $ClN(SO_2F)_2$ with iodoperfluoroalkanes provided a route to the first perfluoroalkyl-$N(SO_2F)_2$ derivatives (Scheme 5). Derivative **2** can be synthesized in better yields than by the method described in Scheme 3 by reaction of $ClN(SO_2F)_2$ with CF_3CH_2I.

Scheme 5

$$ClN(SO_2F)_2 + R_FI \xrightarrow[-\ 0.5\ Cl_2,\ -\ 0.5\ I_2]{60\ ^\circ C/4\ d} R_FN(SO_2F)_2$$

$$R_F = CF_3\ \mathbf{(6)},\ C_2F_5\ \mathbf{(7)},\ n\text{-}C_3F_7\ \mathbf{(8)},\ n\text{-}C_4F_9\ \mathbf{(9)}$$
$$CF_3CH_2\ \mathbf{(2)}$$

Chlorine and iodine were identified as byproducts. We believe that this reaction proceeded via a radical mechanism. The reaction of $ClN(SO_2F)_2$ with CF_3Br under identical conditions did not produce **6**. Instead, we observed the formation of $ClSO_2F$, which indicates fragmentation of $ClN(SO_2F)_2$. No other decomposition products were isolated or identified. Photolysis of mixtures of $ClN(SO_2F)_2$ and R_FI also produced the perfluoroalkyl-$N(SO_2F)_2$ derivatives but only in low yields (Scheme 6).

Scheme 6

$$ClN(SO_2F)_2 + R_FI \xrightarrow{h\nu/\ 24\ h} R_FN(SO_2F)_2$$
$$R_F = n\text{-}C_3F_7\ \mathbf{(8)},\ n\text{-}C_4F_9\ \mathbf{(9)}$$

The ^{19}F NMR spectra of compounds **3**, **4a**, and **6**−**9** showed two resonances for the SF fluorine atoms. This phenomenon was also observed for $CF_3CFClCF_2N(SO_2F)_2$ and $(CF_3)_2CClN(SO_2F)_2$.[9] We believe that this is due to a staggered conformation of the SO_2F groups in the $N(SO_2F)_2$ moiety which resulted in inequivalence of the SF fluorine atoms. Variable-temperature experiments in the range of 25−60 °C with **8** showed that increasing the temperature to 60 °C did not affect this inequivalence. Derivatives **1**, **2**, and **5** showed a single resonance for the SF fluorine atoms that is the same as that observed for $CH_3CF_2N(SO_2F)_2$, $CH_2ClCF_2N(SO_2F)_2$, and $CH_3CH_2CH(CH_3)N$-

---

(20) Ruff, J. K. *Inorg. Chem.* **1966**, *5*, 732.
(21) Becke-Goehring, M.; Fluck, E. *Inorg. Synth.* **1966**, *8*, 105.
(22) Ruff, J. K.; Lustig, M. *Inorg. Synth.* **1968**, *11*, 138.
(23) Vij, A. Ph.D. Dissertation, Panjab University, India, 1991; Chapter 7.
(24) Singh, S.; DesMarteau, D. D. *Inorg. Chem.* **1986**, *25*, 4596.
(25) Ruff, J. K. *Inorg. Chem.* **1965**, *4*, 1446.

Table 1. Crystallographic Data for $HN(SO_2X)_2$ (X = F or Cl) and $CF_3CH_2N(SO_2F)_2$

	$HN(SO_2Cl)_2$	$HN(SO_2F)_2$	$CF_3CH_2N(SO_2F)_2$
empirical formula	$HCl_2NO_4S_2$	$HF_2NO_4S_2$	$C_2H_2F_5NO_4S_2$
formula weight	214.04	181.14	263.17
temperature (°C)	−60(2)	−100(2)	−60(2)
crystal system	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$ (No. 14)	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)
a (Å)	7.7331(3)	5.1619(5)	11.1245(1)
b (Å)	10.0542(2)	7.8153(8)	28.8003(4)
c (Å)	9.3197(3)	6.8028(7)	7.7120(0)
β (deg)	109.495(1)	100.411(2)	90
volume(Å^3), *Z*	683.07(4), 4	269.92(5), 2	2470.90(4), 12
ρ_{calcd} (g cm^{-3})	2.081	2.229	2.122
μ (cm^{-1})	15.05	9.76	7.26
F(000)	424	180	1560
θ range for data (deg)	2.79−28.25	3.04−28.20	1.96−28.24
limiting indices	$-8 \le h \le 10$	$-6 \le h \le 6$	$-14 \le h \le 14$
	$-13 \le k \le 11$	$-7 \le k \le 10$	$-38 \le k \le 31$
	$-12 \le l \le 11$	$-9 \le l \le 8$	$-9 \le l \le 10$
reflections collected/unique	8015, 1614	1750, 886	14723, 5783
R_{int}	0.0295	0.041	0.0257
data/restraints/ parameters	1614/0/87	886/0/87	5783/0/404
goodness of fit on F^2	1.113	1.082	1.097
*R*1, *wR*2 [$2\sigma(I)$ data]^a	0.0368, 0.0880	0.0256, 0.0674	0.0386, 0.0903
*R*1, *wR*2 [all data]^a	0.0427, 0.0917	0.0263, 0.0676	0.0468, 0.0942
extinction coefficient	0.011(2)	0.079(11)	0.0041(3)
largest diff. peak (e Å^{-3})	0.454	0.302	0.350
largest diff. hole (e Å^{-3})	−0.359	−0.354	−0.309

[a] $w = 1/[\sigma^2(F_o^2) + (0.0417P)^2 + 0.6062P]$, where $P = (F_o^2 + 2F_c^2)/3$.

$(SO_2F)_2$,[10] suggesting an eclipsed conformation of the SO_2F groups. For **3**, we observed the presence of both conformers in the ^{19}F NMR spectrum in a ratio of 11:1 (staggered/eclipsed) and were able to assign the resonances (see the Experimental Section).

The ^{14}N NMR spectra of compounds **1**−**9** measured in $CDCl_3$ showed broad resonances (line widths of 350−700 Hz) in the range of −200 to −250 ppm relative to nitromethane. These shifts and line widths lie in the range typical for nitrogen resonances having sulfonamide structures.[26]

Although $HN(SO_2Cl)_2$ and its derivatives have been known for over 3 decades, no structures with the $N(SO_2Cl)_2$ moiety have been reported.[27] There has been a recent increase in interest in the structures of compounds containing the $N(SO_2X)_2$ moiety.[3,5,6,8,28] The modifications we have made to the synthetic procedure for the preparation of $HN(SO_2F)_2$ afford this acid, as well as its fluorinated analogue in high purity. The availability of diffraction quality crystals formed at low temperatures for these acids and $CF_3CH_2N(SO_2F)_2$ provided an opportunity to study the cryogenic crystal and molecular structures of these compounds. All of the crystallographic data are listed in Table 1.

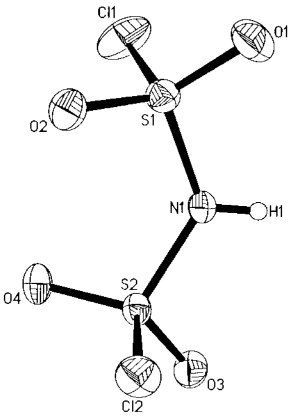

Figure 1. Molecular structure of $HN(SO_2Cl)_2$ with thermal ellipsoids at 30% probability

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) and Bond Lengths and Angles for $HN(SO_2Cl)_2$^{a}

a. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

	x	*y*	*z*	*U*(eq)
Cl(1)	−2092(1)	8721(1)	681(1)	70(1)
Cl(2)	4007(1)	5900(1)	1754(1)	45(1)
S(1)	−788(1)	6985(1)	1100(1)	35(1)
S(2)	3097(1)	7703(1)	2019(1)	30(1)
O(1)	−1684(3)	6152(3)	1844(3)	59(1)
O(2)	−474(3)	6596(2)	−252(2)	43(1)
O(3)	4334(3)	8259(2)	3369(2)	43(1)
O(4)	2652(3)	8365(2)	593(2)	40(1)
N(1)	1195(3)	7399(3)	2372(3)	37(1)

b. Bond Lengths and Angles

bond	length (Å)	bond	length (Å)
Cl(1)−S(1)	1.9880(11)	S(2)−O(3)	1.417(2)
Cl(2)−S(2)	1.9894(9)	S(2)−O(4)	1.422(2)
S(1)−O(1)	1.408(2)	S(2)−N(1)	1.639(2)
S(1)−O(2)	1.415(2)	N(1)−H(1)	0.78(4)
S(1)−N(1)	1.649(2)		

bond	angle (deg)	bond	angle (deg)
O(1)−S(1)−O(2)	122.18(14)	O(4)−S(2)−N(1)	108.75(12)
O(1)−S(1)−N(1)	106.77(13)	O(3)−S(2)−Cl(2)	107.93(10)
O(2)−S(1)−N(1)	108.38(12)	O(4)−S(2)−Cl(2)	107.22(9)
O(1)−S(1)−Cl(1)	108.57(12)	N(1)−S(2)−Cl(2)	103.49(9)
O(2)−S(1)−Cl(1)	107.11(10)	S(2)−N(1)−S(1)	125.75(14)
N(1)−S(1)−Cl(1)	102.04(10)	S(2)−N(1)−H(1)	117(3)
O(3)−S(2)−O(4)	121.74(12)	S(1)−N(1)−H(1)	117(3)
O(3)−S(2)−N(1)	106.26(12)		

