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Solvolyis reactions of perfluoro-5-aza-4-nonene, C_3F_7–CF=N–C_4F_9

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Abstract

Hydrolysis of the imine perfluoro-5-aza-4-nonene, C_3F_7–CF=N–C_4F_9, in ether was studied by several spectroscopic techniques including ^{17}O NMR. The initial product is C_3F_7–CO–NH–C_4F_9 which is converted to $(C_3F_7CO)_2NH$ and then to $C_3F_7CONH_2$ and $C_3F_7CO_2H$. Solvolysis in liquid ammonia afforded the amidine C_3F_7–C(=NH)NH_2. Reaction with hydrazine produced 3,5-bis(heptafluoropropyl)-1,2,4-triazole whose crystal structure is reported.

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1. Introduction

We have reported that successive addition of a wide variety of primary amines such as aniline to the imine perfluoro-5-aza-4-nonene, C_3F_7–CF=N–C_4F_9 (**1**), and hydrogen fluoride elimination, leads to a new class of compounds, perfluoroalkyl triazapentadienides, exemplified by PhN=C(C_3F_7)–N=C(C_3F_7)–NHPh [1]. This paper presents a study of similar nucleophilic addition—HF elimination reactions of water, ammonia and hydrazine.

2. Results and discussion

To moderate the exothermic hydrolysis of **1**, an immiscible cosolvent was used. Dropwise addition of two equivalents of water to a solution of the imine in diethyl ether resulted in its slow dissolution through reaction and was intended to prevent high local concentrations of water. Infrared analysis revealed that the principle products from **1** and two equivalents of water were perfluorobutyramide, $C_3F_7CONH_2$ (**2**), perfluorobutyric acid and small amounts of two additional products described below.

More incisive characterization of intermediates was achieved by shorter reaction times and use of stoichiometric amounts of $H_2{}^{17}O$ so that ^{17}O NMR could be used to aid in product characterization (vide infra) in addition to ^{19}F NMR and infrared and mass spectroscopy. In this case, the initial products were found to be the secondary amide C_3F_7–CO–NH–C_4F_9 (**3**), along with smaller amounts of the imide $(C_3F_7CO)_2NH$ (**4**). Compounds **2–4** exhibit distinctive infrared spectroscopic features that enable their identification in mixtures of the three (cf. Table 1). The primary amide **2** exhibits symmetric and asymmetric NH stretching bands at 3405 and 3203 cm^{-1}, a NH_2 deformation mode at 1622 cm^{-1} and a NH_2 rocking mode at 1124 cm^{-1} which are all characteristic of its NH_2 group. In addition, its ^{1}H NMR spectrum (in CD_3CN) demonstrates two resonances at 7.3 and 6.9 ppm due to non-equivalent *cis*- and *trans*-N*H* protons in the stereochemically rigid amide group.

The infrared spectra of the secondary amides **3** and **4** both display amide II bands, that is, a combination of C–N stretching and CHN in-plane bending modes, at 1534 and 1519 cm^{-1}, respectively. There also occur Fermi resonances, which are overtones of these bands, at 3045 and 3017 cm^{-1}, respectively. The ^{19}F NMR spectrum of **3**, compared to **2** and **4**, is unique on account of the "extra" CF_2 resonance contained in the C_4F_9 moiety.

The fluorochemical amides **2–4** have distinctive ^{17}O chemical shifts, 330, 389 and 435 ppm, respectively, a consequence of the large range of shifts for this nucleus [2]. Scheme 1 displays the proposed mechanism for the hydrolysis of C_3F_7–CF=N–C_4F_9. The intermediates formed

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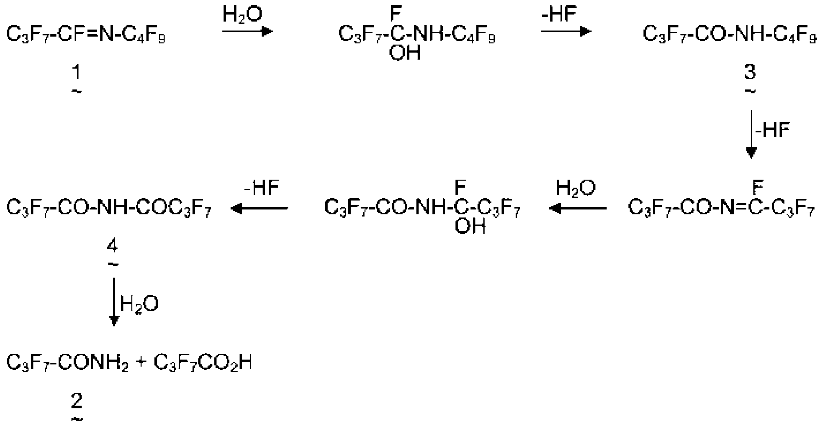
Table 1
Infrared spectral data (cm^{-1})

