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Pentafluorosulfanylnitramide Salts

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The synthesis and properties of a new class of inorganic salts, named pentafluorosulfanylnitramide salts (or pentafluorosulfanylnitraminic acid salts) [$Z^+SF_5NNO_2^-$], are described. A number of SF_5-nitramide salts ($Z^+SF_5NNO_2^-$) were successfully prepared via nucleophilic displacements from carbamates and/or ion exchange techniques, but some salts [$M(SF_5NNO_2)_x$; M = Li, Mg, Al] decomposed during isolation procedures and appear to be unstable in the solid state. Single-crystal X-ray diffraction was used to fully characterize the $Z^+SF_5NNO_2^-$, and their properties/structures are compared with those of the corresponding dinitramide salts (or dinitraminic acid salts), $Z^+N(NO_2)_2^-$. X-ray crystallography revealed major structural differences between $N(NO_2)_2^-$ and $SF_5N(NO_2)^-$ salts concerning the N−N distances and the angles subtended at the central nitrogen atom. In the $N(NO_2)_2^-$ salts, there are two nonequivalent N−N (average lengths 1.372(2) and 1.354(2) Å) distances and an average N−N−N angle of 115.8(3)° (falls between sp^3 and sp^2 hybridization). In the $SF_5NNO_2^-$ salts, the average N−N distance is much shorter, 1.308(9) Å, and the average N−N−S angle is 120.0(5)° (closely fits sp^2 hybridization). The $SF_5NNO_2^-$ salts show a remarkable metrical similarity for the SF_5 moiety in all structures, indicating a lack of sensitivity to its steric and electronic environment. This is in marked contrast to $N(NO_2)_2^-$, where there is a wide variation in conformations adopted by these anions which can be related to their environment.

Introduction

Recent articles[2] report investigations in the U.S.A. and Russia concerning the syntheses and crystal structures of dinitramide salts, $Z^+N(NO_2)_2^-$ [salts of dinitraminic acid, $HN(NO_2)_2$]. Ammonium dinitramide, $NH_4^+N(NO_2)_2^-$, is of special interest as a non-chlorine-containing oxidizer in rocket propellants and offers significant advantages over currently used oxidizers such as ammonium perchlorate, especially from an environmental standpoint, given that chlorine-containing combustion products are generally not environmentally benign materials.

Dinitramide salt analogs, $Z^+N(X)(NO_2)^-$, in which a nitro group in a dinitramide salt is substituted by group X, are being investigated in an effort to provide salts with improved physical and energetic properties (e.g., increased density, oxidant level, etc.). This report, concerning the syntheses/properties/crystal structures of pentafluorosulfanylnitramide salts ($Z^+SF_5NNO_2^-$; X = SF_5), describes a continuation of our research in the area of SF_5 chemistry, which has included the synthesis of SF_5 materials/intermediates, as well as the determination of the physical and chemical property changes that occur in various materials with the incorporation of an SF_5 group.[3] Previous investigations include a demonstration that the SF_5 group can act as an oxidizing moiety (producing HF and O=C=S as oxidation products),[3c] suggesting that $Z^+SF_5NNO_2^-$ may be useful as oxidizer ingredients.

Results and Discussion

Syntheses. The synthetic strategy toward $Z^+SF_5NNO_2^-$ (**1**) was to identify and synthesize SF_5-containing precursors (SF_5NHR_1) which potentially could be nitrated to produce $SF_5NNO_2R_1$ and from which R_1 could later be removed to produce the desired salt. Groups R_1 under consideration included $COOCMe_3$ and CMe_3 (removal under acidic conditions) and $COOCH_2CH_2SiMe_3$ (removal by treatment with fluoride).[4]

$Z^+\ SF_5NNO_2^-$

1

1a: Z = NH_4; **1b**: Z = K; **1c**: Z = Na;
1d: Z = $NH_2C(=NH_2)NH_2$; **1e**: Z = $NH_2C(=NH_2)NHNH_2$

Also under consideration, as a potential synthesis route to **1**, was a method analogous to that developed at NSWC for $NH_4^+N(NO_2)_2^-$. This method for $NH_4^+N(NO_2)_2^-$ generates

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(4) Similar to the preparation of dinitramide salts from $(NO_2)_2NCH_2CH_2SiMe_3$ as described in ref 2a.

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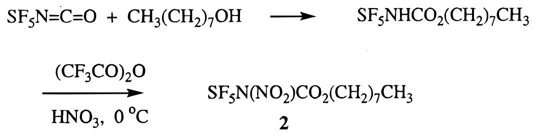
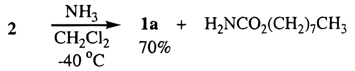
the dinitramide salt via a displacement reaction from dinitrocarbamate [$(NO_2)_2NCO_2Et$].[5] For the analogous synthesis of **1,** the required $SF_5NNO_2CO_2R_2$ are available via nitration of $SF_5NHCO_2R_2$, obtained by condensation of $SF_5N{=}C{=}O$ with R_2OH.[3d] The particular $SF_5NNO_2CO_2R_2$ chosen for the synthesis of **1** was *N*-(pentafluorosulfanyl)-*N*-nitro octyl carbamate (**2**) (see eq 1), mainly because of its ease of handling (low volatility).

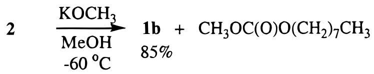


$$SF_5N{=}C{=}O + CH_3(CH_2)_7OH \longrightarrow SF_5NHCO_2(CH_2)_7CH_3 \xrightarrow[HNO_3,\ 0\ ^{\circ}C]{(CF_3CO)_2O} \underset{\mathbf{2}}{SF_5N(NO_2)CO_2(CH_2)_7CH_3} \quad (1)$$

The first SF_5-nitramide salt synthesized via **2** was **1a** (eq 2),[6] which was then employed to prepare **1b** via ion exchange.[6] However, an improved synthesis of **1b**, directly from **2**, has now been developed (eq 3).



$$\mathbf{2} \xrightarrow[CH_2Cl_2,\ -40\ ^{\circ}C]{NH_3} \underset{70\%}{\mathbf{1a}} + H_2NCO_2(CH_2)_7CH_3 \quad (2)$$

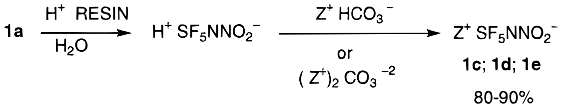


$$\mathbf{2} \xrightarrow[MeOH,\ -60\ ^{\circ}C]{KOCH_3} \underset{85\%}{\mathbf{1b}} + CH_3OC(O)O(CH_2)_7CH_3 \quad (3)$$

We also had interest in metal SF_5-nitramide salts, $M(SF_5NNO_2)_x$, that would offer (in comparison to the potassium salt **1b**) increased fluorine levels relative to the weight of metal. The fluorine-to-metal ratios (atoms of F/g of M) in various M $(SF_5NNO_2)_x$ show the following order: Li ($x = 1$), $5/7 = 0.71$; Al ($x = 3$), $15/27 = 0.56$; Mg ($x = 2$), $10/42 = 0.42$; Na ($x = 1$), $5/23 = 0.22$; K ($x = 1$), $5/39 = 0.13$. From the standpoint of increased fluorine level, $Li(SF_5NNO_2)$ appears particularly attractive, followed by the Al and Mg salts.