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

The molecular structure of $HN(SO_2Cl)_2$ is shown in Figure 1. The atomic coordinates, equivalent isotropic displacement parameters, bond lengths, and bond angles for $HN(SO_2Cl)_2$ are given in Table 2. As found in other nitrogen acids,[8,29−31] the S−NH−S arrangement is planar because of the delocalization of the nitrogen lone pair over the O−S−N−S−O π framework (average angle around nitrogen ≈120°). The point group for the molecule is C_2. A crystallographic C_2 axis along the H−N bond bisects the S−N−S bond. The chlorine atoms are located on opposite sides of the S−N−S plane, similar to the positions of the trifluoromethyl groups in the CF_3-containing analogue. The S−N and S−O bond distances in $HN(SO_2Cl)_2$ are comparable to those reported in $HN(SO_2CF_3)_2$,[8] but the S−N−S angles are compressed to 125.7(2)° from the value of 128.4(2)° found in the latter case.

---

(26) Mason, J. Nitrogen. In *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 12, p 350.

(27) *Cambridge Structural Database System*; Cambridge Crystallographic Data Center, April 1997.

(28) Vij, A. Crystal and molecular structures of $AgN(SO_2CF_3)_2(H_2O)L$ [L = C_6H_6, $C_6H_5CH_3$, and $C_6H_4(1,2\text{-}CH_3)_2$]. Unpublished results.

(29) Cotton, F. A.; Stokely, P. F. *J. Am. Chem. Soc.* **1970**, *92*, 294.

(30) Blaschette, A.; Wieland, E.; Schomburg, D.; Adelhelm, M. *Z. Anorg. Allg. Chem.* **1986**, *533*, 7.

(31) DesMarteau, D. D.; Zuberi, S. S.; Pennington, W. T.; Randolph, B. B. *Eur. J. Solid State Inorg. Chem.* **1992**, *29*, 777.

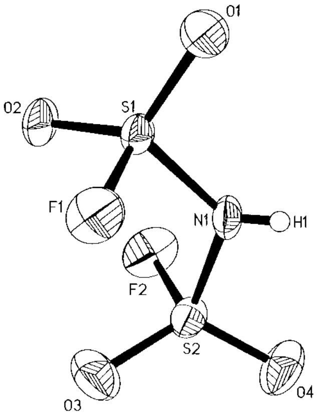

Figure 2. Molecular structure of HN(SO$_2$F)$_2$ with thermal ellipsoids at 50% probability.

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å^2 $\times$ 10^3) and Bond Lengths and Angles for HN(SO$_2$F)$_2$[a]

a. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

	x	*y*	*z*	*U*(eq)
S(1)	6835(1)	677(1)	8961(1)	21(1)
S(2)	7766(1)	−2064(1)	6336(1)	25(1)
F(1)	7295(4)	−459(3)	10830(3)	36(1)
F(2)	5704(4)	−1369(3)	4617(3)	43(1)
O(1)	8018(4)	2263(4)	9507(3)	34(1)
O(2)	4158(3)	489(3)	8090(3)	30(1)
O(3)	6415(5)	−3147(3)	7456(4)	40(1)
O(4)	9960(5)	−2587(4)	5522(4)	43(1)
N(1)	8596(5)	−288(3)	7551(4)	24(1)

b. Bond Lengths and Angles

bond	length (Å)	bond	length (Å)
S(1)−O(1)	1.402(3)	S(2)−O(4)	1.408(2)
S(1)−O(2)	1.409(2)	S(2)−F(2)	1.532(2)
S(1)−F(1)	1.534(2)	S(2)−N(1)	1.633(3)
S(1)−N(1)	1.621(3)	N(1)−H(1)	0.64(6)
S(2)−O(3)	1.405(2)		

bond	angle (deg)	bond	angle (deg)
O(1)−S(1)−O(2)	123.4(2)	O(4)−S(2)−F(2)	107.48(14)
O(1)−S(1)−F(1)	107.29(13)	O(3)−S(2)−N(1)	110.36(13)
O(2)−S(1)−F(1)	106.33(13)	O(4)−S(2)−N(1)	106.8(2)
O(1)−S(1)−N(1)	107.70(13)	F(2)−S(2)−N(1)	99.64(13)
O(2)−S(1)−N(1)	108.36(13)	S(1)−N(1)−S(2)	124.8(2)
F(1)−S(1)−N(1)	101.66(12)	S(1)−N(1)−H(1)	117(6)
O(3)−S(2)−O(4)	123.5(2)	S(2)−N(1)−H(1)	114(6)
O(3)−S(2)−F(2)	106.5(2)		

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

HN(SO$_2$F)$_2$ crystallizes in a polar space group $P2_1$, and refinement of Flack's parameter gives a value of 0.02(12), which suggests that the assigned absolute configuration is accurate. The fluorine atoms are in a staggered conformation (Figure 2), imparting to the molecule approximate C_2 symmetry. Table 3b contains the bond lengths and angles for HN(SO$_2$F)$_2$. Substitution of the chlorine atoms in HN(SO$_2$Cl)$_2$ by fluorine causes shortening of both the S−O and the S−N bond distances from 1.412(2) and 1.644(2) Å to 1.406(2) and 1.627(3) Å, respectively. Consequently, the S−N−S angle is further compressed from 125.8(1) in HN(SO$_2$Cl)$_2$ to 124.8(2)° in HN(SO$_2$F)$_2$. Compression of the S−N−S angle in HN(SO$_2$X)$_2$ follows the order X = CF$_3$ > Cl > F and can be explained on the basis of decreasing steric crowding about the sulfur atoms.

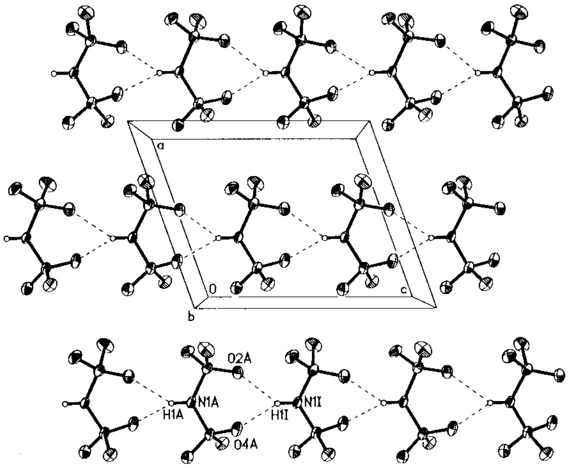

Figure 3. Intermolecular forked H···O bonding shown in the crystal packing diagram of HN(SO$_2$Cl)$_2$ viewed down the *b* axis.

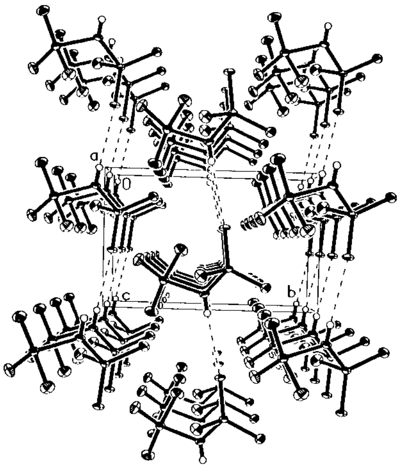

Figure 4. Intermolecular chain-type H···O bonding shown in the crystal packing diagram of HN(SO$_2$F)$_2$ viewed down the *a* axis.