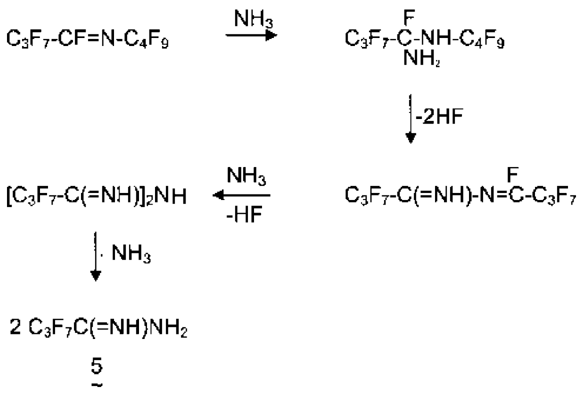
Band	$C_3F_7CONH_2$	$(C_3F_7CO)_2NH$	$C_3F_7CONHC_4F_9$	$C_3F_7C(=NH)NH_2$
Fermi resonance[a]		3017	3045	
NH asymmetric stretch	3405			3363
NH symmetric stretch	3203	3238	3285	3162
C=O stretch	1703	1794	1750	
NH_2 deformation	1622			1626
C–N stretch	1430	1519[a]	1534[a]	1664
NH_2 rock	1124			1119

[a] Enhanced overtone of ~1550 cm^{-1} which is combination of C–N stretch and CNH in-plane bend (amide II band).



Scheme 1.

by addition of water are, by their very nature, hypothetical but identification of the products formed is secure. A plausible alternative could involve simple displacement of fluoride on the sp^2 carbon atom by hydroxide ion; however, as the reaction progresses, the pH falls due to formation of HF and $C_3F_7CO_2H$. In the event, the initial product, secondary amide **3**, arises from localized hydrolysis of the CF=N group. It is the only product in which the N–$CF_2CF_2CF_2CF_3$ portion of **1** remains intact. Subsequent reaction with water leads to loss of fluorine from the carbon atom adjacent to nitrogen and conversion of that CF_2 group to the carbonyl of $(C_3F_7CO)_2NH$. Hydrolysis of imide **4** presumably proceeds by nucleophilic attack at the carbonyl carbon and leads to $C_3F_7CONH_2$ and $C_3F_7CO_2H$. Compound **4** was independently prepared by reaction of $(C_3F_7CO)_2O$ with $C_3F_7CONH_2$ [3]. NMR showed that its reaction in CD_3CN with $H_2{}^{17}O$ resulted in disappearance of the ^{17}O peak at 435 ppm and development of new peaks at 330 and 250 ppm due to the amide **2** and carboxylic acid, respectively, thus confirming the last step in Scheme 1.



Scheme 2.

Ammonolysis of C_3F_7–CF=N–C_4F_9 also appears to proceed by nucleophilic addition followed by HF elimination as proposed in Scheme 2. This reaction is much less complex than the triethylamine-catalyzed addition of urea to **1** which produced **2** and also 4,6-bis(heptafluoropropyl)-1H-[1,3,5]triazin-2-one and 2-fluoro-4,6-bis(heptafluoropropyl)-1,2-dihydro-[1,3,5]triazin-2-ol [4]. Here, the isolated products were $[NH_4]F$ and the volatile, moisture sensitive amidine C_3F_7–C(=NH)NH_2 (**5**). This compound was characterized by mass spectroscopy. The infrared spectrum of the solid shows two NH (symmetric and antisymmetric stretching) bands, at 3363 and 3162 cm^{-1}, NH_2 deformation and rocking modes at 1626 and 1119 cm^{-1}, respectively, and a strong C=N stretching band at 1664 cm^{-1} (cf. Table 1). Assignment of the latter band is consistent with a value of 1690 cm^{-1} reported for $CF_3C(=NH)NH_2$ [5]. The ^1H NMR spectrum in CD_3CN shows a single, broad ($w/2$ 106 Hz) resonance at 5.3 ppm, indicative of fast exchange between the $=NH$ and NH_2 protons. Hydrolysis of **5** in CD_3CN with $H_2{}^{17}O$ was found by ^{17}O NMR to give a quantitative yield of **2**.