An initial attempt to prepare $Li(SF_5NNO_2)$ by the treatment of **2** with $LiOCH_3$/MeOH (similar to the preparation of **1b**; see Experimental Section) appeared to give a high concentration of the desired lithium salt in the reaction solution (by TLC analysis; visualization with UV light). However, all attempts to isolate the salt from the solution resulted in decomposition to products that were no longer UV active, a strong indication that the $SF_5NNO_2^-$ moiety was no longer present.

Another approach to the synthesis of $Li(SF_5NNO_2)$ was from **1a** via ion exchange, using a method similar to that developed for $Z^+N(NO_2)_2^-$ (a method based on the formation of $H^+N(NO_2)_2^-$, which is prepared in aqueous solution and shortly thereafter neutralized to give various $Z^+N(NO_2)_2^-$).[2a] In this study, we determined that pentafluorosulfanylnitraminic acid, $H(SF_5NNO_2)$, can be prepared from **1a** via ion exchange and then neutralized with the appropriate bicarbonate or carbonate to give the sodium, guanidinium, and aminoguanidinium SF_5-nitramide salts (**1c**,**d**,**e**) (eq 4).



$$\mathbf{1a} \xrightarrow[H_2O]{H^+\ RESIN} H^+\ SF_5NNO_2^- \xrightarrow[(Z^+)_2\,CO_3^{-2}]{Z^+\ HCO_3^-\ \text{or}} \underset{\substack{\mathbf{1c};\ \mathbf{1d};\ \mathbf{1e}\\ 80\text{-}90\%}}{Z^+\ SF_5NNO_2^-} \quad (4)$$

However, when $H(SF_5NNO_2)$ in H_2O was similarly neutralized with Li_2CO_3 to give the lithium salt in solution (analyzed by TLC and ^{19}F NMR), all attempts to isolate the salt resulted in its decomposition. Similarly, the Mg and $Al(SF_5NNO_2)_x$ salts also decomposed during attempts to isolate them from their aqueous solutions. (A description of the attempts to prepare and isolate these salts is given in the Experimental Section).

Stabilities of M $(SF_5NNO_2)_x$. The Li, Mg, and $Al(SF_5NNO_2)_x$ salts appear to be inherently unstable in the solid state. A possible rationale for this instability is that preferential metal complexation with oxygen vs nitrogen in these salts results in loss of resonance stabilization, leading to decomposition.

Another potential driving force for the instability of the Li, Mg, and $Al(SF_5NNO_2)_x$ salts is the precipitation of insoluble fluoride salts[7] from concentrated solutions of these SF_5-nitramide salts.

Characterization of 1. (a) ^{19}F NMR Spectral Data. The ^{19}F NMR spectra of **1** exhibit only a doublet and a quintet, an absorption pattern that is characteristic of the SF_5 group (four F syn and one F anti to the NNO_2 group).

(b) IR Spectral Data. The infrared spectra of **1** contain two strong peaks of about equal intensity in the 1400−1300 cm^{-1} region (characteristic of $R{-}N{-}NO_2^-$). In addition, the IR spectra contain strong absorptions in the 900−800 cm^{-1} region, which is characteristic of the SF_5 group.

(c) Physical Properties. The melting points and densities of **1** are listed in Table 1 and are compared with data for $Z^+N(NO_2)_2^-$. It is seen that compounds **1** are significantly more dense than the corresponding $Z^+N(NO_2)_2^-$ but are less thermally stable.

Description of the Crystal Structures of SF_5-Nitramide Salts: $NH_4(SF_5NNO_2)$ (1a), $K(SF_5NNO_2)$ (1b), $NH_2C({=}NH_2)NH_2(SF_5NNO_2)$ (1d), and $NH_2C({=}NH_2)NHNH_2(SF_5NNO_2)$ (1e). In recent times, there has been considerable interest in the structural chemistry of the SF_5 moiety, as evidenced by its appearance in numerous reports containing X-ray crystal structures. In these articles, the SF_5 group appears as an anion,[8a] as part of an oxyanion,[8b] and as part of larger anions.[8c−f] It

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(6) Koppes, W. M.; Sitzmann, M. E. Pentafluorosulfanylnitramide Salts. U.S. Patent 5,441,720, 1995.

(7) *The Merck Index, 10th ed.*; Merck & Co., Inc.: Rahway, NJ, 1983. The solubilities of the Li, Mg, and Al fluoride salts in water are 0.13 g/100 mL (25 °C), 87 mg/L (18 °C), and 0.559 g/100 mL (25 °C), respectively. By contrast, the solubilities of the K, Na, and NH_4 fluoride salts are 96.4 g/100 mL (21 °C), 4.3 g/100 mL (25 °C), and 100 g/100 mL, respectively.

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Table 1. Comparison of Physical Properties of Pentafluorosulfanylnitramide and Dinitramide Salts

Z	mp (°C)[a]		density (g/cm^3)	
	$Z^+SF_5NNO_2^-$	$Z^+N(NO_2)_2^-$	$Z^+SF_5NNO_2^-$	$Z^+N(NO_2)_2^-$
NH_4	93	94	2.16	1.80
K	137	139	2.56	2.20
$H_2NC({=}NH_2)NH_2$	127	135	1.94	1.67
$H_2NC({=}NH_2)NHNH_2$	70	91	1.96	1.65
Na	78	107		

[a] Decomposition point for $Z^+SF_5NNO_2^-$; slow decomposition for $Z^+N(NO_2)_2^-$.

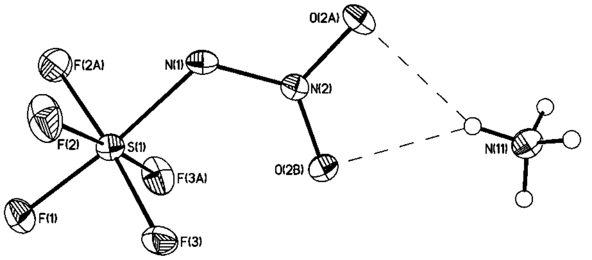

Figure 1. Formula unit and labeling scheme used for ammonium pentafluorosulfanylnitramide (**1a**).