Intermolecular hydrogen bonding in nitrogen acids is known to occur in different fashions. These range from a linear N···H bond resulting in chain formation as seen in HN(SO$_2$C$_6$H$_5$)$_2$[29] (O···H = 2.854(6) Å) to dimeric units in HN(SO$_2$C$_2$H$_5$)$_2$[30] (O···H = 2.87 Å). Recently, a bifurcated hydrogen bond has been observed in the crystal lattice of HN(SO$_2$CF$_3$)$_2$ (O···H $\approx$2.26 Å), where the N−H interacts with the two oxygen atoms of the SO$_2$ groups located on the neighboring molecule. The packing diagram of HN(SO$_2$Cl)$_2$ along the *b* axis is shown in Figure 3. In this case, the hydrogen-bonding networks form six-membered rings arranged in a polymeric fashion. The N−H interacts with two oxygen atoms of a neighboring molecule in a bifurcated manner, as seen in HN(SO$_2$CF$_3$)$_2$, with N1−H1···O2^a = 2.51(4) Å and N1−H1···O4^a = 2.23(4) Å ($a = x$, $^3/_2 - y$, $^1/_2 + z$). The corresponding N1···O2^a and N1···O4^a contact distances are 3.082(3) and 2.935(3) Å, respectively. In the case of crystal packing of HN(SO$_2$F)$_2$, the intermolecular hydrogen bonding is chain-type with only one hydrogen bond linking the N−H proton to the sulfonyl oxygen of the neighboring molecule (Figure 4): N1−H1···O2^b = 2.25(6) Å; N1···O2^b = 2.892(3) Å ($b = 1 + x, y, z$). This observation suggests that bifurcated intermolecular hydrogen bonding is not unique to nitrogen acids where a strong electron-withdrawing group is bonded to the sulfur atom. A comparison of intermolecular hydrogen bond

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) and Bond Lengths and Angles for $CF_3CH_2N(SO_2F)_2$[a]

a. Atomic Coordinates and Equivalent Isotropic Displacement Parameters

	x	*y*	*z*	*U*(eq)		*x*	*y*	*z*	*U*(eq)
S(1)	−1 294(1)	192(1)	3 056(1)	33(1)	O(1)	−1 088(2)	46(1)	1 348(3)	50(1)
S(2)	1 277(1)	154(1)	3 183(1)	33(1)	O(2)	−2 193(2)	511(1)	3 519(3)	48(1)
S(3)	3 596(1)	1537(1)	6 667(1)	34(1)	O(3)	1 128(2)	−327(1)	2 909(3)	45(1)
S(4)	6 160(1)	1468(1)	6 834(1)	36(1)	O(4)	2 202(2)	341(1)	4 195(3)	50(1)
S(5)	8 552(1)	1837(1)	11 833(1)	31(1)	O(5)	2 653(2)	1348(1)	5 691(4)	57(1)
S(6)	11 126(1)	1846(1)	11 811(1)	32(1)	O(6)	3 772(2)	2016(1)	6 884(3)	53(1)
F(1)	−1 501(2)	−249(1)	4 123(3)	53(1)	O(7)	5 954(2)	1636(1)	8 505(4)	67(1)
F(2)	1 363(2)	380(1)	1 392(3)	54(1)	O(8)	7 042(2)	1140(1)	6 405(4)	49(1)
F(3)	−1 098(2)	302(1)	7 280(3)	59(1)	O(9)	7 617(2)	2127(1)	11 271(3)	41(1)
F(4)	806(2)	254(1)	7 412(3)	57(1)	O(10)	8 734(2)	1713(1)	13 570(3)	48(1)
F(5)	−72(3)	885(1)	8 209(3)	68(1)	O(11)	12 051(2)	2033(1)	10 805(4)	58(1)
F(6)	3 497(2)	1333(1)	8 478(3)	62(1)	O(12)	11 010(2)	1374(1)	12 195(3)	43(1)
F(7)	6 417(2)	1896(1)	5 685(3)	60(1)	N(1)	−7(2)	379(1)	3 901(3)	27(1)
F(8)	4 877(3)	768(1)	1 716(3)	70(1)	N(2)	4 862(2)	1293(1)	5 992(3)	29(1)
F(9)	5 961(2)	1338(1)	2 597(3)	61(1)	N(3)	9 835(2)	2041(1)	11 023(3)	27(1)
F(10)	4 058(2)	1414(1)	2 473(3)	64(1)	C(1)	−15(3)	744(1)	5 249(4)	28(1)
F(11)	8 444(2)	1382(1)	10 807(3)	50(1)	C(2)	−96(3)	542(1)	7 047(4)	37(1)
F(12)	11 165(2)	2102(1)	13 557(3)	59(1)	C(3)	4 833(3)	923(1)	4 670(4)	27(1)
F(13)	8 762(2)	1971(1)	7 645(3)	66(1)	C(4)	4 931(3)	1115(1)	2 850(4)	36(1)
F(14)	10 668(2)	1935(1)	7 520(3)	66(1)	C(5)	9 828(3)	2416(1)	9 699(4)	28(1)
F(15)	9 773(3)	2560(1)	6 746(3)	73(1)	C(6)	9 758(3)	2218(1)	7 888(4)	38(1)

b. Bond Lengths and Angles

bond	length (Å)	bond	length (Å)	bond	length (Å)	bond	length (Å)
S(1)−O(1)	1.402(2)	S(4)−F(7)	1.545(2)	S(2)−N(1)	1.664(2)	S(6)−O(11)	1.397(2)
S(1)−O(2)	1.403(2)	S(4)−N(2)	1.662(2)	S(3)−O(5)	1.402(2)	S(6)−F(12)	1.536(2)
S(1)−F(1)	1.531(2)	S(5)−O(10)	1.402(2)	S(3)−O(6)	1.403(2)	S(6)−N(3)	1.658(2)
S(1)−N(1)	1.663(2)	S(5)−O(9)	1.403(2)	S(3)−F(6)	1.520(2)	N(1)−C(1)	1.478(4)
S(2)−O(4)	1.400(2)	S(5)−F(11)	1.536(2)	S(3)−N(2)	1.658(2)	N(2)−C(3)	1.475(4)
S(2)−O(3)	1.409(2)	S(5)−N(3)	1.665(2)	S(4)−O(7)	1.396(3)	N(3)−C(5)	1.486(4)
S(2)−F(2)	1.530(2)	S(6)−O(12)	1.396(2)	S(4)−O(8)	1.401(2)		

bond	angle (deg)	bond	angle (deg)	bond	angle (deg)	bond	angle (deg)
O(1)−S(1)−O(2)	123.6(2)	O(10)−S(5)−O(9)	123.7(2)	O(4)−S(2)−F(2)	107.1(2)	S(3)−N(2)−S(4)	119.1(2)
O(1)−S(1)−F(1)	106.26(14)	O(12)−S(6)−O(11)	124.1(2)	O(3)−S(2)−F(2)	106.85(14)	C(5)−N(3)−S(6)	120.2(2)
O(2)−S(1)−F(1)	107.36(14)	C(1)−N(1)−S(1)	120.0(2)	O(4)−S(2)−N(1)	107.14(13)	C(5)−N(3)−S(5)	120.6(2)
O(1)−S(1)−N(1)	108.92(14)	C(1)−N(1)−S(2)	121.1(2)	O(3)−S(2)−N(1)	109.38(13)	S(6)−N(3)−S(5)	119.06(14)
O(2)−S(1)−N(1)	107.61(13)	S(1)−N(1)−S(2)	118.8(2)	F(2)−S(2)−N(1)	100.80(13)	N(1)−C(1)−C(2)	111.9(2)
F(1)−S(1)−N(1)	100.79(12)	C(3)−N(2)−S(3)	120.3(2)	O(5)−S(3)−O(6)	123.4(2)	N(2)−C(3)−C(4)	112.0(2)
O(4)−S(2)−O(3)	123.3(2)	C(3)−N(2)−S(4)	120.5(2)	O(7)−S(4)−O(8)	124.5(2)	N(3)−C(5)−C(6)	111.2(2)

[a] *U*(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

distances suggests that the relative acidity in $HN(SO_2X)_2$ increases in the order $X = CF_3 \approx F > Cl > C_2H_5 \approx C_6H_5$.

A variety of new per- and polyfluoroalkyl derivatives of $N(SO_2F)_2$ are reported in this study. However, with the exception of the low melting $CF_3CH_2N(SO_2F)_2$, all of these derivatives are liquids. Only one other alkyl derivative, $CH_2[N(SO_2F)_2]_2$,[32] has been studied using single-crystal X-ray diffraction.

The unit cell shows three crystallographically independent molecules for **2**. Selected bond lengths and angles are listed in Table 4. The molecular structure of $CF_3CH_2N(SO_2F)_2$ (**2**), shown in Figure 5, contains a planar sp^2-hybridized nitrogen atom with the alkyl chain lying in a plane perpendicular to the plane containing the S−N−S bond. This is consistent with the torsion angles: S1−N1−C1−C2 = 89.9(3)°, S2−N1−C1−C2 = −91.0(3)°, S3−N2−C3−C4 = 90.6(3)°, S4−N2−C3−C4 = −89.9(3)°, S6−N3−C5−C6 = 95.3(3)°, S5−N3−C5−C6 = −89.0(3)°.