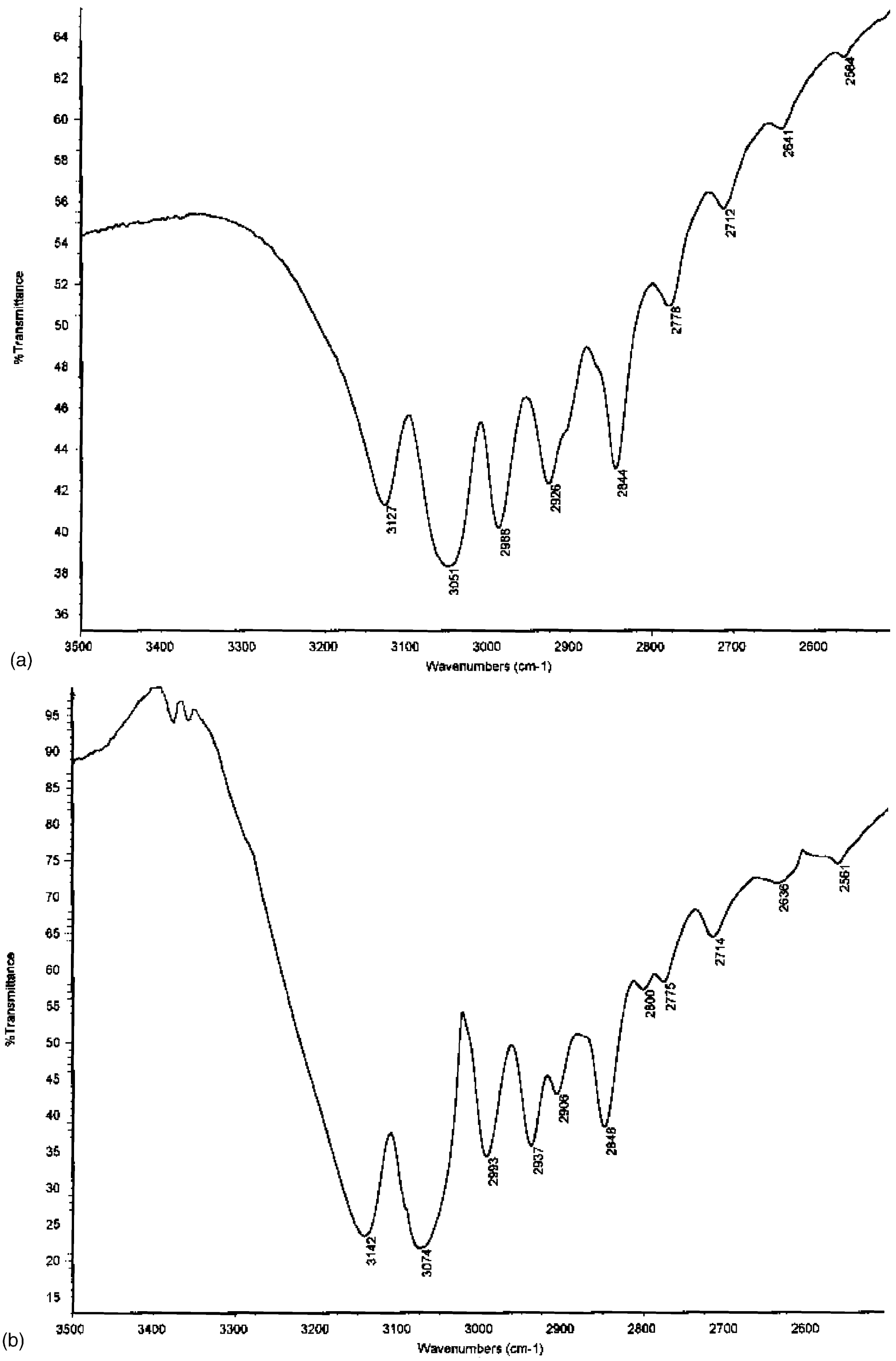


Fig. 1. Infrared spectra of solid **6** (a), **6** in CH_3CN (b) and solid **6**-N-*d* (c).

In the vigorous reaction of **1** with anhydrous hydrazine in diethyl ether, the N–N bond was retained and volatile, crystalline 3,5-bis(perfluoropropyl)-1,2,4-triazole (**6**), resulted. Its ^1H NMR spectrum in CD_3CN shows a single, broad N*H* peak at 10.8 ppm. The ^{19}F NMR spectrum demonstrates only one set of C_3F_7 resonances, indicating rapid movement of the N*H* proton between the N(1) and N(2) sites so that the molecule has effective C_2 symmetry on the NMR time scale. Here, the nitrogen atoms are designated according to the numbering scheme used to describe the molecular structure, vide infra.