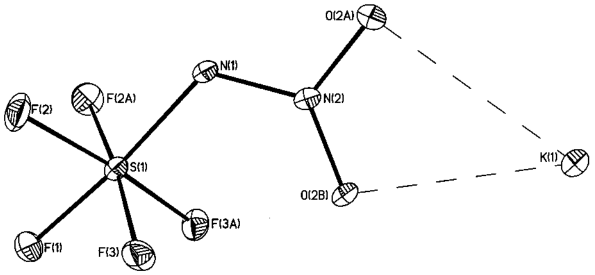

Figure 2. Formula unit and labeling scheme used for potassium pentafluorosulfanylnitramide (**1b**).

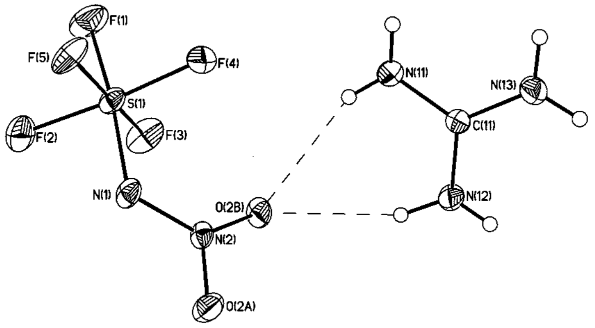

Figure 3. Formula unit and labeling scheme used for guanidinium pentafluorosulfanylnitramide (**1d**).

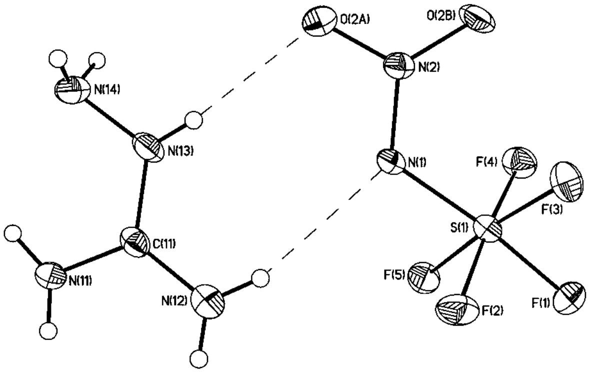

Figure 4. Formula unit and labeling scheme used for aminoguanidinium pentafluorosulfanylnitramide (**1e**).

Table 2. Metrical Parameters (Å, deg) for the Pentafluorosulfanyl Moiety in Its Anions

	nitramide ion			
	1a	**1b**	**1d**	**1e**
S1−F1	1.573(3)	1.574(2)	1.574(2)	1.583(3)
S1−F2	1.572(2)	1.5803(17)	1.571(2)	1.575(3)
S1−F3	1.567(2)	1.5783(16)	1.566(2)	1.562(3)
S1−F4	1.567(2)[a]	1.5783(16)[a]	1.562(2)	1.574(3)
S1−F5	1.572(2)[a]	1.5803(17)[a]	1.559(2)	1.580(3)
N1−S1−F1	174.7(2)	174.61(13)	174.6(1)	174.4(2)
N1−S1−F2	88.9(1)	88.84(9)	88.7(1)	88.8(2)
N1−S1−F3	95.8(1)	96.33(9)	95.5(1)	96.8(2)
N1−S1−F4	95.8(1)[a]	96.33(9)[a]	96.1(2)	96.1(2)
N1−S1−F5	88.9(1)[a]	88.84(9)[a]	88.9(1)	88.7(2)
F1−S1−F2	87.3(1)	87.33(9)	86.9(2)	87.5(2)
F1−S1−F3	87.8(1)	87.43(9)	87.5(1)	87.5(2)
F1−S1−F4	87.8(1)[a]	87.43(9)[a]	88.2(2)	87.4(2)
F1−S1−F5	87.3(1)[a]	87.33(9)[a]	87.9(1)	86.9(2)
F2−S1−F3	89.4(2)	89.49(11)	89.3(2)	90.2(2)
F2−S1−F4	175.0(1)[a]	174.67(9)	175.0(1)	174.7(2)
F2−S1−F5	89.2(2)[a]	89.31(16)[a]	88.7(2)	88.6(2)
F3−S1−F4	91.5(2)[a]	91.23(14)[a]	91.4(2)	91.2(2)
F3−S1−F5	175.0(1)[a]	174.67(9)[a]	175.2(1)	174.3(2)
F4−S1−F5	89.4(2)[a]	89.49(11)[a]	90.3(1)	89.5(2)

[a] In **1a**,**b**, F2/F5 and F3/F4 are related by a crystallographically imposed mirror symmetry.

also appears attached to carbon in many neutral organic[8g−n] and organometallic[8d,j,o−q] compounds.

In seven previously determined structures containing the N−SF$_5$ moiety,[3e,8j,r,s] the observed geometries are remarkably similar (see Table S30 in the Supporting Information). In the absence of steric effects due to substituents on the central nitrogen atoms, equivalent bond lengths and bond angles of the N−SF$_5$ moiety show remarkable agreement. In all of these N−SF$_5$ structures a similar numbering scheme has been chosen to facilitate comparisons. If one looks down the F(1)−S−N axis with the projection of the N−N vector in the vertical plane, the equatorial F atoms are numbered from F(2) to F(5) in a counterclockwise sense starting from the bottom left. Figures 1−4 show the formula units for each structure and illustrate the numbering scheme used.

Using this numbering scheme, some general trends can be observed in the seven previous structures containing the N−SF$_5$ moiety as well as those in this study. The N−S−F2 and N−S−F5 angles are always less than 90°, and the N−S−F3 and N−S−F4 angles are always greater than 90°. In **1a**,**b**,**d**,**e** the average of the former is 88.83(8)° while the average of the latter is 96.10(38)°. This corresponds to a tipping of the SF$_5$ group away from the direction of greatest congestion, the substituent on the central amine N atom (cf. Figure 4). Table 2 contains comparative metric data for the four new SF$_5$NNO$_2$ salts reported herein.