The average C−N bond length of 1.479(4) Å in **2** is similar to that found in $CH_3N(SO_2CH_3)_2$ at room temperature (1.479 Å)[33] and at −95 °C (1.484 Å),[34] in $CH_2[N(SO_2F)_2]_2$ (1.486 Å),[32] and in $[CH_3NSO_2]_3$ (1.487 Å)[35] but significantly shorter than the corresponding distances found in $C_6H_5CH_2CH_2N(SO_2C_6H_4$-

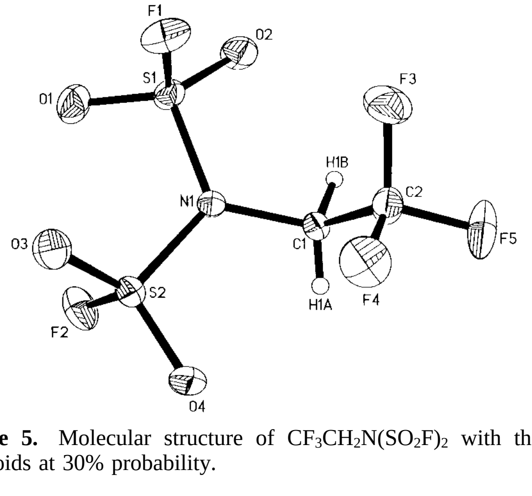

Figure 5. Molecular structure of $CF_3CH_2N(SO_2F)_2$ with thermal ellipsoids at 30% probability.

---

(32) Zak, Z.; Ruzicka, A. *Z. Anorg. Allg. Chem.* **1987**, *549*, 67.

(33) Schomburg, D.; Blaschette, A.; Wieland, E. *Z. Naturforsch., B: Chem. Sci.* **1986**, *41*, 1112.

(34) Blaschette, A.; Naveke, M.; Jones, P. G. *Z. Naturforsch., B: Chem. Sci.* **1991**, *46*, 46.

(35) Hazell, A. C. *Acta Crystallogr.* **1974**, *B30*, 2724.

Table 5. Comparative Structural Characteristics of Some Derivatives Containing the O−S−N−S−O π-framework

	av bond lengths (Å)			av bond angles (deg)	
compound	S−O	S−N	S−F	S−N−S	O−S−O
$HN(SO_2Cl)_2$[a]	1.412(2)	1.644(2)		125.8(1)	122.2(1)
$HN(SO_2CF_3)_2$[8]	1.409(2)	1.644(1)		128.4(2)	123.9(1)
$HN(SO_2F)_2$[a]	1.406(2)	1.627(3)	1.533(2)	124.8(2)	123.5(2)
$CF_3CH_2N(SO_2F)_2$[a]	1.402(2)	1.662(2)	1.533(2)	119.0(2)	123.8(2)
$CH_2[N(SO_2F)_2]_2$[32]	1.402(5)	1.658(5)	1.525(5)	119.8(4)	123.1(3)
$S[N(SO_2F)_2]_2$[8]	1.378(4)	1.688(4)	1.502(5)	118.4(2)	123.2(4)
$FXeN(SO_2F)_2$[17]	1.405(3)	1.626(3)	1.532(3)	120.5(2)	123.3
$[XeN(SO_2F)_2^+][Sb_3F_{16}^-]$[15]	1.375	1.69		123.6	125.5
$AgN(SO_2F)_2 \cdot C_6H_6$[53,b]	1.407(8)	1.571(6)	1.403(10)	120.1(7)	112.2(12)
$(C_6H_5)_4AsN(SO_2F)_2$[43]	1.415(3)	1.567(3)	1.574(3)	121.4(2)	110.3
$CsN(SO_2F)_2$[3]	1.421(3)	1.577(3)	1.566(2)	121.2(2)	119.7(2)
$(CH_3)_3PbN(SO_2F)_2$[3]	1.418(6)	1.593(6)	1.555(5)	119.3(4)	120.0(4)
$(C_6H_5)_3PHN(SO_2F)_2$[5]	1.419(2)	1.563(2)	1.566(2)	120.8(1)	118.6(9)
$(C_6H_5)_3CHN(SO_2F)_2$ 5	1.414(3)	1.561(3)	1.565(2)	122.0(2)	119.1(2)

[a] Present work. [b] The oxygen and fluorine atoms in the $N(SO_2F)_2$ group are disordered.

NO_2-*p*)$_2$ (1.508 Å)[36] and $C_6H_5CH_2N(SO_2C_6H_{11})(SO_2C_6H_4Br$-*p*) (1.512 Å).[37] However, the C−N distance of 1.342 Å found in $CH_3N(SO_3K)_2$[38] is very short compared to those of the other compounds listed above. The S−N bond shows a concomitant increase in length as the C−N bond length decreases. For example, in $CH_3N(SO_3K)_2$,[38] the S−N bond length is 1.750 Å, compared to 1.665 Å observed in the case of $C_6H_5CH_2N(SO_2C_6H_{11})(SO_2C_6H_4Br$-*p*). The S−N bond distance value of 1.662(2) Å compares well with the corresponding value of 1.658(5) Å found in $CH_2[N(SO_2F)_2]_2$.

A comparison of the structural parameters of $N(SO_2F)_2$-containing derivatives (Table 5) shows that with an increase in the covalent nature of the $R-N(SO_2F)_2$ bond the S−O and S−F bond lengths are shortened and the S−N bonds are elongated. In the case of $H_3N^+SO_3^-$,[39] the S−N bond length of 1.772 Å corresponds to a S−N single bond. The S−N bond distances of 1.627(3) Å in $HN(SO_2F)_2$ [almost identical to the S−N bond distance of 1.626(3) Å in $FXeN(SO_2F)_2$],[17] 1.662(2) Å in $CF_3CH_2N(SO_2F)_2$, and 1.688(4) Å in $S[N(SO_2F)_2]_2$[8] indicate a decrease in the contribution of the nitrogen lone pair to N−S dative bonding, thereby indicating an increase in the S−N bond order.

In covalent $R-N(SO_2F)_2$ derivatives, the S−O bond distances lie in the range 1.375−1.405 Å, which is close to the S−O bond length found in SO_2F_2 (1.405 Å), where the S−O bond order is assigned as 2.0 by Gillespie et al.[40] These S−O distances are, however, shorter than the corresponding bond lengths found in $CsN(SO_2F)_2$ [1.421(3) Å],[3,6] $(C_6H_5)_3XN(SO_2F)_2$ [X = C, 1.414(3) Å; X = P, 1.419(2) Å],[5] $Me_3PbN(SO_2F)_2$ [1.418(6) Å],[3] $NH_2(SO_3)^-$ (1.457 Å),[41,42] $NH(SO_3)_2^{2-}$ [1.449 Å],[43,44] and $N(SO_3)_3^{3-}$ (1.468 Å).[45] An increase in S−O bond order is observed in going from an ionic to a covalently bonded $R-N(SO_2F)_2$ derivative. A similar trend is also observed for the S−F bond lengths, which fall around 1.53 Å for the covalent $R-N(SO_2F)_2$ derivatives. For the ionic analogues, this bond distance is ~1.56 Å.

The effects of these structural changes can be seen in fluorine NMR and infrared spectroscopic data for both ionic and covalent $R-N(SO_2F)_2$ compounds. For example, the ν_{asSO_2} frequency for the covalent derivatives[10,20] (see the Experimental Section) is observed at ~1500 cm^{-1}, which is ~100 cm^{-1} higher than that observed for ionic derivatives such as $CsN(SO_2F)_2$ (1380 cm^{-1}).[25] A short S−F bond in covalently bonded $R-N(SO_2F)_2$ compounds is consistent with a deshielded fluorine nucleus, based on the decrease in S−F bond polarity expected for the covalent derivatives. Consequently, covalent $R-N(SO_2F)_2$ compounds[10,20] show a S−F resonance ~+60 ppm in the ^{19}F NMR spectrum whereas the ionic counterparts resonate at ~+52 ppm.[25] Compounds that exhibit intermediate S−F chemical shifts are compounds that contain a highly polarized $N(SO_2F)_2$ moiety.[4]

The O−S−O bond angles also show an increase in going from ionic to covalent bonding. As seen from Table 5, the O−S−O bond angle in $(C_6H_5)_4AsN(SO_2F)_2$[46] of 110.3° is close to tetrahedral. However, in a covalent molecule like $CF_3CH_2N(SO_2F)_2$, this O−S−O angle increases to 123.8(2)°. In the case of a cationic species such as $[XeN(SO_2F)_2]^+$,[15] the O−S−O value reaches a very high value of 125.5°. This effect is consistent with the order of bond-pair−bond-pair repulsion between the S−O bonds possessing considerable double bond character, which is expected to be at a maximum for the $[XeN(SO_2F)_2]^+$ species.