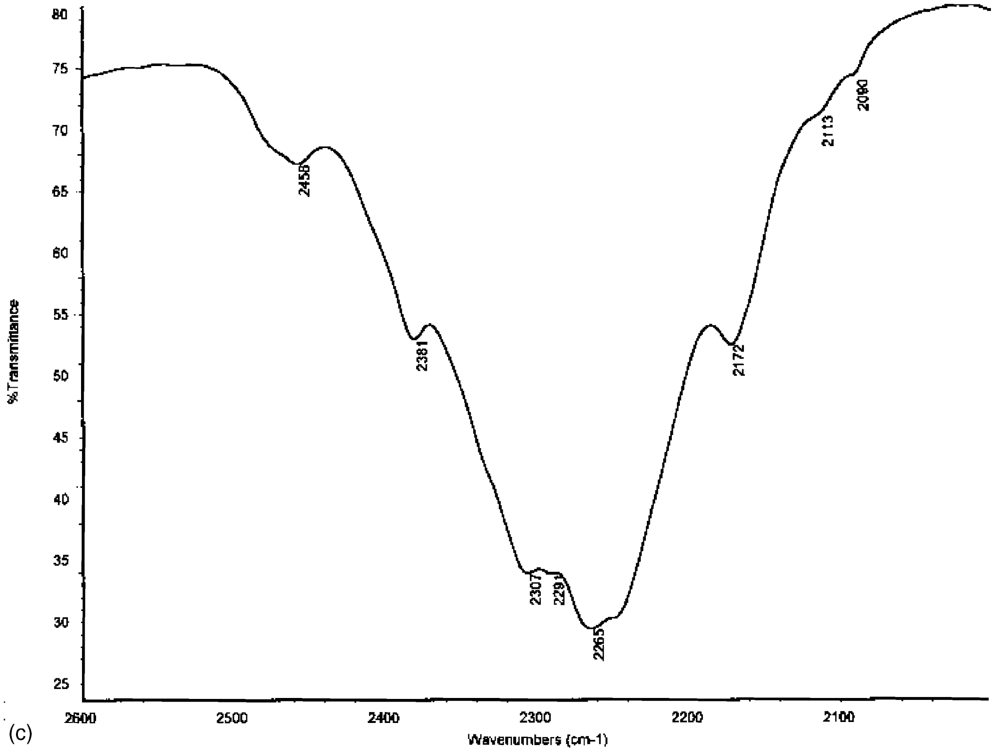


Fig. 1. (*Continued*).

A curious feature of the infrared spectrum of **6** is the occurrence of an envelope of nine closely spaced bands between 3127 and 2564 cm^{-1} (Fig. 1a). The spectroscopic features of **6** are clearly associated with hydrogen bonding and are therefore solvent-dependent. The infrared spectrum of this compound in acetonitrile is similar to that in the solid state, having eleven peak maxima between 3142 and 2561 cm^{-1} (cf. Fig. 1b). However, in chloroform, a solvent capable of forming hydrogen bonds with it, only a featureless, broad ($w/2$ 56 cm^{-1}) band centered at 3400 cm^{-1} occurs. The N–D stretching region of the N-deuterated analog of **6** also exhibits fine structure, with five bands between 2458 and 2172 cm^{-1} (Fig. 1c). The envelope formed by these peaks is, however, narrower and more symmetric than that of the N–H compound in which peak intensities decrease on going to lower frequency. The origin of such multiple infrared absorption maxima in triazoles [6] and other strongly hydrogen bonded solids [7] has been discussed in terms of Fermi resonances [8]. More recently, the vibrational spectrum of triazole has been analyzed in detail [9]. In the solid state, this compound has, as does **6**, a broad structured N–H stretching band in the infrared. This band shape was attributed to coupling of the N–H bending mode with fundamentals in the 1550–1100 cm^{-1} region; binary overtones and combinations in Fermi resonance with the N–H stretching fundamental lead to a large number of sub-bands [9]. C–H bending modes are not required for there are none in **6**. Whatever the details of the coupling mechanism, it appears to be in part intermolecular and to involve aggregation by means of hydrogen bonds, bonding that should be favored by the electronegative effect of two C_3F_7 groups. This is evident from the effect of solvent on the N–H stretching band shape of **6**.

Synthesis of 3,5-bis(perfluoropropyl)-1,2,4-triazole has been previously reported: the 4*H* tautomer was obtained

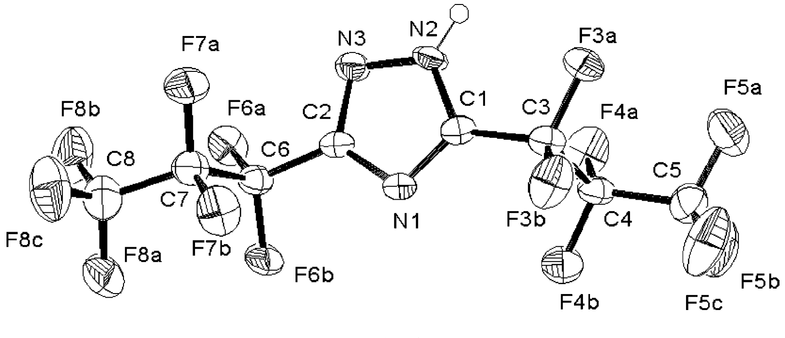


Fig. 2. ORTEP plot of 2,5-$(C_3F_7)_2$-1,3,4-C_2N_3.

