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Polynitroalkyl derivatives of $SF_5N{=}CCl_2$: nitrations of SF_5 imines

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Abstract

Polynitroalkyl SF_5 imines have been synthesized from $SF_5N{=}CCl_2$ via nucleophilic substitution and nitration reactions. Only in one instance was the SF_5 imino moiety ($SF_5N{=}C-$) affected by a nitration reagent; the product was the fluorosulfonyl compound; very similar SF_5 materials were not affected by the nitration reagent. The $SF_5N{=}C-$ moiety, when compared to the carbonyl group ($O{=}C-$), exhibited a strong tendency to lower the melting points of nitro compounds. The crystal structures of three SF_5 imines and one fluorosulfonyl imine have been determined.

Introduction

Reactions of pentafluorosulfanyldichloroimine ($SF_5N{=}CCl_2$) (**1**) with nucleophiles (alkoxides, amines) have been described previously [1]. As part of a study to determine the effect of the SF_5 group on the properties of nitro compounds (effect on sensitivity, density, stability, energy, etc.) [2, 3], the synthesis of polynitroalkyl derivatives of **1** was undertaken. Some of these polynitroalkyl derivatives were expected to be available by direct nucleophilic substitution, but in other cases nitrations of SF_5 imines would be necessary to product the desired materials. One concern was that the SF_5 imino moiety ($SF_5N{=}C-$) might be vulnerable to the concentrated acids and strongly oxidizing conditions often present during nitrations. Another concern was that the highly electronegative (and bulky) SF_5 group might prevent the desired nitrations which would often be occurring at positions in close proximity to the SF_5 group.

Results and discussion

The initial nitrations of SF_5 imines were performed during the conversion of the SF_5 imino imidazolidone (**2**) to the mono- (**3**) and the di- (**4**) nitro

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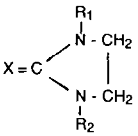
derivatives. Compound **2**, prepared from **1** and ethylenediamine, was found to nitrate readily with concentrated sulfuric/nitric acids to give the mononitro derivative **3** in good yield. For further nitration of **3** to **4**, trifluoroacetic anhydride/nitric acid was required, and this conversion also proceeded in high yield. In neither nitration was there any evidence of substantial attack on the $SF_5N{=}C-$ group by the nitration reagents.



2: $R_1, R_2 = H; X = NSF_5$
3: $R_1 = H; R_2 = NO_2; X = NSF_5$
4: $R_1, R_2 = NO_2; X = NSF_5$
5: $R_1, R_2 = NO_2; X = O$

The properties of **3** and **4** were determined to allow comparison with similar non-SF_5 nitro compounds. The crystal density of **3** was measured (X-ray) to be 2.02 g cm^{-3}, but the X-ray structure and density of **4** could not be determined due to difficulty in growing suitable crystals (forming either very fine crystals or solvates). The density of **4** was calculated* to be 2.03 g cm^{-3}, a density that represents a significant increase over that of the corresponding carbonyl compound **5** (X-ray density of **5** is 1.79 g cm^{-3}). More notable is the difference in melting point between **4** and **5** (melting points of 41 °C and 216 °C [5]), respectively. This large difference in melting point suggested that replacing $C{=}O$ with $C{=}NSF_5$ in other nitro compounds might lead to low-melting SF_5 nitro compounds that would be useful as energetic plasticizers. Thus, other polynitroalkyl derivatives of **1** which could be anticipated to have attractive melting points were investigated. One such compound, $SF_5N{=}C[OCH_2CF(NO_2)_2]_2$ (**6**) [6] was found to exhibit a lowered melting point (-4 °C) respective to both the carbonyl compound $O{=}C[OCH_2CF(NO_2)_2]_2$ (m.p. 46 °C) [7] and to the dihydro compound $H_2C[OCH_2CF(NO_2)_2]_2$ (**7**) (m.p. 14 °C) [8]. Compound **6** exhibits other attractive properties as an energetic plasticizer: the liquid density of **6** is 1.82 g cm^{-3} compared to 1.60 g cm^{-3} for **7**; the volatility of **6** is only about one-half that of **7** (rates of weight loss at 117 °C are 0.054% min^{-1} and 0.104% min^{-1} [9], respectively).

Displacement of one of the chlorine atoms in **1** by a nucleophile often provides materials in which the remaining chlorine reacts sluggishly [1]. This sluggishness was also observed when polynitroalcohols were employed as nucleophiles when chloro intermediates such as **8** and **9** were easily produced.

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*See ref. 4. For solids, the atomic volume of an SF_5 group is calculated to be 51.4 cm^3 mol^{-1}; for liquids, the value is 49.2 cm^3 mol^{-1}.

$$\mathbf{1} + ROH \longrightarrow SF_5N{=}C(Cl)(OR)$$

$$(\mathbf{8})\ R = CH_2CF(NO_2)_2$$

$$(\mathbf{9})\ R = CH_2CH_2C(NO_2)_3$$

The remaining chlorine in **8** was displaced by various nucleophiles to produce products (**10**, **11**) or intermediates such as **12** that could be further nitrated (see Table 1).