Perhaps the most interesting features of the crystal structure of $CF_3CH_2N(SO_2F)_2$ are the intra- and intermolecular hydrogen bonding networks. These interactions are listed in Table 6 and shown in Figure 6. Within the same asymmetric unit, the molecule containing the atom C5 shows only intramolecular bonds with the sulfonyl oxygen atoms O9 and O11 at 2.52(3) and 2.33(4) Å, respectively. However, the other two crystallographically independent molecules that are present are linked via bifurcated intermolecular hydrogen bonds, forming a four-membered center. This type of bifurcated hydrogen bonding originating from an alkyl proton has recently been reported by Gard et al.[47] Figure 7 shows intermolecular hydrogen-bonding networks resulting from the interaction of the molecules from different unit cells. These distances range from 2.43(3) to 2.89-

---

(36) Curtis, V. A.; Pavkovik, S. F. *Acta Crystallogr.* **1983**, *C39*, 1077.
(37) Higgins, T.; Bruke, P. O.; Spillane, W. J.; Cunningham, P. D.; McArdle, P. *Acta Crystallogr.* **1989**, *C45*, 685.
(38) Morris, A. J.; Kennard, C. H. L.; Hall, J. P.; Smith, G. *Inorg. Chim. Acta* **1982**, *62*, 247.
(39) Bats, J. W.; Coppens, P.; Koetzle, *Acta Crystallogr.* **1977**, *B33*, 37.
(40) Gillespie, R. J.; Robinson, E. A. *Can. J. Chem.* **1963**, *41*, 2047.
(41) Cox, G. W.; Sabine, T. M.; Padmanabhan, Ban, N. T.; Chung, M. K.; Surjadi, A. S. *Acta Crystallogr.* **1967**, *23*, 578.
(42) Jeffery, G. J.; Stadler, J. *J. Chem. Soc. A* **1951**, 1467.
(43) Jeffery, G. J.; Jones, D. W. *Acta Crystallogr.* **1956**, *9*, 238.
(44) Hodgson, P. G.; Moore, F. H.; Kennard, C. H. L. *J. Chem. Soc., Dalton Trans.* **1976**, 1443.
(45) Tillack, J. V.; Kennard, C. H. L. *J. Chem. Soc. A* **1970**, 1637.
(46) Isenberg, W.; Noltemayer, M.; Sheldrick, G. M. *Acta Crystallogr.* **1982**, *B38*, 2887.
(47) Braden, D. A.; Gard, G. L.; Weakly, T. J. R. *Inorg. Chem.* **1996**, *35*, 1912.

Table 6. Intra- and Intermolecular Hydrogen Bond Distances in $CF_3CH_2N(SO_2F)_2$

Intramolecular Interactions

bond	distance (Å)
C1−H1A···O4	2.49(2)
C1−H1B···O2	2.28(3)
C3−H3A···O8	2.46(2)
C3−H3B···O4	2.34(3)
C3−H3A···O5	2.32(3)
C5−H5A···O11	2.33(4)
C5−H5B···O9	2.52(3)

Intermolecular Interactions

bond	distance (Å)	symmetry operation
O1···H3A	2.60(3)	$^1/_2 - x, -y, -^1/_2 + z$
O2···H3A	2.89(3)	$-1 + x, y, z$
O3···H3A	2.65(3)	$^1/_2 - x, -y, -^1/_2 + z$
O6···H5B	2.77(3)	$-^1/_2 + x, ^1/_2 - y, 2 - z$
O7···H5A	2.50(4)	$-^1/_2 + x, ^1/_2 - y, 2 - z$
O8···H1B	2.67(3)	$1 + x, y, z$
O9···H5A	2.43(4)	$-^1/_2 + x, ^1/_2 - y, 2 - z$
O10···H1B	2.50(3)	$1 + x, y, 1 + z$
O11···H5B	2.70(3)	$^1/_2 + x, ^1/_2 - y$, 2 - z
O12···H1A	2.68(3)	$1 + x, y, 1 + z$

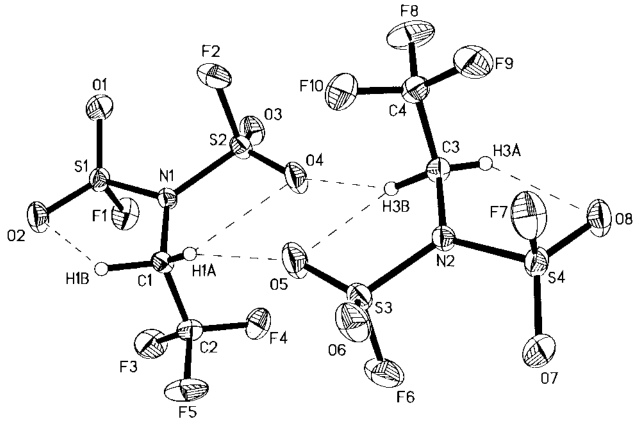

Figure 6. Intramolecular hydrogen bonding in $CF_3CH_2N(SO_2F)_2$ forming four-membered H_2O_2 units.

(3) Å as seen in Table 6. In addition to these intermolecular hydrogen bonds, there are numerous other fluorine−fluorine contacts at a distance of ∼2.9 Å.

Studies involving the chemistry of these per- and polyfluoroalkyl-N(SO_2F)$_2$ derivatives are continuing.

Experimental Section

Materials. $HN(SO_2Cl)_2$[21] and $Hg[N(SO_2F)_2]_2$[24] were prepared by the literature methods. SbF_3 (Ozark-Mahoning, Tulsa, OK) was sublimed in a vacuum prior to use.

General Considerations. A conventional vacuum system, consisting of a Pyrex glass vacuum line fitted with Teflon needle stopcocks and equipped with Heise Bourdon tube and Televac thermocouple gauges, was used to handle gases and volatile liquids. Standard pressure−volume−temperature techniques were used to quantitate starting materials or products. Fractional condensation (trap-to-trap distillation) was used for the purification of products. Infrared spectra were recorded on a Perkin-Elmer 1710 FT-IR spectrometer with a 10-cm glass cell equipped with AgCl windows. ^1H, ^{13}C, ^{14}N, and ^{19}F NMR spectra were obtained on a Bruker AC200 or AC300 FT-NMR instrument using $CDCl_3$ as solvent at room temperature unless otherwise noted. Chemical shifts were reported with respect to $(CH_3)_4Si$, CH_3NO_2, or $CFCl_3$. Mass spectra were obtained with a Varian VG 7070 HS mass spectrometer by using the electron-impact (EI) technique. Peak assignments of chlorine-containing fragments were based on ^{35}Cl. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany. Photolysis reactions were carried out in quartz reaction vessels irradiated in a Rayonet photochemical reactor with 3000-Å UV lamps.

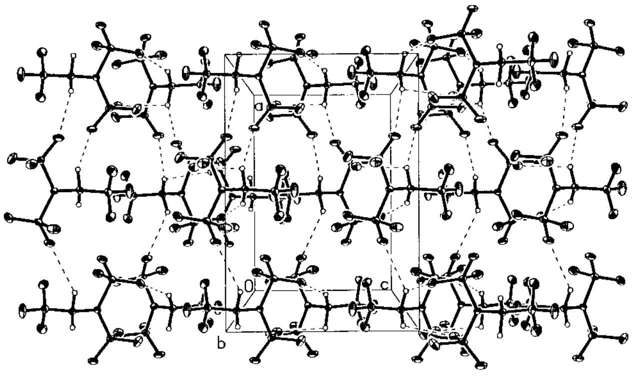

Figure 7. Packing diagram of $CF_3CH_2N(SO_2F)_2$ viewed along the *b* axis showing the intermolecular H···O contacts.