Table 2
Bond distances (Å) and angles (°) in **6** [and 1,3,4-triazole]

N(1)–C(1)	1.314(6) [1.324(3)]
N(1)–C(2)	1.351(6) [1.359(3)]
C(1)–N(2)	1.342(6) [1.331(3)]
C(1)–C(3)	1.498(7)
N(2)–N(3)	1.344(6) [1.359(3)]
N(2)–H(2A)	0.880
N(3)–C(2)	1.330(6) [1.323(3)]
C(2)–C(6)	1.495(7)
C(1)–N(1)–C(2)	102.8(4) [103.0(2)]
N(1)–C(1)–N(2)	110.3(4) [110.1(2)]
N(2)–C(1)–C(3)	122.1(4)
C(1)–N(2)–N(3)	110.0(4) [110.2(2)]
C(1)–N(2)–H(2A)	125.0
C(2)–N(3)–N(2)	102.1(4) [102.1(2)]
N(3)–C(2)–C(1)	121.2(4)
N(3)–C(2)–N(1)	114.8(4) [114.6(2)]

from $N_2H_4 \cdot H_2O$ and the $1H$ tautomer from propionylhydrazine [10]. Although this compound rapidly tautomerizes in solution (vide supra), its structure in the solid state was uncertain. The crystal structure at −100 °C was determined to resolve this issue.

An ORTEP drawing of the structure, showing the numbering system employed, is provided in Fig. 2. Selected bond distances and angles for **6** are given in Table 2 along with analogous data for 1,2,4-triazole itself [11,12] for comparative purposes. An interesting aspect of the molecular packing is the one-dimensional hydrogen bonding of triazole along the *c* axis. The staggered packing of the molecules permits close contact of N(3) with the perfluoropropyl fluorine atoms F(3B) and F(4B) at 2.95 and 2.88 Å, respectively. Additional close contacts between fluorine atoms on adjacent molecules are observed with $F(5A) \cdots F(8A)$ and $F(3A) \cdots F(6B)$ being 2.79 and 2.81 Å, respectively (cf. Fig. 3). The triazole ring is strictly planar and pendant carbon atoms C(3) and C(6) are minimally displaced by only −0.034 and 0.050 Å, respectively. The dihedral angle between triazole ring planes is 98.4°. The $N(2)\text{–}H \cdots N(1)$ bond distance is 2.097(6) Å and the $N\text{–}H \cdots N$ bond angle is 157.5(2)°. These data demonstrate a weaker hydrogen bond than that observed [12] in triazole which has $N\text{–}H \cdots N$ values of 1.789(2) Å and 168.2(1)°. The N*H* hydrogen atom is located on N(2), one (of two) adjacent nitrogen atoms in the ring and thus the compound crystallizes as the $1H$ tautomer (as does triazole, both being described here using the CAS numbering system). More interesting than the absolute metrical data is a comparison of the two structures which show how the structure of the N_3C_2 triazole ring changes as a result of replacing both C*H* hydrogen atoms with C_3F_7 groups. Three changes are conspicuous: (1) the N–N bond contracts by 0.015 Å; (2) both C–N bonds involving the central nitrogen atom, N(1)–C(1) and N(1)–C(2) in Fig. 1, contract; (3) C(1)–N(2) and N(3)–C(2), the bonds between carbon and the pair of adjacent nitrogen atoms both expand by 0.011 and 0.007 Å, respectively.

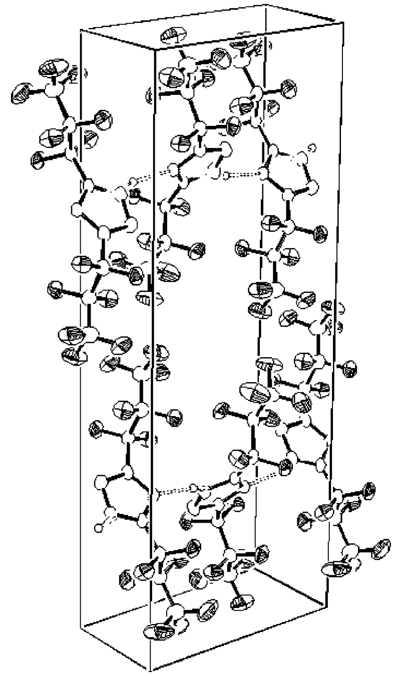
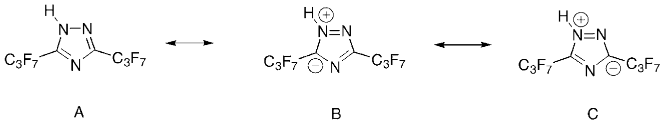


Fig. 3. Packing diagram for $2,5\text{-}(C_3H_7)_2\text{-}1,3,4\text{-}C_2N_3$. The *b*-axis is vertical; H-bonds run along *c*-axis.