For compound **10**, the corresponding carbonyl compound $O{=}C(NH_2)[OCH_2CF(NO_2)_2]$ (**15**) has been reported [10] but was described as a liquid and no melting point was given. We determined the melting point of **15** to be 23 °C and indeed **15** represents the only case where we have observed the carbonyl compound as melting at a lower temperature than the corresponding SF_5 imine. The trinitropropyl compound, $SF_5N{=}C(NH_2)[OCH_2CH_2C(NO_2)_3]$ (**16**) analogous to **10** has a melting point of 43 °C compared to 82 °C for $O{=}C(NH_2)[OCH_2CH_2C(NO_2)_3]$ (**17**).

Thus, there appears to be a strong tendency for the $SF_5N{=}C-$ moiety, as compared to the carbonyl group, to lower the melting points of nitro compounds. This lowering of melting point is probably due to a number of factors which include the bulkiness of the SF_5 group as well as the tendency of fluorinated compounds to have reduced intermolecular forces. Another factor that would be expected to influence the melting points is the relative contribution to the dipole moment associated with the $SF_5N{=}C-$ and $O{=}C-$ groups.

Nitration of **12** provided the only case in which the SF_5 imino group was attacked by the nitration reagent. When a dilute solution of **12** in dichloromethane was stirred with 90% nitric acid at 0 °C for 1.5 h, a good yield of the SF_5 imino derivative **13** was produced. However, a more concentrated solution of **12** in dichloromethane treated with 90% nitric acid under the same conditions produced the fluorosulfonyl compound $FSO_2N{=}C[NH(CH_2)_2ONO_2][OCH_2CF(NO_2)_2]$ (**18**). Compound **13**, isolated as a pure material and then exposed to 90% nitric acid under concentrated

TABLE 1

The properties of $SF_5N{=}C(R)[OCH_2CF(NO_2)_2]$

Compound No.	R	Melting point (°C)	Density (g cm^{-3})
10	NH_2	28	1.81[a]
11	$OCH_2CH_2C(NO_2)_3$	2	–
12	$NH(CH_2)_2OH$	–	–
13	$NH(CH_2)_2ONO_2$	4	1.75[b]
14	$NNO_2(CH_2)_2ONO_2$	75	1.98[c]

[a] Liquid density at 30 °C.
[b] Liquid density at 25 °C.
[c] Crystal density (X-ray).

conditions, was also converted to **18**. Thus, it seems probable that **12** is first converted to **13** and then to **18**, but **12** cannot be totally ruled out as an intermediate to **18** since small (equilibrium) amounts of **12** would be expected to be present from **13** in contact with 90% nitric acid. Remarkably, SF_5 compounds very similar to **12**, such as **10** and $SF_5NHC(O)OCH_2CF(NO_2)_2$ [11], remained unchanged under the concentrated conditions with 90% nitric acid. It would appear that the $NH(CH_2)_2OH$ and/or the $NH(CH_2)_2ONO_2$ group can somehow assist in the degradation of the SF_5 moiety. The SF_5 group in **13** was, however, unaffected by further nitration with trifluoroacetic anhydride/nitric acid and the $N-NO_2$ compound **14** was produced in nearly quantitative yield.

Single-crystal X-ray diffraction analyses

Data were collected for four crystalline compounds (**3**, **4**, **14** and **18**) on an automated Siemens R3m/V diffractometer equipped with an incident beam monochromator. All structures were solved and refined with the aid of the SHELXTL system of programs [12].

A pentafluorosulfanyl group attached to an imino nitrogen atom occurs in **3**, **4** and **14** as well as in an earlier crystal structure [13]. In each case, the bond angles deviate from regular octahedral symmetry. The equatorial $S-F$ bonds bend slightly toward the axial $S-F$ bond, as shown below (Table 2). Also, the axial bond is always longer than the average of the equatorial bonds, but the difference is too slight to be considered significant.

Crystal data for compound **3**: $C_3H_5F_5N_4O_2S$: formula weight$=256.2$; monoclinic; space group, $P2_1/a$; $a=8.970(1)$, $b=17.203(3)$, $c=11.170(2)$ Å, $\beta=102.60(1)°$, $V=1682.0(4)$ Å^3, $Z=8$, D_c (X-ray, calc.)$=2.023$ mg mm^{-3}, $\lambda(\text{CuK}\alpha)=1.54184$ Å, $\mu=4.256$ mm^{-1}, $F(000)=1024$, $T=295$ K.

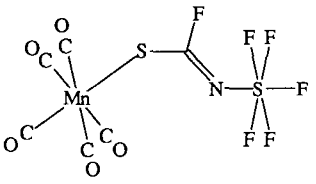
Data were collected on a clear colorless $0.18\times0.30\times0.41$ mm crystal in the shape of a rectangular prism. Lattice parameters were determined from 25 centered reflections within $53\leqslant2\theta\leqslant69°$. The data collection of hkl was $-9\leqslant h\leqslant9$, $0\leqslant k\leqslant18$, $0\leqslant l\leqslant12$, with $[(\sin\theta)/\lambda]_{\text{max.}}=0.538$. Three standards, monitored after every 97 reflections, exhibited random variations with deviations of up to $\pm3.0\%$ during data collection. A set of 2421 reflections was collected in the $\theta/2\theta$ scan mode with a scan width $[2\theta(\text{K}\alpha_1)-0.45]$ to $[2\theta(\text{K}\alpha_2)+0.45]°$ and an ω scan rate (a function of the count rate) from 3.3° min^{-1} to 30.0° min^{-1}. There were 2190 unique reflections, and 2011 were observed with $F_0>3\sigma(F_0)$. The full-matrix least-squares refinement varied 302 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms; the hydrogen atom coordinates were refined, and the $U_{\text{iso}}(\text{H})$ values were set equal to $1.1\times U_{\text{eq}}$(neighboring C). Final residuals were $R=0.032$ and $Rw=0.044$ with final difference Fourier excursions of 0.22 and -0.18 e Å^{-3}.