The X-ray diffraction data were collected on a Siemens SMART 3-circle diffractometer (χ axis fixed at 54.74°) equipped with a CCD detector maintained near −54 °C. The frame data were acquired with the SMART[48] software with a Siemens 3-circle platform using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Because HN(SO_2X)$_2$ (X = Cl or F) and $CF_3CH_2N(SO_2F)_2$ are low-melting compounds, in addition to being highly moisture-sensitive, a single colorless crystal of each was mounted in a glass capillary fixed on a copper pin premounted on a goniometer head and then transferred onto the diffractometer platform under a stream of cold nitrogen. The cell constants were determined from 60 10-s frames. A complete hemisphere of data was scanned on ω (0.3°) with a run time of 10 s/frame at a detector resolution of 512 × 512 pixels. A total of 1271 frames were collected in three sets, and a final set of 50 frames, identical to the first 50 frames, were also collected to determine crystal decay. The frames were then processed on a SGI-Indy/IndigoII workstation by using SAINT software[49] to give the *hkl* file corrected for Lorentz polarization. The data were corrected for absorption using the SADABS[50] program. The structures were solved by the direct method using the SHELX-90[51] program and refined by least-squares method on F^2 using SHELXTL version 5.03.[52] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from the difference electron density maps and refined isotropically. The crystal used for the diffraction study showed no decomposition during data collection.

Preparation of $HN(SO_2F)_2$ by Fluorination of $HN(SO_2Cl)_2$ with SbF_3. Freshly sublimed SbF_3 (0.472 mol) was added in three portions to 0.506 mol of $HN(SO_2Cl)_2$ under an atmosphere of dry nitrogen in a 250-mL, round-bottomed flask equipped with a reflux condenser. After a few minutes, the mixture liquified and was slightly exothermic. After ca. 30 min, the reaction temperature returned to 25 °C, and the mixture was stirred for a total of 4 h. The resulting slurry was distilled repeatedly (five times) at 25 °C/0.01 Torr to ensure complete removal of $SbCl_3$ which sublimed slowly along with $HN(SO_2F)_2$. The receiver flask was cooled with N_2 (l). The liquid $HN(SO_2F)_2$ was separated from small amounts of solid $SbCl_3$, by removal of the liquid with a glass pipet. The yield of pure $HN(SO_2F)_2$ obtained by this process was 70%. The ^1H and ^{19}F NMR data agreed with the literature values.[25]

---

(48) *SMART, Software for the CCD Detector System*, version 4.043; Siemens Analytical Instruments Division: Madison, WI, 1995.

(49) *SAINT, Software for the CCD Detector System*, version 4.035; Siemens Analytical Instruments Division: Madison, WI, 1995.

(50) *SADABS, Siemens Area Detector Absorption Correction Program*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(51) Sheldrick, G. M. *SHELXS-90, Program for the Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1990.

(52) *SHELXTL 5.03, Program Library for Structure Solution and Molecular Graphics*; Siemens Analytical Instruments Division: Madison, WI, 1995.

(53) Begley, M. J.; Sowerby, D. B.; Verma, R. D.; Vij, A. *J. Organomet. Chem.* **1994**, *481*, 243.

In addition to the ^{14}N NMR shift, we list the IR spectrum in the gas phase. The liquid-phase spectrum has been reported previously.[25]

$HN(SO_2F)_2$: IR (gas) 3419 m (ν_{NH}), 1495 s (ν_{asSO}), 1321 m, 1224 m (ν_{sSO}), 992 w, 912 m (ν_{SN}), 888 w, 837 m (ν_{SF}), 568 cm^{-1}; ^{14}N NMR δ -241 [δ -182 $HN(SO_2Cl)_2$; -231 $Hg[N(SO_2F)_2]_2$ (CD_3CN)].

$[N(SO_2F)_2]_2$: prepared according to ref 20; IR (gas) 1509 s/1491 m (ν_{asSO}), 1246 s (ν_{sSO}), 921 m (ν_{SN}), 867 m, 847 s (ν_{SF}), 797 w (ν_{NN}), 603 m, 577 s, 463 m cm^{-1}.

Preparation of $ClN(SO_2F)_2$ by Chlorination of $Hg[N(SO_2F)_2]_2$. Chlorine (67 mmol) was condensed into a 160-mL, stainless-steel vessel which contained 28 mmol of $Hg[N(SO_2F)_2]_2$. The contents were kept at 25 °C for 5 days. Distillation through traps cooled to -20 and -80 °C gave $ClN(SO_2F)_2$ in 89% yield in the -80 °C trap.

Alkylation of $Hg[N(SO_2F)_2]_2$ with RI (R = *i*-$C_3F_7CH_2CH_2$ and CF_3CH_2). To 2 mmol of $Hg[N(SO_2F)_2]_2$ loaded in a 80-mL stainless-steel vessel was condensed 6 mmol of alkyl iodide. For R = *i*-$C_3F_7CH_2CH_2$, the vessel was kept at 70 °C for 12 h whereas for R = CF_3CH_2 the vessel was kept at 120 °C for 48 h. Distillation of the respective contents through traps at -30 °C [*i*-$C_3F_7CH_2CH_2N(SO_2F)_2$ (**1**) retained] and at -60 °C [$CF_3CH_2N(SO_2F)_2$ (**2**) retained] removed the excess alkyl iodides. The yields were 64% **1** (colorless liquid) and 33% **2** [large colorless rectangular crystals (mp 35−36 °C)].

Spectral data for *i*-$C_3F_7CH_2CH_2N(SO_2F)_2$ (1): IR (gas) 1496 s/1467 m (ν_{asSO}), 1332 m, 1297 m, 1269 m, 1233 s (ν_{sSO}), 1173 m, 1123 m, 1089 m, 954 w, 896 m, 845 m, 827 m, 796 w, 573 m cm^{-1}; ^{19}F NMR δ 58.9 (SF, t, 2F, $^4J_{F-H} = 1.0$ Hz), -77.0 (CF_3, d, 6F, $^3J_{F-F} = 6.4$ Hz), -186.5 (CF, m, 1F); ^{1}H NMR δ 4.25 (CH_2N, m, 2H), 2.64 ($CFCH_2$, m, 2H); $^{13}C\{^1H\}$ NMR δ 120.4 (CF_3, qd, $^1J_{C-F} = 286.9$ Hz, $^2J_{C-F} = 27.2$ Hz), 90.0 (CF, dsept, $^1J_{C-F} = 206.2$ Hz, $^2J_{C-F} = 33.3$ Hz), 47.5 (CH_2N, d, $^3J_{C-F} = 6.7$ Hz), 28.1 (CH_2CF, d, $^2J_{C-F} = 20.1$ Hz); ^{14}N NMR δ -236; MS (EI) [*m*/*e* (species, intensity)] 358 ($M^+ - F$, 67), 256 ($M^+ - 2F - SO_2F$, 31), 197 [$(CF_3)_2CFCH_2CH_2^+$, 19], 194 [$CH_2N(SO_2F)_2^+$, 100], 177 [$(CF_3)_2CCHCH_2^+$, 5], 128 ($CFNSO_2F^+$, 4), 114 ($CF_3CFCH_2^+$, 6), 93 ($C_3F_3^+$, 10). Anal. Calcd for $C_5H_4F_9NO_4S_2$: C, 15.92; H, 1.07. Found: C, 16.39; H, 1.19.

Spectral data for $CF_3CH_2N(SO_2F)_2$ (2): IR (gas) 3044 w, 3001 w, 1499 s/1474 m (ν_{asSO}), 1430 m, 1401 m, 1337 m, 1285 m, 1235 s (ν_{sSO}), 1188 s, 1123 m, 997 s, 921 w, 830 s, 739 w, 665 m, 607 m, 575 s, 470 m cm^{-1}; ^{19}F NMR δ 59.2 (SF, qt, 2F, $^5J_{F-F} = 3.7$ Hz, $^4J_{F-H} = 1.5$ Hz), -71.4 (CF_3, tt, 3F, $^3J_{F-H} = 7.5$ Hz); ^{1}H NMR δ 4.52 (CH_2, tq, 2H); $^{13}C\{^1H\}$ NMR δ 121.6 (CF_3, q, $^1J_{C-F} = 279.9$ Hz), 52.4 (CH_2, q, $^2J_{C-F} = 38.5$ Hz); ^{14}N NMR δ -238; MS (EI) [*m*/*e* (species, intensity)] 244 ($M^+ - F$, 18), 223 ($M^+ - 2HF$, 4), 194 [$CH_2N(SO_2F)_2^+$, 100], 179 ($CF_3CHNSO_2F^+$, 5), 110 ($CHNSO_2F^+$, 8), 92 ($CH_2NSO_2^+$, 19), 86 (SOF_2^+, 19), 83 ($SO_2F^+/CF_3CH_2^+$, 5), 69 (CF_3^+, 7), 67 (SOF^+, 5). Anal. Calcd for $C_2H_2F_5NO_4S_2$: C, 9.13; H, 0.77. Found: C, 9.38; H, 0.86.