These changes can be rationalized in terms of three of the resonance structures of triazole written by Goldstein et al. [11] as shown below. The two dipolar forms, B and C, have, as is observed, shorter N–N and longer C–NN bonds than structure A. Structures B and C each bear a formal −1 charge at carbon and should be stabilized by electronegative groups, such as C_3F_7, at C(1) and C(2).



Triazole (**6**) itself is a monoprotic acid and was converted to the $(C_4H_9)_4N^+$ salt of its conjugate base, **7**, by reaction with $[(C_4H_9)_4N][OH]$ in methanol–water.

3. Experimental

NMR spectra were recorded on CD_3CN or $CDCl_3$ (dried with molecular sieves) solutions in 5 mm tubes on a Varian INOVA 400 spectrometer operating at 54.3 MHz for ^{17}O. Spectra of enriched samples (20 at.% ^{17}O) were typically collected with 90° pulses, 0.1 s acquisition times, 0.2 s relaxation delays and a 67 kHz sweep width. Excellent signal/noise was observed in 1500 transients obtained in 6 min. ^{17}O chemical shifts in ppm are referenced to external $H_2{}^{17}O$; ^1H, ^{13}C and ^{19}F chemical shifts are in ppm relative to internal Me_4Si and $CFCl_3$, respectively. Coupling constants are in Hz. Raman spectra were obtained using solid samples and 782 nm laser excitation.

Perfluoro-5-aza-4-nonene was prepared by a modification of methodology reported by Petrov et al. [13] which involves cracking of perfluoro(tributylamine) and elimination of C_4F_{10} in a reaction catalyzed by strong Lewis acids. The procedure reported here uses a small flask as a continuous reactor, allowing a relatively large quantity of substrate to be processed with minimum use of catalyst. It emphasizes efficiency over yield.

Fluoroimine **1** was prepared by dropwise addition under nitrogen of 90 g $(C_4F_9)_3N$ (3M) to stirred SbF_5, 36 g, contained in a 100 ml flask and heated to ca. 120–140 °C with an oil bath. The rate of addition was adjusted so as to provide brisk evolution of the product, which was removed as it formed by distillation through a short-path distillation head; 72 g was collected. An alembic is useful for this purpose for it minimizes contact between **1** and hot SbF_5. This is advantageous because these two compounds can react further with elimination of C_4F_{10} and formation of C_3F_7CN. The combined distillates from several such reactions, 603 g, were washed twice with 150 ml ice water then dried over $CaCl_2$ to give 450 g crude product. Distillation through a 16 in. spinning band column gave 206 g (44%) of **1**, bp 99–102 °C. The compound was handled in a well-ventilated hood.

Imide **4** was prepared from $C_3F_7CONH_2$ and excess $(C_3F_7CO)_2O$ [3]. Distillation gave a product that, by ^1H and ^{17}O NMR analysis, contained 80% **4** and 20% unreacted **2**. This, and other moisture sensitive compounds, were handled (and Nujol mulls for IR spectra prepared) under nitrogen in a drybox.

3.1. Hydrolysis of C_3F_7–$CF{=}N$–C_4F_9

(A) Water (0.166 g, 9.2 mmol) was added slowly by microliter syringe to a stirred solution of 2.0 g (4.6 mmol) **1** in 30 ml dry ether. After 16 h, the solution was transferred to a sublimer and the ether was removed under high vacuum. The sublimer probe was cooled to −78 °C and heating to 45° then led to collection of 1.0 g of white, waxy sublimate. This was extracted with 20 ml Freon 113 (CF_2Cl–$CFCl_2$). Infrared analysis showed that the insoluble material, 0.65 g, was mostly $C_3F_7CONH_2$; and that the soluble material (0.35 g) contained $(C_3F_7CO)_2NH$ along with smaller amounts of C_3F_7–CO–NH–C_4F_9 and $C_3F_7CO_2H$.

(B) A solution of 1.89 g (4.4 mmol) **1** in 15 ml ether was treated with 0.073 g $H_2{}^{17}O$ (20 at.% ^{17}O, 4.1 mmol). After 30 min, volatiles were removed on the vacuum line. Analysis by infrared and ^1H and ^{17}O NMR spectroscopy of the residue, 1.1 g, revealed a 79:19:2 mixture of **3**, **4** and **2**.