Dinitramides, and the four SF$_5$-nitramide salts reported herein, contain nitramine (N−NO$_2$) groups, but the characteristics of the N−NO$_2$ moieties are quite different. The N−N bond lengths most clearly illustrate this. In dinitramide salts, the two N−N bonds in each anion are usually asymmetric, averaging 1.381

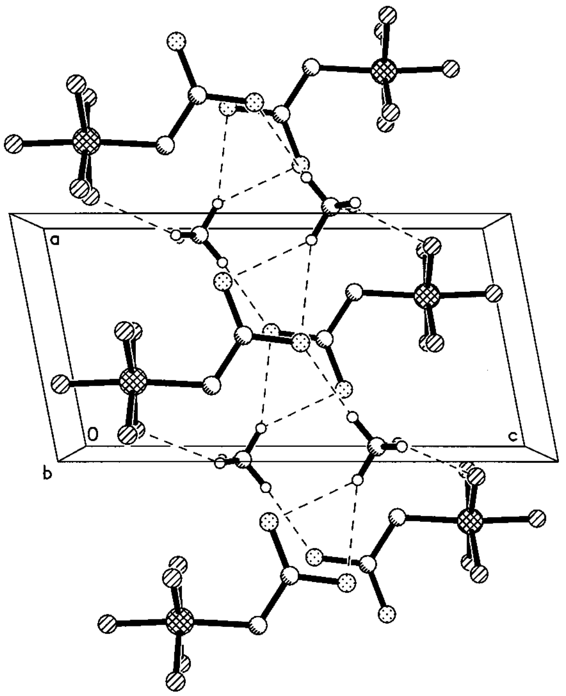

Figure 5. Packing diagram for ammonium pentafluorosulfanylnitramide (**1a**).

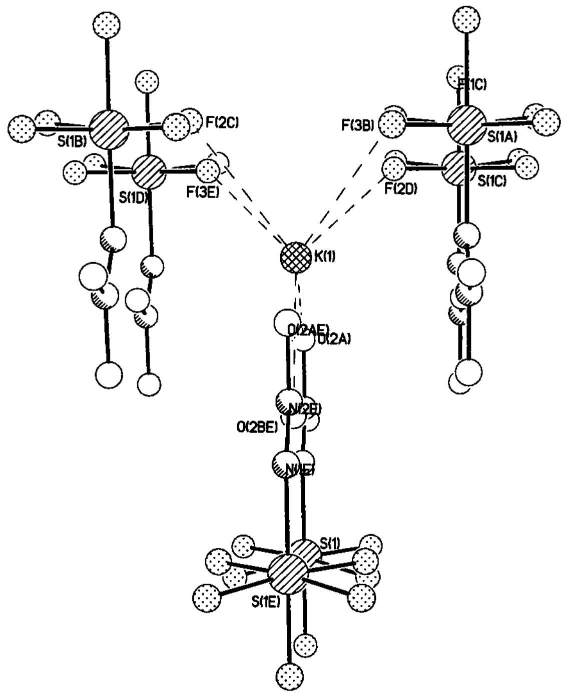

Figure 6. Packing diagram for potassium pentafluorosulfanylnitramide (**1b**) showing the trigonal prismatic coordination environment about the potassium ion.

Å for the longer and 1.356 Å for the shorter.[2b−2i] In the N−SF$_5$ salts, there is just one N−N bond length, which is considerably shorter than either of these lengths at 1.297(6), 1.316(4), 1.301(4), and 1.317(5), for **1a**,**b**,**d**,**e**, respectively. Thus, in these latter salts, this bond has values which place it much closer to N=N compared to N−N and this indicates that, in all N−SF$_5$ structures, N(1) is sp^2 hybridized. This is also borne out by the S−N−N angle which is very close to 120° in all cases compared to the N−N−N angles in the dinitramide structures which have an average value of 114.9°.

A search of the Cambridge Structural Database for compounds containing the N−NO$_2$ moiety gave 408 hits. For the N−N bond, a mean value of 1.374(38) Å was obtained with minimum and maximum values of 1.266 and 1.494 Å. A survey of all those examples where the N−N distance was less than 1.340 Å showed 27 examples, of which 5 were charged compounds, 13 were neutral compounds, and 9 were compounds in which the N−NO$_2$ was a ligand in a metal complex. In these three types of nitramine compounds containing short N−N bonds, the average length of this bond was 1.310(18), 1.322(13), and 1.294(17) Å, respectively, for those containing charged, uncharged, and chelated nitramine moieties. For compounds **1a**−**e** which contain the (NO$_2$)N(SF$_5$)$^-$ ion, the average N−N bond length of 1.308(9) Å is similar to those of other structures containing an anionic N−NO$_2$ moiety.

The packing of **1a** is dominated by the hydrogen-bonding interactions of the ammonium protons with the anion. Two protons link anions in the *ac* plane to form two antiparallel chains in the *a* direction (see Figures S1−S3 in Supporting Information). These two antiparallel chains are linked via hydrogen bonds between the other two protons of the ammonium ion and fluorine atoms of adjoining anions to form zigzag chains in the *bc* plane in the *c* direction; the overall packing scheme is illustrated in Figure 5.

In **1b**, the potassium ion is in an eclipsed trigonal prismatic environment, being surrounded by four fluorine and two oxygen atoms, as is shown in Figure 6. This can also be clearly seen in the bond angles subtended at K where the largest trans angle is only 138.9(1)°.

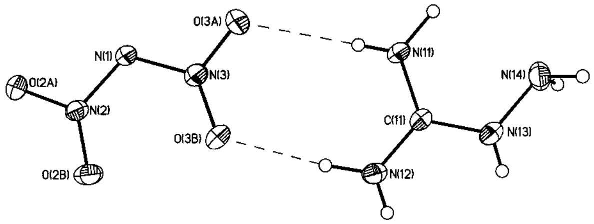

Figure 7. Formula unit and labeling scheme used for the monoclinic polymorph of aminoguanidinium dinitramide (**3a**).

The packing assemblies of both **1d** and **1e** are dominated by multiple hydrogen-bonding interactions between the cation protons and the oxygen and fluorine atoms of the anion. In **1d**, the hydrogen bonding is such that there are sheets primarily in the *bc* plane made up of six pairs of anions and cations linked in a circular fashion. These sheets are linked together by further hydrogen bonds to make up a three-dimensional network.

Description of Two Crystal Structures for Aminoguanidinium Dinitramide NH$_2$C(=NH$_2$)NHNH$_2$[N(NO$_2$)$_2$] (3). Monoclinic (**3a**) and triclinic (**3b**) crystal forms have been found in samples of **3**. The two forms have been analyzed by X-ray diffraction and, though different, both are extensively linked by hydrogen bonding. Figures 7 and 8 show the formula unit and atom labeling for **3a**,**b**, respectively. In structures containing the dinitramide anion, there is often considerable asymmetry[2b−i] in the two halves of the anion, apart from those examples where there is crystallographically imposed symmetry.[2d,f] To facilitate comparisons between the structures of dinitramide salts, a consistent labeling scheme has been used on the basis of this asymmetry in which the N1−N2 bond is longer than the N1−N3 bond and O2A and O3A are the exterior (anti) oxygen atoms while O2B and O3B are the interior (syn) oxygen atoms.