There are two molecules of **3** in the asymmetric unit which are essentially identical (except for their packing surroundings) (see Fig. 1). In both molecules, the nitro groups are *trans* to the SF_5 groups across the imino double bond,

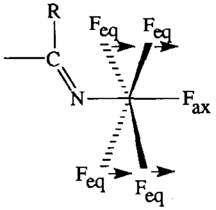
TABLE 2

Selected SF_5 imino structural parameters[a]

Molecule	Bond angle (°)				Bond length (Å)			
	R–C=N	C=N–S	$N-S-F_{eq}$	$F_{ax}-S-F_{eq}$	C=N	N–S	$S-F_{eq}$	$S-F_{ax}$
3	135.0	122.6	93.2	86.9	1.290	1.638	1.578	1.588
4	132.1	127.2	91.8	88.2	1.250	1.691	1.553	1.575
14	130.2	126.3	92.0	88.0	1.251	1.679	1.553	1.577
19 [13]	123.9	124.8	92.8	87.3	1.267	1.677	1.571	1.587



19



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[a] The values listed are averages over the pertinent bonds; in **3** and **4**, two independent molecules in the asymmetric unit have been averaged. For **3**, **4** and **14**, the estimated standard deviations of the individual distances contributing to the averages range from 0.002–0.005 Å, and the individual angle estimated standard deviations are 0.1–0.2°. The diagram at the right depicts the labeling scheme used in the heading, and indicates, by exaggerated arrows, the distortion from octahedral symmetry indicated by the parameters. The values listed above for **19** were calculated from coordinates reported in ref. 13.

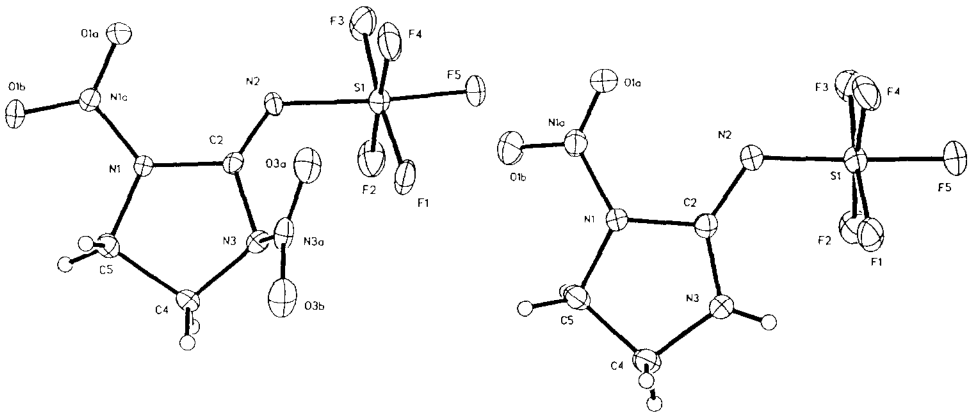

Fig. 1. Thermal ellipsoid drawings of **4** (left) and **3** (right). Both contain an imino double bond, N2–C2, and show evidence of crowding in its vicinity on the side *cis* to the pentafluorosulfanyl group. Bond angles increased beyond 120° are S1–N2–C2, 122.6(2)° in **3** and 127.2(4)° in **4**, and N2–C2–N3, 135.0(2)° in **3** and 132.1(4)° in **4**. Each bond angle is the average of two determinations; the digit in parentheses here and elsewhere in this paper represents the estimated standard deviation in the last digit of the reported number.

which minimizes the intramolecular repulsions. There are no appreciable out-of-plane twists. The packing is dominated by NH· · ·nitro H-bonds that link successive molecules related by the crystallographic screw axis; this creates polarized chains that are parallel and antiparallel, in equal number, to the *b* axis of the unit cell.

Crystal data for compound **4** (benzene solvate): $C_3H_4F_5N_5O_4S \cdot 0.5C_6H_6$: formula weight = 340.2; triclinic; space group, $P-1$; $a = 6.450(2)$, $b = 12.011(3)$, $c = 16.481(4)$ Å, $\alpha = 101.40(2)$, $\beta = 99.83(2)$, $\gamma = 92.38(2)°$, $V = 1229.4(6)$ Å^3, $Z = 4$, D_c (X-ray, calc.) = 1.838 mg mm^{-3}, $\lambda(\text{MoK}\alpha) =$ 0.71073 Å, $\mu = 0.340$ mm^{-1}, $F(000) = 684$, $T = 201$ K.