$C_3F_7CONH_2$: NMR (CD_3CN): ^1H: δ 7.3, 6.9 ($\mathrm{N}H_2$). ^{17}O: δ 330. ^{19}F: δ −80.6 (t, 9, $\mathrm{C}F_3$), −120.0 (q, 9 $\mathrm{C}F_2\mathrm{CO}$), −126.8 (s, $\mathrm{C}F_2\mathrm{CF_3}$).

C_3F_7–CO–NH–C_4F_9: NMR (CD_3CN): ^1H: δ 9.6 ($\mathrm{N}H$). ^{17}O: δ 389. ^{19}F: δ −80.3 (t, 9, C_3F_7 $\mathrm{C}F_3$), −80.6 (tt, 10, 3, C_4F_9 $\mathrm{C}F_3$), −93.9 (t, 13, NH–$\mathrm{C}F_2$), −119.7 (q, 9, $\mathrm{C}F_2\mathrm{CO}$), −123.0 (m, C_4F_9 $\mathrm{CF_3CF_2C}F_2$), −125.8 (m, C_4F_9 $\mathrm{C}F_2\mathrm{CF_3}$), −126.4 (s, C_3F_7 $\mathrm{C}F_2\mathrm{CF_3}$).

$(C_3F_7CO)_2NH$: NMR (CD_3CN): ^1H: δ 10.7 ($\mathrm{N}H$). ^{17}O: δ 435. ^{19}F: δ −80.1 (t, 9, $\mathrm{C}F_3$), −118.9 (q, 9, $\mathrm{C}F_2\mathrm{CO}$) and −125.7 (s, $\mathrm{C}F_2\mathrm{CF_3}$).

3.2. Ammonolysis of C_3F_7–$CF{=}N$–C_4F_9

Liquid ammonia, 5 ml, was condensed upon 2.65 g **1** at −176°. The reaction mixture was warmed to −78°. Unreacted ammonia and **1** were pumped away. The residue was fractionated on a high vacuum line by distillation through a series of U-traps. A liquid, which passed slowly through a −78° trap, was collected. On standing at 30°, it slowly crystallized to give clear, colorless blades of **5**, 0.4 g (31%). Anal. Calcd. for $C_4H_3F_7N_2$: C, 22.6; H, 1.4; N, 13.2. Found: C, 22.4; H, 1.4; N, 13.1. Mass spectrum: *m/z* 212.1076 (M^+, Calcd. 212.1079); self-CI MS: *m/z* 213 ($M^+ + H$). NMR (CD_3CN): ^1H: δ 5.3 (*w*/2 106 Hz); ^{19}F: δ −80.3 (t, 9, $\mathrm{C}F_3$), −120.2 (q, 9, $\mathrm{C}F_2\mathrm{CN}$), −126.8 (s, $\mathrm{C}F_2\mathrm{CF_3}$).

The X-ray powder pattern of the non-volatile residue, 1.2 g, demonstrated that it was $[NH_4]F$ along with about 5% $[NH_4][HF_2]$.

3.3. Reaction of C_3F_7–$CF{=}N$–C_4F_9 with hydrazine

Hydrazine (97%, anhydrous, 0.78 g, 24 mmol) was suspended with stirring in 30 ml anhydrous diethyl ether and cooled to 4 °C. Fluoroimine **1**, 2.16 g (4.9 mmol), was added dropwise. After warming to room temperature, the ether phase was filtered off, washed with water and dried over $MgSO_4$. The residue remaining after evaporation of the ether was sublimed under vacuum and the sublimate recrystallized from carbon tetrachloride to give 0.55 g (28%) **6** as tiny, colorless needles, mp 106–106.5 °C (sealed capillary). Anal. Calcd. for $C_8HF_{14}N_3$: C, 23.7; H, 0.2; N, 10.4. Found: C, 24.0; H, 0.3; N, 10.5. Electron impact mass spectrum: *m/z* 386 ($M^+ - F$), 286 ($M^+ - C_2F_5$). Negative ion FAB MS: *m/z* 404 ($M^+ - H$). NMR (CD_3CN): ^1H: δ 10.8 ($\mathrm{N}H$). ^{13}C: δ 151.5 (t, $^2J_{CF} = 30$, $C\mathrm{N}$), 118.6 (qt, 287, 34, $C\mathrm{F_3}$), 111.6 (tt, 256, 31, $C\mathrm{F_2CN}$), 109.4 (th, 266, 37, $C\mathrm{F_2CF_3}$). ^{19}F: δ −80.1 (t, 9, $\mathrm{C}F_3$), −112.5 (q, 8, $\mathrm{C}F_2\mathrm{CN}$), −126.6 (s, $\mathrm{C}F_2\mathrm{CF_3}$). IR (thin film): 3127, 3051, 2988, 2926, 2844, 2778, 2712, 2641, 2564, 2474, 1453, 1346, 1218, 1123, 1036, 893, 886. 743, 669, 607 and 543 cm^{-1}. IR (CD_3CN): 3142, 3074, 2993, 2937, 2906, 2828, 2800, 2775, 2714, 2636 and 2561 cm^{-1}. Raman: 1551, 1499, 1353, 1323, 1328, 1039, 895, 783, 733, 676, 624, 381, 352 and 305 cm^{-1}. Ultraviolet spectrum (CH_3CN): λ_{max} 207 nm (log ε 2.88).