Alkylation of $ClN(SO_2F)_2$ with Ethenes $CF_2{=}CHal_2$ ($CHal_2$ = CF_2, CFCl, and CCl_2). Mixtures consisting of 3 mmol of $ClN(SO_2F)_2$ and 6 mmol of ethene were kept in 80-mL stainless-steel vessels at 25 °C for 3 days. Distillation of the contents through traps at -50 °C [$CF_2ClCF_2N(SO_2F)]_2$ (**3**) (60%); $CF_2ClCFClN(SO_2F)_2/CFCl_2CF_2N(SO_2F)_2$ mixture (**4a**/**4b**) (78%)] and -30 °C [($CCl_3CF_2N(SO_2F)_2$ (**5**) (46%)] gave the products as colorless liquids.

Spectral data for $CF_2ClCF_2N(SO_2F)_2$ (3): IR (gas) 1510 m/1464 s/1428 s (ν_{asSO}), 1329 m, 1238 s (ν_{sSO}), 1192 m, 1151 m, 1096 s, 977 s, 882 m, 861 m, 840 m, 821 m, 771 m, 726 w, 658 w, 574 m, 564 m cm^{-1}; ^{19}F NMR (two conformers 11:1) major (staggered) δ 61.0 (SF, d, 1F, $^4J_{F-F} = 7.3$ Hz), 59.1 (SF, dt, 1F, $^4J_{F-F} = 10.8$ Hz, $^5J_{F-F} = 7.0$ Hz), -73.2 (CF_2Cl, t, 2F, $^3J_{F-F} = 1.7$ Hz), -83.6 (C*F*FN, AB system of dm, 1F, $^2J_{F-F} = 125.8$ Hz, $^4J_{F-F} = 6.5$ Hz), -84.7 (CF*F*N, AB system of dm, 1F, $^4J_{F-F} = 11.1$ Hz), minor (eclipsed) δ 65.2 (SF, tt, 2F, $^4J_{F-F} = 7.6$ Hz, $^5J_{F-F} = 2.2$ Hz), -69.2 (CF_2Cl, m, 2F), -85.5 (CF_2N, tm, 2F, $^4J_{F-F} = 7.6$ Hz); ^{13}C NMR δ 118.6 (CF_2, tt, $^1J_{C-F} = 301.5$ Hz, $^2J_{C-F} = 38.5$ Hz), 116.3 (CF_2, tt, $^1J_{C-F} = 300.4$ Hz, $^2J_{C-F} = 38.9$ Hz); ^{14}N NMR δ -239; MS (EI) [*m*/*e* (species, intensity)] 296 ($M^+ - F$, 7), 280 ($M^+ - Cl$, 34), 230 ($M^+ - CF_2Cl$, 91), 164 [$N(SOF)SO_2F^+$, 21], 142 [$N(SO_2)_2^+$, 45], 135 ($CF_2ClCF_2^+$, 67), 128 ($CFNSO_2F^+$, 100), 100 ($CF_2CF_2^+$, 5), 97 (NSO_2F^+, 4), 85 (CF_2Cl^+, 39), 83 (SO_2F^+, 26), 67 (SOF^+, 13). Anal. Calcd for $C_2ClF_6NO_4S_2$: C, 7.61; F, 36.12. Found: C, 7.57; F, 36.0.

The mixture of **4a**/**4b**, (2.5:1), obtained from the reaction of $ClN(SO_2F)_2$ with $CF_2{=}CFCl$, was distilled repeatedly through -40 °C traps. The major isomer, according to the ^{19}F NMR spectrum, is retained at -40 °C, but the minor isomer is more volatile and slowly passed this trap. Analysis of the ^{19}F NMR spectrum of the purified, less volatile isomer was consistent with the structure of **4a** and displayed a more complicated NMR spectrum, because of the asymmetric CFClN carbon center. For the minor isomer **4b**, which could only be obtained in 60% purity, only NMR data are given.

Spectral data for $CF_2ClCFClN(SO_2F)_2$ (4a): IR (gas) 1462 m/1424 s (ν_{asSO}), 1234 s (ν_{sSO}), 1192 m, 1151 m, 1087 m, 1006 m, 943 w, 874 m, 846 m, 561 m cm^{-1}; ^{19}F NMR δ [61.1 (d, $^4J_{F-F} = 7.4$ Hz)/60.9 (d, $^4J_{F-F} = 7.4$ Hz)/60.3 (dd)/59.2 (t, $^4J_{F-F} = 7.3$ Hz)/58.5 (dt)] (SF, 2F), -70.09/-70.11 (CF_2Cl, d, 2F, $^3J_{F-F} = 5.9/6.3$ Hz), -75.4/-81.9 (CF, m, 1F); ^{13}C NMR δ 121.1 (CF_2Cl, dt, $^1J_{C-F} = 302.4$ Hz, $^2J_{C-F} = 33.7$ Hz)/118.1 (CF_2Cl, dt, $^1J_{C-F} = 300.0$ Hz, $^2J_{C-F} = 34.1$ Hz), 118.3 (CFCl, td, $^1J_{C-F} = 311.1$ Hz, $^2J_{C-F} = 39.3$ Hz)/118.1 (CFCl, td, $^1J_{C-F} = 311.5$ Hz, $^2J_{C-F} = 39.1$ Hz)/111.4 (CFCl, td, $^1J_{C-F} = 341.1$ Hz, $^2J_{C-F} = 35.9$ Hz); ^{14}N NMR δ -242; MS (EI) [*m*/*e* (species, intensity)] 296 ($M^+ - Cl$, 1), 246 ($M^+ - CF_2Cl$, 1), 194 ($CF_2CClNSO_2F^+$, 2), 164 ($N(SOF)SO_2F^+$, 45), 151 ($CF_2ClCFCl/CFCl_2CF_2^+$, 100), 101 ($CFCl_2^+$, 35), 85 (CF_2Cl^+, 28), 83 (SO_2F^+, 17), 67 (SOF^+, 39). Anal. Calcd for $C_2Cl_2F_5NO_4S_2$: C, 7.23; Cl, 21.35. Found: C, 7.40; Cl, 21.08.

Spectral data for $CFCl_2CF_2N(SO_2F)_2$ (4b): ^{19}F NMR δ 65.8 (SF, d m, 2F, $^5J_{F-F} = 14.5$ Hz), -63.3 (C*F*FN, AB system of dt, 1F, $^2J_{F-F} = 168.4$ Hz, $^3J_{F-F} = 6.9$ Hz, $^4J_{F-F} = 2.3$ Hz), -64.4 (CF*F*N, AB system of dt, 1F, $^2J_{F-F} = 168.1$ Hz, $^3J_{F-F} = 5.2$ Hz, $^4J_{F-F} = 1.7$ Hz), -91.2 (CF, t of $^+$,s, 1F); ^{13}C NMR δ 123.3 (CF_2N, dt, $^1J_{C-F} = 304.9$ Hz, $^2J_{C-F} = 36.7$ Hz), 112.3 ($CFCl_2$, dt, $^1J_{C-F} = 282.8$ Hz, $^2J_{C-F} = 38.7$ Hz).

Spectral data for $CCl_3CF_2N(SO_2F)_2$ (5): IR (gas) 1502 s/1480 m (ν_{asSO}), 1247 m (ν_{sSO}), 1172 m, 1046 w, 983 m, 908 w, 839 m, 607 w, 571 m cm^{-1}; ^{19}F NMR δ 69.1 (SF, t, 2F, $^4J_{F-F} = 2.2$ Hz), -61.4 (CF_2, t, 2F); ^{13}C NMR δ 125.9 (CF_2, t, $^1J_{C-F} = 305.2$ Hz), 96.1 (CCl_3, t, $^2J_{C-F} = 37.3$ Hz); ^{14}N NMR δ -202; MS (EI) [*m*/*e* (species, intensity)] 312 ($M^+ - Cl$, 24), 262 ($M^+ - Cl - CF_2$, 52), 194 ($CClCF_2NSO_2F^+$, 6), 144 ($CClNSO_2F^+$, 39), 101 ($CFCl_2^+$, 35), 85 (CF_2Cl^+, 70), 83 (SO_2F^+, 100), 67 (SOF^+, 18). Anal. Calcd for $C_2Cl_3F_4NO_4S_2$: C, 6.89; Cl, 30.51. Found: C, 7.34; Cl, 30.49.