Data were collected on a clear colorless 0.08×0.06×0.65 mm crystal in the shape of a needle. Lattice parameters were determined from 25 centered reflections within $19 \leqslant 2\theta \leqslant 30.5°$. The data collection range of *hkl* was $0 \leqslant h \leqslant 6$, $-11 \leqslant k \leqslant 11$, $-15 \leqslant l \leqslant 15$, with $[(\sin\ \theta)/\lambda]_{\text{max.}} = 0.481$. Three standards, monitored after every 97 reflections, exhibited random variations with deviations of up to ± 5.0% during data collection. A set of 2631 reflections was collected in the $\theta/2\theta$ scan mode with a scan width $[2\theta(\text{K}\alpha_1) - 0.45]$ to $[2\theta(\text{K}\alpha_2) + 0.45]°$ and an ω scan rate (a function of the count rate) from 5.0° min^{-1} to 30.0° min^{-1}. There were 2310 unique reflections, and 1733 were observed with $F_0 > 3\sigma(F_0)$. The full-matrix least-squares refinement varied 380 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms; H atoms were included, but not refined, by using a riding model [coordinate shifts of C applied to attached H atoms, C–H distances set to 0.96 Å, H angles idealized, $U_{\text{iso}}(\text{H})$ values set equal to $1.1 \times U_{\text{eq}}(\text{C})$]. Final residuals were $R = 0.041$ and $Rw = 0.042$ with final difference Fourier excursions of 0.35 and -0.23 e Å^{-3}.

There are two independent molecules of **4** in the asymmetric unit (see Fig. 1). In both molecules, the bonding geometry of one of the two imidazole ring nitrogen atoms is relatively planar ($\sim sp^2$ hybrid), while the other is clearly pyramidal ($\sim sp^3$ hybrid). In each case, the pyramidal ring N atom is *cis* to the SF_5 group across the imine double bond, suggesting that pyramidalization occurs to minimize repulsive interactions between the nitro and pentafluorosulfanyl groups. Two benzenes are located near the center of the unit cell, and the repetition of these two by the short a axis of the unit cell produces continuous channels of benzene that extend through the whole crystal; at room temperature, this included solvent starts escaping as soon as the crystals are taken from the mother liquor. Data were collected from a crystal which was rapidly cooled to -50 °C whilst still wet. Recrystallization attempts from several other solvents did not produce single crystals.

Crystal data for compound **14**: $C_5H_6F_6N_6O_{10}S$: formula weight; monoclinic; space group, $P2_1/n$; $a = 14.845(4)$, $b = 5.847(1)$, $c = 18.588(6)$ Å, $\beta = 108.14(2)°$, $V = 1533.2(7)$ Å^3, $Z = 4$, D_c (X-ray, calc.) = 1.976 mg mm^{-3}, λ(MoKα) = 0.71073 Å, $\mu = 0.335$ mm^{-1}, $F(000) = 912$, $T = 293$ K.

Data were collected on a clear colorless $0.12 \times 0.16 \times 0.46$ mm rod-shaped crystal. Lattice parameters were determined from 25 centered reflections within $20 \leq 2\theta \leq 30°$. The data collection range of hkl was $0 \leq h \leq 16$, $-6 \leq k \leq 0$, $-20 \leq l \leq 18$, with $[(\sin\theta)/\lambda]_{max.} = 0.538$. Three standards, monitored after every 97 reflections, exhibited an overall increase of 7.5% with short-term random deviations of approximately ±2.5% during data collection. A set of 2361 reflections was collected in the $\theta/2\theta$ scan mode with a scan width $[2\theta(K\alpha_1) - 0.5]$ to $[2\theta(K\alpha_2) + 0.5]°$ and a constant ω scan rate of 10.2° min^{-1}. There were 2020 unique reflections, and 1439 were observed with $F_O > 3\sigma(F_O)$. The full-matrix least-squares refinement varied 272 parameters: atom coordinates and anisotropic thermal parameters for all non-H atoms; H atoms were included using a riding model [coordinate shifts of C applied to attached H atoms, C—H distances set to 0.96 Å, H angles idealized, U_{iso}(H) values set equal to $1.1 \times U_{eq}$(C)]. Final residuals were $R = 0.045$ and $Rw = 0.041$ with final difference Fourier excursions of 0.31 and -0.29 e Å^{-3}. Figure 2 gives a thermal ellipsoid drawing for **14**.

Crystal data for compound **18**: $C_5H_7F_2N_5O_{10}S$: formula weight = 367.2; triclinic; space group, $P-1$; $a = 8.683(4)$, $b = 10.524(6)$, $c = 15.069(7)$ Å, $\alpha = 76.18(4)$, $\beta = 87.14(3)$, $\gamma = 80.46(4)°$, $V = 1319(1)$ Å^3, $Z = 4$, D_c (X-ray, calc.) = 1.850 mg mm^{-3}, λ(MoKα) = 0.71073 Å, μ = 0.324 mm^{-1}, $F(000) = 744$, $T = 243$ K.