Ab initio and other theoretical calculations[2c,9] on the dinitramide anion have concluded that the potential energy

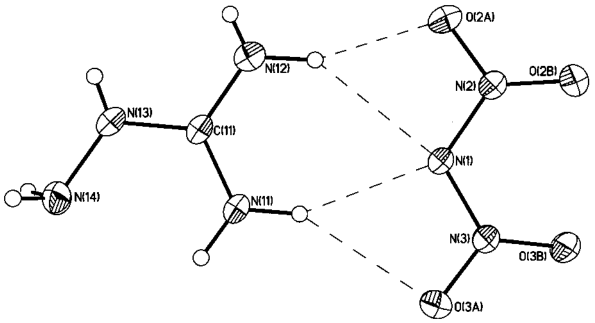

Figure 8. Formula unit and labeling scheme used for the triclinic polymorph of aminoguanidinium dinitramide (**3b**).

surface for rotation of the nitro groups is very shallow. It was found[2c] that the important factors in producing molecular orbitals similar to those found for experimental geometries were inequivalent N−N bond lengths, some twisting of the nitro groups, and a smaller NNN angle than that predicted from optimized geometry. Of particular interest in dinitramide structures is both the asymmetry in the N−N bond lengths and the value of the NNN bond angle. In all dinitramide structures this angle is intermediate between that expected for sp^2 and sp^3 hybridization of the central N atom. If this atom was sp^2 hybridized, this would allow complete delocalization of the π electrons while sp^3 hybridization allows the two independent conjugated halves of the molecule to twist while still remaining conjugated to one of the lone pairs on the central N atom. Calculations suggest that a 27° twist of the NO_2 out of the NNN plane as the best geometry for a conjugated system with a sp^3-hybridized central N atom and a 0° twist for a sp^2-hybridized central N atom.[10] From these studies, it can be seen that the metrical parameters of the dinitramide ion can be strongly influenced by its environment.

Previous structural determinations[2b−i] of salts containing the dinitramide ion have shown that this entity actually does exhibit considerable flexibility. Table 3 lists the metrical parameters, while Table 4 lists conformational parameters relating to the dinitramide ions in **3a**,**b**. Since **3a**,**b** are polymorphs, any differences in the metrical parameters of the dinitramide ion in these structures can be ascribed to the differences in their packing and in their hydrogen-bonding scheme. As it turns out, the hydrogen-bonding arrangements and the anionic conformations are similar in many respects, but there are qualitative differences. For both **3a**,**b**, all except one of the hydrogen bonds are nearly parallel to the plane of the dinitramide ion. This has the effect of constraining the conformations adopted by the terminal NO_2 groups to be very close to planar. The dinitramide ions in **3a**,**b** adopt conformations (see Table 4) in which the terminal NO_2 groups are rotated by only 2.9 and 3.3° (for **3a**) and 6.0 and 7.8° (for **3b**) from the N1−N2−N3 plane. In structures of other less constrained dinitramide ions, rotations of up to 30.3° [2e] have been observed. Figures 7 and 8 show, in each case, the bidentate planar hydrogen bonding between the cation and anion in the formula unit. However, there is a fundamental difference; in **3a**, the two hydrogen bonds are accepted by a nitro group at one end of the anion, while in **3b** they are accepted by the central nitrogen atom and two nitro oxygen atoms at the side of the anion. Other hydrogen bonds link the ions into sheets; in **3b**, there is also one out-of-plane hydrogen bond linking these sheets.

Conclusions

Certain SF_5-nitramide salts, $Z^+SF_5NNO_2^-$, were successfully prepared via nucleophilic displacements from carbamates and/or ion exchange techniques. Although these same methods appeared to give solutions containing high concentrations of Li, Mg, and $Al(SF_5NNO_2)_x$, these particular salts are apparently unstable in the solid state and decomposed during isolation procedures. The instabilities of these salts may be due to metal complexation with oxygen which causes a loss of resonance stabilization. Another possible driving force for these instabilities is the formation of insoluble fluoride salts. Compared to the corresponding dinitramide salts, the SF_5-nitramide salts are less thermally stable but are significantly more dense.

The structures reported herein contain two related types of anions, $N(NO_2)_2^-$ and $SF_5N(NO_2)^-$. From a structural point of view, the major difference between them concerns the N−N distances and the angles subtended at the central nitrogen atom. In **3**, there are two nonequivalent N−N (average lengths 1.372(2) and 1.354(2) Å) with an average N−N−N angle of 115.8(3)°. On the other hand, in **1a**,**b**,**d**,**e** the average N−N distance is 1.308(9) Å and the average N−N−S angle is 120.0(5)°. For the former this clearly indicates a hybridization of the central N which is neither sp^3 nor sp^2 while in the latter the hybridization of the central N is clearly more closely related to sp^2. The dinitramide anions are only slightly distorted from planarity due to predominantly in-plane hydrogen-bonding interactions.

The most striking feature of the pentafluorosulfanylnitramide anion is its remarkable metrical similarity in all crystal structures. The structure of this anion is apparently intrinsically rigid; this is in marked contrast to the dinitramide salts where there is a range in the conformations adopted by the anions in different environments.[2b−i]

Experimental Section

CAUTION! *Compounds* **1** *are energetic oxidizers and can be explosive under certain conditions. They should be handled with care behind adequate shielding.*

Reagents. The preparation and purification of $SF_5N{=}C{=}O$,[3a] $SF_5N{=}CCl_2$,[11] and $SF_5N(NO_2)CO_2(CH_2)_7CH_3$ (**2**)[3d] have been described previously. $KOCH_3$/MeOH was prepared by cautious addition of potassium metal (washed with hexane to remove mineral oil) to MeOH, which was under N_2 and cooled in an ice bath. Other reagents used were commercially available.

Measurements. ^{19}F NMR spectra for **1** were recorded from H_2O solutions using a Varian XL-200 spectrometer with $CFCl_3$ as the external reference at 0 ppm. Infrared spectra were from solids in pressed KBr pellets and were recorded in cm^{-1} with a Perkin-Elmer model 1600 series FT-IR spectrometer. Melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. TLC was performed using 250 μm Silica gel GF plates with CH_3CN/CH_2Cl_2 (50/50) as the developer (all **1** exhibit an R_F of approximately 0.3 under these conditions).