Alkylation of $ClN(SO_2F)_2$ with R_FI (R_F = CF_3, C_2F_5, *n*-C_3F_7, *n*-C_4F_9, CF_3CH_2). Mixtures consisting of 6 mmol of $ClN(SO_2F)_2$ and 11 mmol iodoperfluoroalkane or CF_3CH_2I were kept in 80-mL, stainless-steel vessels at 60 °C for 4 days. Distillation of the contents through traps at -20 and -90 °C [$CF_3N(SO_2F)_2$ (**6**)], -80 °C [$C_2F_5N(SO_2F)_2$ (**7**) or *n*-$C_3F_7N(SO_2F)_2$ (**8**)], and -60 °C [*n*-$C_4F_9N(SO_2F)_2$ (**9** or **2**)] retained the products as mixtures with iodine. Removal of iodine was achieved by keeping the mixtures over fresh mercury until complete decolorization. Yields of the products as pure colorless liquids are 87% **6**, 43% **7**, 29% **8**, 23% **9**, and 45% **2**.

Photolysis of $ClN(SO_2F)_2$ with R_FI (R_F = *n*-C_3F_7, *n*-C_4F_9). Mixtures consisting of 4 mmol of $ClN(SO_2F)_2$ and 9 mmol of R_FI were photolyzed in a 300-mL, quartz vessel for 24 h at 3000 Å. Distillation of the contents through traps at -20 and -80 °C (**8**) or -60 °C (**9**) gave the products as mixtures with iodine. After the mixtures were kept over fresh mercury until complete decolorization, **8** (15%) and **9** (14%) were obtained in pure form.

Spectral data for $CF_3N(SO_2F)_2$ (6): IR (gas) 1465 s/1430 s (ν_{asSO}), 1303 s, 1277 s, 1236 s (ν_{sSO}), 1122 vs, 973 s, 876 m, 836 m, 811 m, 741 w, 694 w, 600 m, 578 m, 549 m cm^{-1}; ^{19}F NMR δ 61.1 (SF, d, 1F, $^4J_{F-F} = 7.3$ Hz), 56.5 (SF, m, 1F), -53.5 (CF_3, d, 3F, $^4J_{F-F} = 6.2$ Hz); ^{13}C NMR δ 118.5 (CF_3, q, $^1J_{C-F} = 281.1$ Hz); ^{14}N NMR δ -246; MS (EI) [*m*/*e* (species, intensity)] 249 (M^+, 1), 164 [$N(SOF)SO_2F^+$, 5], 83 (SO_2F^+, 4), 69 (CF_3^+, 100), 67 (SOF^+, 7). Anal. Calcd for $CF_5NO_4S_2$: N, 5.62. Found: N, 5.65.

Spectral data for $CF_3CF_2N(SO_2F)_2$ (7): IR (gas) 1465 s/1430 s (ν_{asSO}), 1391 w, 1254 vs, 1237 s (ν_{sSO}), 1155 s, 1066 s, 976 w, 910 m, 883 m, 863 m, 824 m, 788 m, 742 m, 722 m, 588 w, 568 m, 468 w cm^{-1}; ^{19}F NMR δ 61.1 (SF, d, 1F, $^4J_{F-F} = 7.6$ Hz), 59.5 (SF, m, 1F), -85.3 (CF_3, t, 3F, $^3J_{F-F} = 1.9$ Hz), -85.4 (C*F*FN, AB system of dm, 1F, $^2J_{F-F} = 130.8$ Hz, $^4J_{F-F} = 10.1$ Hz), -86.5 (CF*F*N, AB system of dm, 1F); ^{13}C NMR δ 115.0 (CF_3, qt, $^1J_{C-F} = 286.7$ Hz, $^2J_{C-F} = 38.4$

Hz), 114.7 (CF_2N, tq, $^1J_{C-F} = 299.9$ Hz, $^2J_{C-F} = 46.1$ Hz); ^{14}N NMR δ −241; MS (EI) [*m/e* (species, intensity)] 299 (M^+, 1), 230 ($M^+ - CF_3$, 1), 164 [N(SOF)SO_2F^+, 9], 119 ($C_2F_5^+$, 100), 83 (SO_2F^+, 7), 69 (CF_3^+, 26), 67 (SOF^+, 13). Anal. Calcd for $C_2F_7NO_4S_2$: N, 4.68. Found: N, 4.59.

Spectral data for *n*-$CF_3CF_2CF_2N(SO_2F)_2$ (8): IR (gas) 1465 s/1430 s (ν_{asSO}), 1356 w, 1333 m, 1248 vs, 1237 s (ν_{sSO}), 1161 s, 1099 s, 996 s, 856 m, 822 m, 778 m, 747 m, 720 m, 687 w, 660 w, 564 s, 536 m, 464 w, 403 w cm^{-1}; ^{19}F NMR δ 61.1 (SF, d, 1F, $^4J_{F-F} = 7.3$ Hz), 59.8 (SF, m, 1F), −80.9 (C*F*FN, AB system of m, 1F, $^2J_{F-F} = 134.9$ Hz), −81.0 (CF_3, t, 3F, $^4J_{F-F} = 7.2$ Hz), −82.3 (CF*F*N, AB system of m, 1F), −128.6 (CF_2, s, 2F); ^{13}C NMR δ 116.5 (CF_3, qt, $^1J_{C-F} = 288.4$ Hz, $^2J_{C-F} = 33.0$ Hz), 116.3 (CF_2N, tt, $^1J_{C-F} = 301.6$ Hz, $^2J_{C-F} = 33.7$ Hz), 106.1 (CCF_2C, m); ^{14}N NMR δ −243; MS (EI) [*m/e* (species, intensity)] 349 (M^+, 1), 230 ($M^+ - C_2F_5$, 4), 228 ($M^+ - 2F - SO_2F$, 4), 169 ($C_3F_7^+$, 100), 169 ($C_3F_7^+$, 6), 164 [N(SOF)SO_2F^+, 41], 119 ($C_2F_5^+$, 12), 100 ($C_2F_4^+$, 6), 83 (SO_2F^+, 8), 69 (CF_3^+, 71), 67 (SOF^+, 15). Anal. Calcd for $C_3F_9NO_4S_2$: C, 10.32; N, 4.01. Found: C, 9.89; N, 4.08.

Spectral data for *n*-$CF_3CF_2CF_2CF_2N(SO_2F)_2$ (9): IR (gas) 1465 s/1430 s (ν_{asSO}), 1305 m, 1256 vs, 1238 s (ν_{sSO}), 1154 m, 1134 m, 1106 w, 1076 s, 957 m, 933 m, 917 m, 884 m, 858 m, 821 m, 774 w, 743 m, 688 w, 561 m, 465 w cm^{-1}; ^{19}F NMR δ 61.1 (SF, d, 1F, $^4J_{F-F} = 7.6$ Hz), 59.8 (SF, m, 1F), −80.0 (C*F*FN, AB system of m, 1F, $^2J_{F-F} = 133.8$ Hz), −80.9 (CF_3, t, 3F, $^4J_{F-F} = 8.9$ Hz), −81.3 (CF*F*N, AB system of m, 1F), −125.1 (CF_2, m, 2F), −126.4 (CF_2, m, 2F); ^{13}C NMR δ 116.8 (CF_3, qt, $^1J_{C-F} = 288.4$ Hz, $^2J_{C-F} = 32.4$ Hz), 116.5 (CF_2N, tt, $^1J_{C-F} = 302.1$ Hz, $^2J_{C-F} = 33.3$ Hz), 107.9/107.7 (CCF_2-CF_2C, m); ^{14}N NMR δ −241; MS (EI) [*m/e* (species, intensity)] 278 ($M^+ - 2F - SO_2F$, 1), 230 ($M^+ - C_3F_7$, 1), 219 ($C_4F_9^+$, 40), 169 ($C_3F_7^+$, 6), 164 [N(SOF)SO_2F^+, 63], 131 ($C_3F_5^+$, 48), 119 ($C_2F_5^+$, 21), 100 ($C_2F_4^+$, 18), 83 (SO_2F^+, 11), 69 (CF_3^+, 100), 67 (SOF^+, 26). Anal. Calcd for $C_4F_{11}NO_4S_2$: C, 12.03; N, 3.51. Found: C, 12.17; N, 3.58.

Acknowledgment. We are grateful for the support of British Nuclear Fuels plc and NSF EPSCoR (OSR-9350539). Dr. Gary Knerr is thanked for obtaining the mass spectral data as well as for help with the NMR experiments. The single-crystal SMART CCD X-ray diffraction facility at the University of Idaho was established with the NSF−Idaho EPSCoR program under NSF OSR-9350539 and M. J. Murdock Charitable Trust, Vancouver, WA.

Supporting Information Available: For $HN(SO_2Cl)_2$, $HN(SO_2F)_2$, and $CF_3CH_2N(SO_2F)_2$: tables listing full data collection and processing parameters, bond lengths and angles, atomic coordinates, equivalent isotropic and anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients (21 pages). Ordering information is given on any current masthead page.

IC9800031