Data were collected from a prism-shaped crystal, $0.33 \times 0.42 \times 0.51$ mm. Lattice parameters were determined from 25 centered reflections within $19 \leq 2\theta \leq 36.5°$. The data collection range of hkl was $-10 \leq h \leq 10$, $-12 \leq k \leq 0$, $-17 \leq l \leq 17$, with $[(\sin\theta)/\lambda]_{max.} = 0.595$. Three standards, monitored after every 97 reflections, exhibited random variations with deviations of up to ±2% during data collection. A set of 4963 reflections was collected in the $\theta/2\theta$ scan mode with a scan width $[2\theta(K\alpha_1) - 0.5]$ to $[2\theta(K\alpha_2) + 0.5]°$ and

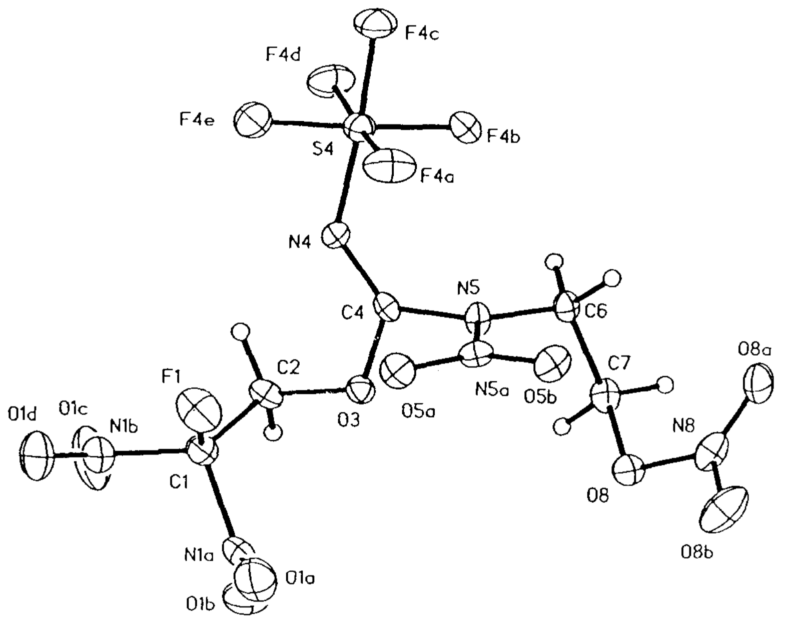

Fig. 2. Thermal ellipsoid drawing of **14**. Bond angles indicative of local crowding are C4—N4—S4, 126.3(4)°, and N4—C4—N5, 130.2(5)°.

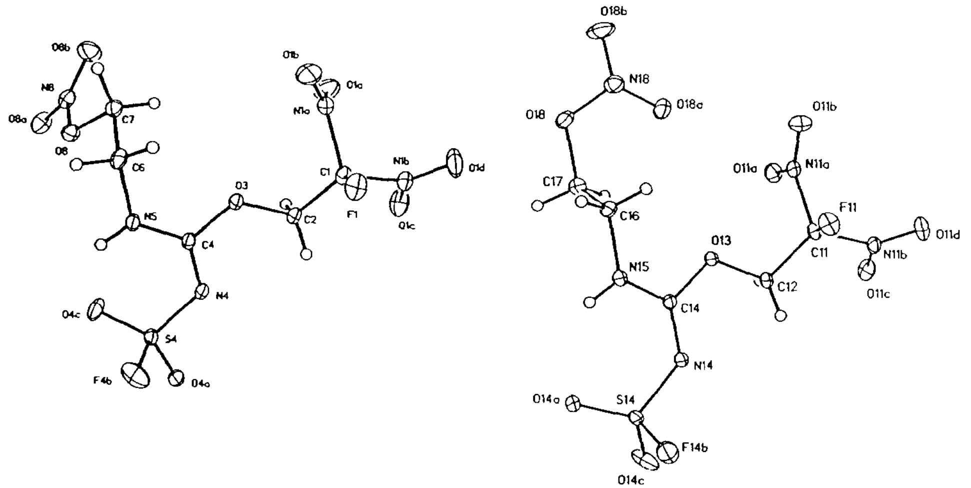

Fig. 3. Thermal ellipsoid drawings of the two distinct conformations of **18** found in the asymmetric unit of the crystal form reported here. Significant torsional differences occur, and are most noticeable in the nitrato-terminated chain seen at the upper left of each drawing.

an ω scan rate (a function of the count rate) from 6.0° min^{-1} to 14.65° min^{-1}. There were 4682 unique reflections, and 3873 were observed with $F_0 > 3\sigma(F_0)$. The full-matrix least-squares refinement varied 458 parameters: atom coordinates for all atoms and anisotropic thermal parameters for all non-H atoms; the U_{iso}(H) values were not refined, but were set equal to $1.1 \times U_{eq}$(neighboring C). Final residuals were $R = 0.038$ and $Rw = 0.042$ with final difference Fourier excursions of 0.33 and -0.26 e Å^{-3}.

Two conformationally distinct molecules of **18** are found in the asymmetric unit of the crystal, with large torsional differences occurring primarily in the nitrato-terminated chain (see Fig. 3).

Supplementary material available

Tables of atomic coordinates, bond distances and angles, anisotropic thermal parameters, and observed and calculated structure factors are available from the NRL author. Coordinates and bond lengths and angles will also be available from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK.

Experimental

Caution: Polynitro compounds are potentially explosive and should be handled with appropriate precautions.

Pentafluorosulfanyldichloroimine (**1**) was purchased from the University of Alabama, Tuscaloosa, AL (Dr Joseph S. Thrasher). The ^{19}F and ^{1}H NMR spectra were recorded with a Varian EM 390 spectrometer; results are given in ppm from CCl_3F and $(CH_3)_4Si$, respectively, used as internal standards. Infrared spectra were recorded with a Perkin-Elmer model 283 spectrometer (quoted in cm^{-1}) and elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Preparation of SF_5 imines from $SF_5N{=}CCl_2$

*(a) 2-Imidazolidone, pentafluorosulfanylimine (**2**) (nc)*

To a solution of ethylenediamine (1.3 g, 0.02 mol) and triethylamine (6 ml, 4.4 g, 0.043 mol) in dry ether (60 ml) stirred in an ice bath, was added a solution of **1** (4.5 g, 0.02 mol) in dry ether (30 ml). The mixture was stirred for 16 h at room temperature and then allowed to stand for 14 d. The insoluble solid was removed by filtration and volatiles were removed from the filtrate to give a semisolid. Dichloromethane (10 ml) was added and the mixture was cooled to −10 °C to give 1.6 g of crystals, m.p. 146–149 °C. The second crop was 0.6 g, m.p. 145–149 °C (52% yield). Crystallization from chloroform raised the melting point to 147–149 °C. IR (KBr) (cm^{-1}): 3530; 3280 (NH); 1640 (C=N); 800–920 (SF_5). ^{1}H NMR ($CDCl_3$) δ: 3.72 (s, 4H); 5.95 (broad s, 2H) ppm. Analysis: Calc. for $C_3H_6F_5N_3S$: C, 17.06; H, 2.86; F, 44.99; N, 19.90; S, 15.18%. Found: C, 16.84; H, 2.84; F, 44.22; N, 19.60; S, 15.38%.

*(b) 2-Fluoro-2,2-dinitroethylchloroformate, pentafluorosulfanylimine (**8**) (nc)*

A solution of **1** (2.85 g, 0.013 mol) and 2-fluoro-2,2-dinitroethanol (2.2 g, 0.014 mol) in dichloromethane (10 ml) was stirred in an ice bath during the dropwise addition of pyridine (1.0 g, 0.0125 mol) in dichloromethane (8 ml) over 15 min. The reaction solution was stirred at 0 °C for 40 min before dilute hydrochloric acid was added, after which the dichloromethane solution was separated and dried over sodium sulfate. The volatiles were removed to give 4.2 g of liquid which was chromatographed on silica gel 40 using dichloromethane/hexane (50:50) as eluant to give 3.6 g (84%) of pure **8** as a liquid. ^{1}H NMR ($CDCl_3$) δ: 5.46 (d) ppm. IR (film) (cm^{-1}): 1665 (C=N); 1610 (NO_2); 880–790 (SF_5). Analysis: Calc. for $C_3H_2ClF_6N_3O_5S$: C, 10.55; H, 0.59; F, 33.37; N, 12.30; S, 9.39%. Found: C, 10.58; H, 0.64; F, 33.27; N, 12.41; S, 10.05%.

*(c) 3,3,3-Trinitropropylchloroformate, pentafluorosulfanylimine (**9**) (nc)*

A solution of **1** (0.9 g, 4 mmol) and 3,3,3-trinitropropanol (0.95 g, 4.8 mmol) in dichloromethane (8 ml) was stirred in an ice bath during the dropwise addition of pyridine (0.35 g, 4.4 mmol) in dichloromethane (3.5 ml). After 1 h at 0 °C, cold dilute hydrochloric acid was added and the dichloromethane solution was separated and dried over sodium sulfate. Removal of volatiles gave 1.70 g of an oil which was chromatographed on silica gel 40 using dichloromethane/hexane (60:40) as eluant to give 1.18 g (77%) of **9** as an oil. ^{1}H NMR ($CDCl_3$) δ: 3.63 (t, 2H); 4.83 (t, 2H) ppm. IR (film) (cm^{-1}): 1660 (C=N); 1610 (NO_2); 920–770 (SF_5).

Preparation of SF_5 imines from $SF_5N{=}C(Cl)(OR)$

*(a) 2-Fluoro-2,2-dinitroethyl carbamate, pentafluorosulfanylimine (**10**) (nc)*

A solution of **8** (2.0 g, 5.8 mmol) in dichloromethane (8 ml) stirred at 0 °C was carefully exposed to ammonia gas for approximately 3 h until thin-layer chromatographic (TLC) analysis indicated that no **8** remained. The reaction mixture was extracted with water (2×20 ml) before the dichloromethane solution was dried over sodium sulfate and the volatiles were removed to give 1.90 g of an oil. Chromatography on silica gel 60 using dichloromethane/hexane (70:30) as eluant gave 1.84 g (98%) of **10**, m.p. 28.5–30 °C. ^{1}H NMR ($CDCl_3$) δ: 5.33 (d); 5.58 (broad, NH_2) ppm. IR (film) (cm^{-1}): 3670, 3455 (NH_2); 1690 (C=N); 1610 (NO_2); 900–800 (SF_5). Analysis: Calc. for $C_3H_4F_6N_4O_5S$: C, 11.18; H, 1.25; F, 35.39; N, 17.39; S, 9.95%. Found: C, 11.06; H, 1.18; F, 35.71; N, 17.57; S, 9.77%.

*(b) (2-Fluoro-2,2-dinitroethyl)(3,3,3-trinitropropyl)carbonate, pentafluorosulfanylimine (**11**) (nc)*

To a solution of **8** (0.7 g, 2 mmol) and 3,3,3-trinitropropanol (0.65 g, 3.3 mmol) in dichloromethane (7 ml), stirred at 0 °C, was added pyridine (0.17 g, 2.2 mmol) in dichloromethane (2 ml). The reaction solution was stored in a refrigerator at approximately 3 °C for 44 h before dilute hydrochloric acid was added. The dichloromethane solution was separated and dried over sodium sulfate before the volatiles were removed to give 1.2 g of an oil.

Chromatography on silica gel 40 using dichloromethane/hexane (50:50) as eluant gave 0.6 g (60%) of pure **11** which was stirred under very cold hexane to give a solid, m.p. 2 °C. ^1H NMR ($CDCl_3$) δ: 3.66 (t, 2H); 4.83 (t, 2H); 5.38 (d, 2H) ppm. IR (film) (cm^{-1}): 1680 (C=N); 1610 (NO_2); 870–790 (SF_5). Analysis: Calc. for $C_6H_6F_6N_6O_{12}S$: C, 14.41; H, 1.21; F, 22.79; N, 16.80; S, 6.41%. Found: C, 14.33; H, 1.27; F, 22.87; N, 16.72; S, 6.63%.

*(c) N-(2-Hydroxyethyl)-2-fluoro-2,2-dinitroethyl carbamate, pentafluorosulfanylimine (**12**) (nc)*

To a solution of **8** (0.7 g, 2 mmol) in dichloromethane (5 ml), stirred at 0 °C, was added ethanolamine (0.25 g, 4 mmol) in dichloromethane (5 ml) dropwise over 10 min. After 1.5 h at 0 °C, dilute hydrochloric acid was added. The dichloromethane solution was separated, dried over sodium sulfate and the volatiles were removed to give 0.8 g (100%) of **12** as an oil. ^1H NMR ($CDCl_3+D_2O$) δ: 3.45 (t, 2H); 3.85 (t, 2H); 5.63 (d, 2H); 6.15 (broad, NH) ppm. IR (film) (cm^{-1}): 3725–3200 (NH, OH); 1670 (C=N); 1610 (NO_2); 900–790 (SF_5).

*(d) 3,3,3-Trinitropropyl carbamate, pentafluorosulfanylimine (**16**) (nc)*

A solution of **9** (0.66 g, 1.7 mmol) in dichloromethane (15 ml) was stirred in an ice bath while ammonia gas was slowly added until thin-layer chromatographic (TLC) analysis showed no starting material remained. The mixture was filtered and the volatiles were removed from the filtrate to give 0.6 g of product. Chromatography on silica gel 40 using dichloromethane/hexane (70:30) as eluant gave 0.55 g (89%) of **16**, m.p. 43–45 °C. ^1H NMR ($CDCl_3$) δ: 3.57 (t, 2H); 4.70 (t, 2H); 5.42 (broad, 2H) ppm. IR (KBr) (cm^{-1}): 3560, 3440 (NH); 1680 (C=N); 1610 (NO_2); 890–790 (SF_5). Analysis: Calc. for $C_4H_6N_5F_5O_7S$: C, 13.23; H, 1.66; N, 19.28; F, 26.16; S, 8.83%. Found: C, 12.92; H, 1.59; N, 18.81; F, 26.55; S, 8.91%.

Nitrations of SF_5 imines

*(a) 1-Nitro-2-imidazolidone, pentafluorosulfanylimine (**3**) (nc)*

To an ice cold mixture of conc. sulfuric acid (10 ml), 90% nitric acid (2.5 ml) and dichloromethane (25 ml) was added **2** (0.55 g, 2.6 mmol) in portions with good stirring. After 30 min at 0 °C, the mixture was poured onto ice and the dichloromethane layer was separated. Removal of volatiles gave 0.55 g (83%) of solid, m.p. 108–113 °C. Crystallization from dichloromethane gave crystals, m.p. 114–116 °C. ^1H NMR (acetone-d_6) δ: 3.85 (t, 2H); 4.57 (t, 2H); 7.95 (broad, NH) ppm. IR (KBr) (cm^{-1}): 3420 (NH); 1700, 1680 (C=N); 1575 (NO_2); 910–830 (SF_5). Analysis: Calc. for $C_3H_5F_5N_4O_2S$: C, 14.06; H, 1.97; F, 37.09; N, 21.87; S, 12.52%. Found: C, 14.09; H, 1.97; F, 37.25; N, 22.11; S, 12.60%.

*(b) 1,3-Dinitro-2-imidazolidone, pentafluorosulfanylimine (**4**) (nc)*

To trifluoroacetic anhydride (10 ml), stirred in an ice bath, was added 100% nitric acid (1.5 ml) after which **3** (0.6 g, 2.3 mmol) was added in portions. After 1 h at 0 °C, the solution was poured onto ice. Extraction with dichloromethane gave 0.55 g of product which was essentially pure (by ^{1}H NMR analysis). Chromatography on silica gel 40 (dichloromethane as eluant) gave 0.45 g of product, m.p. 41–43 °C. ^{1}H NMR ($CDCl_3$) δ: 4.47 (s) ppm. IR (film) (cm^{-1}): 1705 (C=N); 1610 (NO_2); 930–820 (SF_5). Analysis: Calc. for $C_3H_4F_5N_5O_4S$: C, 11.96; H, 1.34; F, 31.54; N, 23.26; S, 10.65%. Found: C, 12.25; H, 1.29; F, 31.12; N, 23.27; S, 10.55%.

*(c) N-(2-Nitroxyethyl)-2-fluoro-2,2-dinitroethyl carbamate, pentafluorosulfanylimine (**13**) (nc)*

A solution of **12** (0.65 g, 1.8 mmol) in dichloromethane (20 ml) was stirred vigorously at 0 °C as 90% nitric acid (2 ml) was added dropwise. After 1.5 h at 0 °C, ice water was added and the dichloromethane solution was separated and dried over sodium sulfate. Removal of the volatiles gave 0.73 g (100%) of an oil which was chromatographed on silica gel 40 (dichloromethane/hexane, 50:50, as eluant) to give 0.59 g (81%) of pure **13** as an oil. Stirring the oil in very cold hexane containing a very small amount of dichloromethane gave crystals, m.p. 4 °C. ^{19}F NMR (acetone) δ: 94.3 (m, SF_{ax}); 75.6 (d of m, SF_{eq}); −110.5 (CF) ppm. ^{1}H NMR ($CDCl_3$) δ: 3.68 (m, 2H); 4.65 (t, 2H); 5.38 (d, 2H); 5.97 (broad, NH) ppm. IR (film) (cm^{-1}): 3490 (NH); 1675 (C=N); 1650 (ONO_2); 1615 (NO_2); 900–790 (SF_5). Analysis: Calc. for $C_5H_7F_6N_5O_8S$: C, 14.60; H, 1.72; F, 27.72; N, 17.03; S, 7.80%. Found: C, 14.67; H, 1.82; F, 27.41; N, 17.33; S, 7.84%.

*(d) N-Nitro-N-(2-nitroxyethyl)-2-fluoro-2,2-dinitroethyl carbamate, pentafluorosulfanylimine (**14**) (nc)*

To trifluoroacetic anhydride (6 ml), stirred in an ice bath, was added 100% nitric acid (0.6 ml) dropwise. Then **13** (0.40 g, 1 mmol) was added and after 1 h at 0 °C, a solid had precipitated from solution. The reaction mixture was poured onto ice to give 0.41 g (93%) of solid, m.p. 75–77 °C. Crystallization from chloroform gave crystals of **14**, m.p. 76–77 °C. ^{19}F NMR (acetone) δ: 79.3 (m, SF_{ax}); 70.6 (m, SF_{eq}); −110.9 (CF) ppm. ^{1}H NMR ($CDCl_3$) δ: 4.27 (t, 2H); 4.85 (t, 2H); 5.49 (d, 2H) ppm. IR (KBr) (cm^{-1}): 1700 (C=N); 1655 (ONO_2); 1615 (NO_2); 1585 ($N-NO_2$); 900–800 (SF_5).

*(e) N-(2-Nitroxyethyl)-2-fluoro-2,2-dinitroethyl carbamate, fluorosulfonylimine (**18**) (nc)*

To a solution of **13** (0.4 g, 1 mmol) in dichloromethane (2.5 ml), stirred in an ice bath, was added 90% nitric acid (5 ml) dropwise. After 1.5 h, ice water (50 ml) was added and the dichloromethane layer was separated, dried (sodium sulfate) and the volatiles removed to give 0.4 g of nearly pure **18** (TLC analysis). Crystallization from chloroform gave 0.25 g (69%) of white crystals, m.p. 42–43 °C. ^{19}F NMR (acetone) δ: 53.6 (SO_2F); −110.3 (CF) ppm. ^{1}H NMR ($CDCl_3+D_2O$) δ: 3.75 (t, 2H); 4.66 (t, 2H); 5.54 (d, 2H) ppm. IR (KBr) (cm^{-1}): 3660 (NH); 1650 (C=N, ONO_2); 1615 (NO_2); 900–790

(SF_5). Analysis: Calc. for $C_5H_7F_2N_5SO_{10}$: C, 16.35; H, 1.92; F, 10.34; N, 19.07; S, 8.73%. Found: C, 16.33; H, 2.05; F, 9.48; N, 18.79; S, 8.47%.

Nitration of **12** using the above conditions gave a similar yield of **18**.

Preparation of carbonyl compounds (carbamates)

(a) 3,3,3-Trinitropropyl carbamate (17) (nc)

Triphosgene (1.8 g, 6 mmol) and 3,3,3-trinitropropanol (3.1 g, 0.016 mol) in dichloromethane (10 ml) were stirred at 0 °C during the dropwise addition of a solution of pyridine (1.5 ml, 0.019 mol) in dichloromethane (5 ml). After 24 h at room temperature, the reaction solution was stirred at −10 °C while conc. ammonium hydroxide (30% NH_3) (2 ml, 0.032 mol) was added dropwise. Insoluble solid was removed by filtration and the filtrate was extracted with water and dilute hydrochloric acid. The volatiles were removed to give 2.75 g of product which was chromatographed on silica gel 40 [using dichloromethane followed by dichloromethane/acetone (80:20) as eluant] to yield 0.65 g of solid, m.p. 82–84 °C. ^1H NMR ($CDCl_3$) δ: 3.50 (t, 2H); 4.60 (t, 2H); 4.85 (broad, s, NH_2) ppm. IR (KBr) (cm^{-1}): 3420, 3360, 3300, 3220 (NH); 1720, shoulder at 1760 (C=O); 1620, 1600 (NO_2). Analysis: Calc. for $C_4H_6N_4O_8$: C, 20.18; H, 2.54; N, 23.53%. Found: C, 20.40; H, 2.53; N, 23.54%.

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