Elemental analyses for **1** were performed by Galbraith Laboratories, Inc., Knoxville, TN. The salts with high oxidant balance (i.e., little or no fuel in Z^+; **1a**−**c**) tended to give poor analyses, whereas the salts containing appreciable fuel in Z^+(**1d**,**e**) gave acceptable results. Thus,

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Table 3. Metrical Parameters (Å, deg) for Dinitramide Anions and Nitramide Fragments in SF_5NNO_2 Anions

	crystal					
	1a	**1b**	**1d**	**1e**	**3a**	**3b**
N1−N2	1.297(6)	1.316(4)	1.301(4)	1.317(5)	1.370(4)	1.375(3)
N1−N3/S1	1.709(4)	1.693(3)	1.692(3)	1.681(4)	1.352(4)	1.355(3)
N2−O2A	1.259(5)	1.252(4)	1.263(3)	1.251(5)	1.233(4)	1.240(3)
N2−O2B	1.258(5)	1.251(3)	1.231(3)	1.252(4)	1.209(4)	1.195(3)
N3−O3A					1.239(5)	1.239(3)
N3−O3B					1.219(4)	1.208(3)
N2−N1−N3/S1	119.5(3)	119.4(2)	120.6(2)	120.4(3)	116.1(3)	115.6(2)
N1−N2−O2A	115.3(4)	114.6(2)	113.6(2)	114.8(3)	111.4(3)	110.6(3)
N1−N2−O2B	126.1(4)	125.8(3)	126.8(3)	125.0(4)	126.6(3)	126.5(3)
O2A−N2−O2B	118.6(4)	119.6(3)	119.6(2)	120.2(4)	122.0(3)	122.8(3)
N1−N3−O3A					111.7(3)	112.2(3)
N1−N3−O3B					126.0(3)	125.9(3)
O3A−N3−O3B					122.3(3)	121.8(2)

Table 4. Selected Twist and Torsion Angles and Distances for the Dinitramide Anions in **3a**,**b**

param	**3a**	**3b**
twist$_i$[a] (deg)	2.9	7.8
twist$_j$[a] (deg)	3.3	6.0
bend$_i$[b] (deg)	0.2	2.7
bend$_j$[b] (deg)	0.4	1.5
O···O[c] (Å)	2.494	2.506
tors[d] (deg)	0.5	12.0
mean dev[e] (Å)	0.016	0.031
dev O2B, O3B[f] (Å)	0.02, 0.009	0.19, 0.18

[a] A measure of the amount by which either nitro group (the *i*th or the *j*th) has rotated out of the N2−N1−N3 plane, which is calculated by averaging the two N−N−N−O torsion angles for a particular nitro group (values are first brought below 90° by adding or subtracting 180°). [b] This represents the pyramidalization of the nitro N atoms with expected values of 0° for ideal sp^2 and 54.8° for ideal sp^3 conformations. [c] The separation of the two closest nitro oxygen atoms. [d] A pseudo-torsion angle defined between the two closest N−O bonds in the molecule belonging to different nitro groups, e.g., O2B−N2···N3−O3B. [e] Mean deviation (Å) from the plane defined by O2A, N2, N1, N3, and O3A. [f] Deviation of O2B and O3B from plane defined above.

our primary evidence of high purity for all **1** is based on their ^{19}F NMR spectra (only peaks present were a doublet and a quintet for the SF_5 group). Additional evidence for the purity of the salts includes their constant melting points, consistent IR spectra, and TLC behavior (exhibiting only one spot).

Preparation of 1a. Treating **2** with NH_3 in CH_2Cl_2 precipitates **1a** with mp 89−92 °C, dec.[6] In this study, additional purification [chromatography on Silica gel 60; CH_3CN/CH_2Cl_2 (50/50) as eluent], was used to give mp 93−94 °C, dec. ^{19}F NMR: δ 83.7 (quintet), 61.7 (d). IR: 3148 (NH), 1404, 1345 (NNO_2), 867−789 (SF_5). Anal. Calcd for $H_4F_5N_3O_2S$: H, 1.97; F, 46.31; N, 20.49; S, 15.63. Found: C, <0.5; H, 1.98; F, 45.88; N, 22.11; S, 16.32.

Preparation of 1b. An improved method for **1b** directly from **2** and $KOCH_3$/MeOH is as follows: A solution containing **2** (0.72 g, 2.09 mmol) in MeOH (5 mL) was stirred at −50 to −60 °C, while adding dropwise a solution (3.7 mL) containing $KOCH_3$ (0.16 g, 2.28 mmol) in MeOH. The solution was allowed to warm and then was held in a water bath at 25 °C while the volatiles were removed under reduced pressure. The residue was stirred with CH_2Cl_2 to give 0.41 g (87%) of white crystals, mp 130−133 °C, dec. Two recrystallizations, by dissolving the product in a small amount of MeOH and adding CH_2Cl_2, gave a 70% yield of crystals, mp 137−138 °C, dec. ^{19}F NMR: δ 83.7 (quintet), 61.7 (d). IR: 1413,1343 (NNO_2), 874−788 (SF_5). Anal. Calcd for $F_5KN_2O_2S$: F, 42.00; K, 17.29; N, 12.39; S, 14.18. Found: F, 36.86; K, 17.58; N, 11.89; S, 13.69.

Preparation of 1c. A solution of **1a** (0.21 g, 1.02 mmol) in 2 mL of distilled H_2O was added onto a column containing 9 g of Dowex 50 × 2-100 ion-exchange resin (prewashed with distilled H_2O). Distilled H_2O was used for elution, and the fractions containing $H(SF_5NNO_2)$ were quickly determined by spotting the fraction onto a TLC plate and visualizing with UV light. The combined fractions (total of 25 mL) were quickly neutralized with sodium carbonate (0.06 g, 0.55 mmol) before the H_2O was allowed to evaporate in a current of air in the hood overnight. The crystalline residue was dried for several hours in a vacuum desiccator (over Drierite) to yield 0.22 g (100%) of product, mp 77−78 °C, dec. Dissolution in a very small amount of MeOH, followed by the addition of CH_2Cl_2, gave 0.19 g (90%) of white crystals, mp 78−79 °C, dec. ^{19}F NMR: δ 83.7 (quintet), 61.7 (d). IR: 1412, 1347 (NNO_2), 867−788 (SF_5). Anal. Calcd for $F_5N_2NaO_2S$: F, 45.22; N, 13.34; S, 15.26. Found: F, 35.97; N, 12.49; S, 14.08.

Preparation of 1d. A solution of $H(SF_5NNO_2)$ was prepared in the same manner as for the synthesis of **1c** described above. Neutralization with guanidine carbonate, $[NH_2C({=}NH)NH_2]_2{\cdot}H_2CO_3$, followed by removal of water as above, gave 100% yield of crystals, mp 122−124 °C, dec. Dissolution in a small amount of CH_3CN, followed by the addition of CH_2Cl_2, gave a 79% yield of white crystals, mp 127−128 °C, dec. ^{19}F NMR: δ 83.7 (quintet), 61.7 (d). IR: 3445−3212 (NH), 1666 (C=N), 1384,1317 (NNO_2), 884−771 (SF_5). Anal. Calcd for $CH_6F_5N_5O_2S$: C, 4.86; H, 2.45; F, 38.44; N, 28.34; S, 12.96. Found: C, 5.10; H, 2.53; F, 37.82; N, 28.47; S, 12.72.