The N-deuterated analog was prepared by dissolving **6** in CH_3OD under nitrogen and then removing the methanol under vacuum. IR (Nujol): 2458, 2381, 2305, 2264, and 2172 cm^{-1}.

3.4. $[Bu_4N][(C_3F_7)_2C_2N_3]$ (**7**)

Triazole (**6**), 0.1 g (0.25 mmol) was dissolved in 3 ml methanol and 1 ml 0.5 M $[Bu_4N][OH]$ in water added. The methanol was slowly removed on a rotary evaporator whereupon the product separated as colorless flakes. It was collected on a filter, washed with water and vacuum dried to give 0.15 g (94%), of **7**, mp 157–158 °C. Anal. Calcd. for $C_{24}H_{36}F_{14}N_4$: C, 44.6; H, 5.6; N, 8.7. Found: C, 44.8; H, 5.3; N, 8.6. NMR (CD_3CN): ^{13}C: δ 151.3 (t, $^3J_{CF} = 26$, *C*N), 119.4 (qt, 288, 35, *C*F_3), 114.2 (tt, 263, 37, *C*F_2CN), 110.3 (th, 263, 34, *C*F_2CF_3). ^{19}F: δ −76.4 (t, 9, C*F*$_3$), −105.6 (q, 9, C*F*$_2$CN), −122.7 ppm (s, C*F*$_2CF_3$). IR (Nujol): 1490, 1478, 1340, 1234, 1182, 882 and 741 cm^{-1}. Raman: 1479, 1451, 1324, 1126, 1012, 915, 884, 759, 740, 617 and 268 cm^{-1}. Ultraviolet spectrum (CH_3CN): λ_{max} 207 nm (log ε 3.96).

3.5. X-ray crystallographic analysis

Numerous solvents for crystallization of **6** were tried. Most gave tiny needles but toluene afforded curled plates. The sample used was trimmed from a larger plate. Poor spot shapes prompted use of wider frames. Twinning was investigated but none found. A fragment of approximate dimensions 0.45 mm × 0.18 mm × 0.14 mm was secured to a 0.1 mm glass capillary and mounted on a Bruker SMART system for data collection at 173(2) K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 20 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 60 reflections. Data collection was carried out with graphite-monochromatized Mo Kα radiation with a frame time of 60 s and a detector distance of 4.9 cm. A randomly oriented region of reciprocal space was surveyed to 1.5 hemispheres and a resolution of 0.84 Å. Three major sections of frames were collected with 0.50° steps in ω at three different ϕ settings and a detector position of -28° in 2θ. The intensity data were corrected for absorption and decay (SADABS) [14]. Final cell constants were calculated from 3555 strong reflections after integration (SAINT V6.1) [15].

The structure was solved using SHELXS-86 (16) and refined with SHELXL-97 [16]. The space group was determined based on systematic absences and intensity statistics. A direct-methods solution was calculated that provided most non-hydrogen atoms from the E-map. Full-matrix least-squares/difference Fourier cycles were performed that located the remaining non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic displacement parameters unless stated otherwise. The hydrogen atom was placed in an ideal position and refined as a riding atom with relative isotropic displacement parameters. A summary of crystal structure data is given in Table 3. Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 209209. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1E2, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

Table 3
Summary of crystal structure data

Formula	$C_8H_1F_{14}N_3$
Fw	405.12
Temperature (K)	173(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 5.2462(18)$ Å, $\alpha = 90^\circ$
	$b = 24/5718(8)$ Å, $\beta = 100.081(14)^\circ$
	$c = 10.067(4)$ Å, $\gamma = 90^\circ$
V (Å^3)	1277.6(8)
D_{calc} (g cm^{-3})	2.106
Z	4
λ (Å)	0.71073
2θ range (°)	1.6–25.11
Intensities (unique, R_i)	8291 (2249, 0.0517)
Data/restraints/parameters	2249/0/226
GOF on F^2	1.170
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0715$, $wR2 = 0.1778$
R indices (all data)	$R1 = 0.1007$, $wR2 = 0.1912$
Largest difference peak and hole (e Å^{-3})	0.326, −0.341

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