Preparation of 1e. Using the same procedure as described above for **1d**, but substituting aminoguanidine bicarbonate $[NH_2C({=}NH)\text{-}NHNH_2{\cdot}H_2CO_3]$ in the neutralization step, gave after crystallization from CH_3CN/CH_2Cl_2 a 70% yield of white crystals, mp 70−72 °C, dec. ^{19}F NMR: δ 83.7 (quintet), 61.7 (d). IR: 3488−3178 (NH), 1681, 1666 (C=N), 1395, 1319 (NNO_2), 892−773 (SF_5). Anal. Calcd for $CH_7F_5N_6O_2S$: C, 4.58; H, 2.69; F, 36.23; N, 32.06; S, 12.23. Found: C, 4.74; H, 2.79; F, 36.41; N, 32.40; S, 12.41.

Attempted Preparation of $Li(SF_5NNO_2)$. Treatment of **2** with $LiOCH_3$/MeOH, similar to the preparation of **1b** described above, gave a methanol reaction solution that appeared by TLC analysis to contain a high concentration of the desired $Li(SF_5NNO_2)$; i.e., there was a very strong spot (visualized with UV light) at $R_F = 0.30$ (same R_F as for all **1**). In all attempts to isolate the salt by removal of the solvent, it was converted to materials that were not visible on a TLC plate with UV light. This loss of UV activity showed that the $SF_5NNO_2^-$ group was no longer present.

An attempt to prepare and isolate $Li(SF_5NNO_2)$, by a method analogous to the preparation of **1c** from $H(SF_5NNO_2)$ as described above (using Li_2CO_3 for neutralization), also failed. Again, TLC analysis of the neutralized aqueous solution indicated a high concentration of the desired $Li(SF_5NNO_2)$, but removal of the water from the aqueous solution left a residue that showed no activity with UV light. An immediate workup of a small sample of the aqueous solution by rapid removal of H_2O under vacuum in a desiccator over Drierite gave the same result (the residue showed no UV activity). The ^{19}F NMR spectrum of the aqueous solution (shortly after its preparation) indicated only the presence of $Li(SF_5NNO_2)$. ^{19}F NMR: δ 83.6 (quintet), 61.7 (d). After standing overnight in the NMR tube, the aqueous solution (by ^{19}F NMR) still contained mainly $Li(SF_5NNO_2)$, but small peaks at δ 42.3, −7.3, and −128 were also present at that time.

Table 5. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

param	**1a**	**1b**	**1d**	**1e**	**3a**	**3b**
formula	$H_4F_5N_3O_2S$	$F_5N_2O_2SK$	$CH_6F_5N_5O_2S$	$CH_7F_5N_6O_2S$	$CH_7N_7O_4$	$CH_7N_7O_4$
M_r	205.12	226.18	247.17	262.19	181.14	181.14
system	monoclinic	monoclinic	monoclinic	triclinic	monoclinic	triclinic
space group	$P2_1/m$	$P2_1/m$	$P2_1/n$	$P\bar{1}$	Pc	$P\bar{1}$
a (Å)	5.3534(4)	5.170(2)	5.3674(3)	7.0662(8)	3.599(1)	7.097(3)
b (Å)	5.5989(4)	5.4260(10)	12.6148(9)	8.096(1)	7.279(1)	7.360(3)
c (Å)	10.5851(9)	10.577(4)	12.544(1)	8.3129(9)	13.938(2)	8.251(3)
α (deg)	90	90	90	92.190(9)	90	105.34(3)
β (deg)	101.055(9)	101.49(3)	93.926(9)	107.875(9)	93.27(2)	94.59(4)
γ (deg)	90	90	90.0	99.145(7)	90.0	115.12(3)
V (Å^3)	311.38	290.76(17)	847.4(1)	444.95(9)	364.5(1)	367.1(3)
Z	2	2	4	2	2	2
D_c (mg/mm^3)	2.188	2.583	1.937	1.957	1.650	1.639
cryst size (mm)	0.34 × 0.30 × 0.03	0.60 × 0.40 × 0.02	0.46 × 0.45 × 0.17	0.47 × 0.12 × 0.02	0.30 × 0.15 × 0.06	0.20 × 0.20 × 0.05
cryst color	colorless	colorless	colorless	colorless	colorless	colorless
temp (°C)	223(2)	293(2)	295(2)	294(2)	293(2)	294(2)
λ (wavelength) (Å)	1.541 78	0.710 73	1.541 78	1.541 78	1.541 78	1.541 78
μ (abs coeff) (mm^{-1})	5.517	1.337	4.261	4.136	1.383	1.374
goodness of fit	1.104	1.074	1.060	1.049	1.162	1.060
R-factors[a] R(F)	0.0518	0.0460	0.0558	0.0638	0.0361	0.1056
(all data) wR(F^2)	0.1353	0.1128	0.1593	0.1187	0.0764	0.1292
R-factors[a] R(F)	0.0468	0.0417	0.0536	0.0426	0.0356	0.0481
$[I > 2\sigma(I)]$ wR(F^2)	0.1303	0.1051	0.1502	0.1021	0.0859	0.1113

[a] R-factors: $R = \sum|F_o| - |F_c||/\sum|F_o|$ and $R_w = \{\sum(w\Delta^2)/\sum[(F_o^2)^2]\}^{1/2}$, wherein $\Delta = (F_o^2 - F_c^2)$. [b] Scattering factors: Atomic scattering factors from ref 13.

Attempted Preparations of $Mg(SF_5NNO_2)_2$ and $Al(SF_5NNO_2)_3$. A column of ion-exchange resin, saturated with either Mg or Al ions, was prepared by passing aqueous $MgSO_4$ or $Al(NO_3)_3{\cdot}9H_2O$, respectively, through Dowex 50 × 2-100 ion-exchange resin (prewashed with distilled H_2O). Aqueous **1a** was added onto the Mg and Al ion-exchange columns which were then washed with water to give solutions appearing to contain the Mg or Al SF_5NNO_2 salt (by TLC analysis with UV light). However, removal of the water from the solutions gave residues that exhibited no UV activity, indicating both salts decomposed under these conditions.

Preparation of $Z^+N(NO_2)_2^-$. $NH_2C(=NH_2)NHNH_2[N(NO_2)_2]$ (3). The aminoguanidinium dinitramide salt was prepared as follows: A mixture of $Ba(OH)_2{\cdot}8H_2O$ (1.05 g, 3.33 mmol, purity = 83% based on H_2O solubility) in distilled water (25 g) was stirred for 15 min before it was filtered to remove insoluble $BaCO_3$. The filtrate was stirred under N_2 while aminoguanidinium sulfate (0.88 g, 3.33 mmol) was added, after which the mixture was filtered to remove the precipitate of $BaSO_4$. The filtrate was stirred under N_2, and ammonium dinitramide (0.96 g, 7.7 mmol) was added in one portion. Removal of the H_2O under reduced pressure and drying the residue gave white crystals (1.20 g, 99%, mp 70−79 °C). Several recrystallizations from ethyl acetate raised the mp to 91−94 °C. Anal. Calcd for $CH_7N_7O_4$: C, 6.63; H, 3.90; N, 54.14. Found: C, 6.79; H, 3.69; N, 53.79.

Preparation of Precursors to SF_5-Nitramide Salts. (a) $SF_5NHCOOCMe_3$. Freshly distilled Me_3COH (3 mL, 32 mmol) was frozen at −196 °C and degassed by several freeze−thaw cycles before $SF_5N{=}C{=}O$ (1.35 g, 8 mmol) was condensed onto the frozen alcohol. After 2 h at 25 °C, the excess alcohol was evaporated and the residue was vacuum sublimed at 35 °C to give 0.94 g (48%) of white crystals, mp 110−111 °C. ^{19}F NMR ($CDCl_3$ + 1% TMS): δ_A 75.6, δ_B 70.9, J_{AB} = 155 Hz. ^1H NMR ($CDCl_3$ + 1% TMS): δ 1.50 (CH_3), 7.26 (NH). ^{13}C NMR ($CDCl_3$ + 1% TMS): δ 28 [$(CH_3)_3$], 84 (CMe_3), 148 (NHCO). Anal. Calcd for $C_3H_{10}F_5NO_2S$: C, 24.69; H, 4.14; N, 5.76; S, 13.18. Found: C, 24.61; H, 4.17; N, 5.74; S, 13.50.

(b) $SF_5NHCOOCH_2CH_2SiMe_3$. Anhydrous ether (2 mL) and freshly distilled $Me_3SiCH_2CH_2OH$ (1.5 mL, 10.5 mmol) were frozen at −196 °C and degassed by several freeze−thaw cycles before $SF_5N{=}C{=}O$ (0.85 g, 5 mmol) was condensed onto the frozen mixture. After 12 h at 25 °C, removal of the solvent and vacuum sublimation of the residue at 35 °C gave 0.73 g (52%) of white crystals, mp 63−64 °C. ^{19}F NMR ($CDCl_3$ + 1% TMS): δ_A 71.9, δ_B 68.8, J_{AB} = 149 Hz. ^1H NMR ($CDCl_3$ + 1% TMS): δ 0.03 ($SiMe_3$), 0.93 (CH_2), 4.19 (OCH_2), 7.32 (NH). ^{13}C NMR ($CDCl_3$ + 1% TMS): δ 1.6 [$Si(CH_3)_3$], 18 (CH_2Si), 66 (OCH_2), 149 (NHCO). Anal. Calcd for $C_6H_{14}F_5NO_2SSi$: C, 25.08; H, 4.91; N, 4.87; S, 11.16. Found: C, 25.11; H, 4.87; N, 4.45; S, 11.29.

(c) $SF_5N{=}C(NHCMe_3)_2$. Anhydrous ether (80 mL), Me_3CNH_2 (3.5 g, 48 mmol), and $SF_5N{=}CCl_2$ (6.6 g, 30 mmol) were combined at −196 °C, after which the mixture was slowly warmed and then stirred at 25 °C for 24 h. The precipitate ($Me_3CNH_2{\cdot}HCl$) was removed (vacuum filtration), additional Me_3CNH_2 (3.5 g, 48 mmol) was added, and after 24 h, precipitate was again removed. Adding more Me_3CNH_2 (3.5 g, 48 mmol) and stirring for 14 d gave a final amount of precipitate which was also removed. The solvent was removed to give a crystalline residue (6 g) from which fractional vacuum sublimation at 35 °C (stopped after ca. 90% was sublimed) produced 5.17 g (59%) of pure product, mp 62−63 °C. ^{19}F NMR ($CDCl_3$ + 1% TMS): δ_A 79.7, δ_B 104.0, J_{AB} = 155 Hz; ^1H NMR ($CDCl_3$ + 1% TMS): δ 1.41 (CH_3), 4.20 (NH), 5.20 (NH); ^{13}C NMR ($CDCl_3$ + 1% TMS): δ 30 (CH_3), 52 (NHC). Anal. Calcd for $C_9H_{20}F_5N_3S$: C, 36.35; H, 6.78; N, 14.14; S, 10.76. Found: C, 36.99; H, 6.96; N, 14.32; S, 11.09.

X-Ray Experimental Details. Data Collection. Clear, colorless crystals of **1a**,**b**,**d**,**e**, and **3a**,**b**, synthesized as described above, were glued to the ends of thin glass fibers and transferred to a Siemens R3/V (for **1e**) or a Siemens P4/S diffractometer using Mo Kα (**1e**) or Cu Kα radiation and a graphite monochromator. Cell dimensions and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of at least 25 accurately centered reflections. These are listed with other relevant crystal data in Table 5.

Structure Solution and Refinement. The structures were solved by direct methods using the SHELXTL package of computer programs.[12] Neutral atom scattering factors were used[13a] with corrections for real and imaginary anomalous dispersion.[13b] All structures were refined by full-matrix least-squares methods based on F^2 using SHELXL-96[14] and used all unique data. Non-hydrogen atoms were refined anisotropically while hydrogen atoms were located in difference Fourier syntheses and refined isotropically. A summary of the refinement details and the resultant refinement agreement factors is contained in Table 5. Fractional coordinates, bond distances and angles, and anisotropic displacement parameters are provided in the Supporting Information.

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(12) Sheldrick, G. M. *SHELXTL, Crystallographic System*; Siemens Analytical Instrument Division, Madison, WI, 1986.

(13) (a) Cromer, D. T.; Waber J. T. *International Tables for X-ray Crystallography*; The Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2. (b) Cromer, D. T. *Ibid.*, Table 2.3.1.

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Supporting Information Available: Tables S1−S31, listing crystal data, atomic coordinates, bond lengths and angles, and anisotropic displacement parameters for **1a**,**b**,**d**,**e**, and **3a**,**b**, geometric data for all SF_5NX structures, and hydrogen bond parameters for **1a**,**d**,**e** and **3a**,**b**, Figures S1−S3, showing packing diagrams for **1a**, and an X-ray crystallographic CIF file. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the six structures have also been deposited with the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. E-mail: deposit@ccdc.cam.ac.uk).

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(14) Sheldrick, G. SHELXTL96 *Acta Crystallogr. A* **1990**, *46*, 467. This is a full-matrix least-squares refinement package that uses all data and refines on F^2 rather than the traditional F. The various parameters used in this refinement process are defined as follows: $R(F) = \sum|F_o - F_c|/\sum F_o$; $R(F^2) = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o) + (aP)^2 + bP]$ and a and b are variable parameters whose optimal values are usually suggested by the program during the refinement process. The goodness-of-fit parameter (s) is based on F^2 and defined as $s = \{\sum[w(F_o^2 - F_c^2)^2]/[n - p]\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined.