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SYNTHESIS OF 4-BENZYLSULFONYL-5-POLYFLUOROALKYL-ν-TRIAZOLES FROM 1,1-DIHYDROPOLYFLUOROALKYL BENZYL SULFONES

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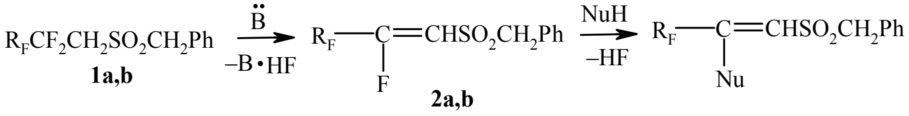
The reaction of 1,1-dihydropolyfluoroalkyl benzyl sulfones with sodium azide or trimethylsilyl azide in the presence of tertiary amines gives ammonium salts of 4-benzylsulfonyl-5-polyfluoroalkyl-ν-triazoles. The proposed reaction scheme includes the participation of catalytic amounts of azide ion in the cyclization of the formed intermediate vinyl azides to triazoles. X-ray analysis of 1,4-diazabicyclo[2.2.2]octane salt of 4-benzylsulfonyl-5-(ω-H-hexafluoropropyl)-ν-triazole has been carried out.

Keywords: 4-benzylsulfonyl-5-polyfluoroalkyl-ν-triazole, 1,1-dihydropolyfluoroalkyl sulfone.

1,1-Dihydropolyfluoroalkyl benzyl sulfones **1a,b** are efficient reagents for the synthesis of fluorine-containing vinyl sulfones, enamines, imines, ketones, and pyrazoles [1-3]. The basis of their synthetic application lies in dehydrofluorination reaction in the presence of base leading to the formation of the reactive fluorovinyl benzyl sulfones **2a,b** which can react readily with nucleophiles like ammonia, amines, and hydrazines [3].



$$R_FCF_2CH_2SO_2CH_2Ph \xrightarrow[-B\cdot HF]{\ddot{B}} R_F{-}\underset{F}{\underset{|}{C}}{=}CHSO_2CH_2Ph \xrightarrow[-HF]{NuH} R_F{-}\underset{Nu}{\underset{|}{C}}{=}CHSO_2CH_2Ph$$

1a,b **2a,b**

1, **2** **a** $R_F = HCF_2$; **b** $R_F = H(CF_2)_3$

In this work we have studied the reaction of sulfones **1a,b** with trimethylsilyl azide and sodium azide and have found that, in the presence of the tertiary amines (triethylamine or 1,4-diazabicyclo[2.2.2]octane) trialkylammonium salts of 4-benzylsulfonyl-5-polyfluoroalkyl-ν-triazoles **3a-d** are formed.

We can therefore propose that in this case, as in the example of the reaction of sulfones **1a,b** with other nucleophiles [2, 3], vinyl fluorides **2a,b** are initially formed which then react with azide. Cyclization of vinyl azides **4a,b** obtained in this way gives the final salts **3a-d** in the presence of base. For confirmation of this proposal we have synthesized vinyl azides **4a,b** by the reaction of vinyl fluorides **2a,b** with trimethylsilyl azide. Vinyl azides **4a,b** were also obtained by brief refluxing of a suspension containing equimolar amounts of sulfone **1a,b** and triethylamine with 15% molar excess of sodium azide in benzene as solvent.

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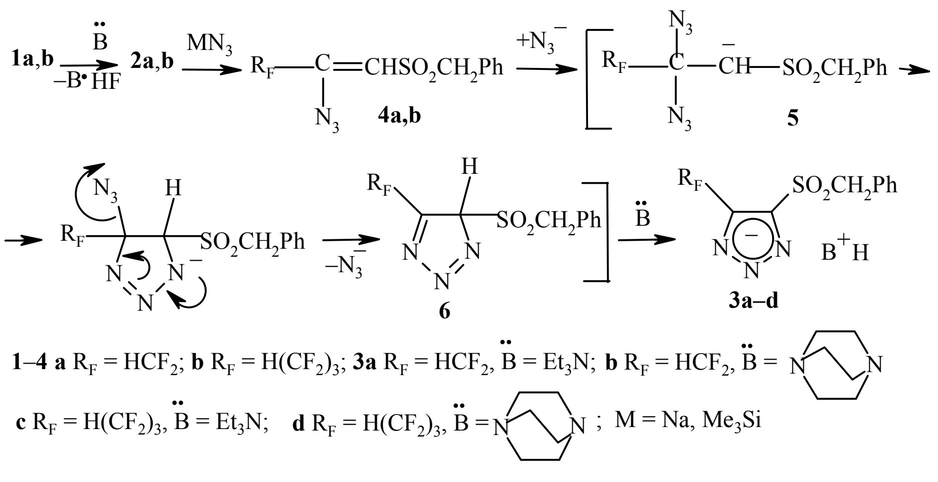
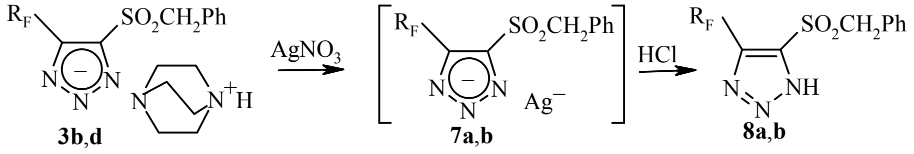


1–4 **a** $R_F = HCF_2$; **b** $R_F = H(CF_2)_3$; **3a** $R_F = HCF_2$, B = Et_3N; **b** $R_F = HCF_2$, B = 1,4-diazabicyclo[2.2.2]octane; **c** $R_F = H(CF_2)_3$, B = Et_3N; **d** $R_F = H(CF_2)_3$, B = 1,4-diazabicyclo[2.2.2]octane; M = Na, Me_3Si

According to literature data, cyclization to triazoles is not characteristic of vinyl azides [4]. However, in agreement with the proposals made in the study [5], such a cyclization can be realized when electron-acceptor substituents are present at the carbon atoms of the C=C double bond in the vinyl azide molecule. The compounds **4a,b** do fit this condition but even prolonged heating of them with tertiary amines did not lead to formation of triazole salts **3a-d**. The latter are only formed when catalytic amounts (5 mole %) of trimethylsilyl azide or sodium azide are added to equimolar mixture of vinyl azides **4a,b** and tertiary amine. This observation allows us to propose a reaction scheme in which the molecule of vinyl azide **4a,b** is able to add the azide anion, which appears in the reaction mixture when adding sodium azide or trimethylsilyl azide (in the latter case as a result of partial hydrolysis). The carbanion formed **5** is cyclized to compound **6** which is then converted to the salts **3a-d** in the presence of base. A similar scheme for cyclization of carbanion which contains azide group in the α-position [6] clearly explains the catalytic role of the azide ion.

The salts **3a,c** are viscous liquids which are soluble in benzene. Triazole and 1,4-diazabicyclo-[2.2.2]octane salts **3b,d** are crystalline substances, poorly soluble in benzene. Treatment of triethylammonium salts **3a,c** with benzene solution of 1,4-diazabicyclo[2.2.2]octane leads to exchange of the ammonium cation. The solubility of compounds **3a-d** in water depends on the chain length of the polyfluoroalkyl substituent. Salts **3a,b** containing difluoromethyl substituent are readily soluble in water whereas the salts **3c,d** are poorly soluble (the latter were, in fact, purified by us by crystallization from water). Compounds **3a-d** are salts of the strong organic NH-acids **8a,b** and these were isolated in the free state by subsequent conversion of the salts **3b,d** to the silver salts **7a,b** and treatment of the latter with hydrochloric acid.



7, 8 **a** $R_F = HCF_2$, **b** $R_F = H(CF_2)_3$

The value of the pK_a of compound **8b** was found to be 2.00, i.e. the acidity of this compound exceeds the acidity of other known triazoles with electron-acceptor substituents [7, 8] by 3-4 orders.

The structure of salt **3d** was confirmed by X-ray diffraction analysis. The general view of the cation and anion in salt **3d** is shown in Figure 1 and their basic geometric parameters are presented in Table 1.

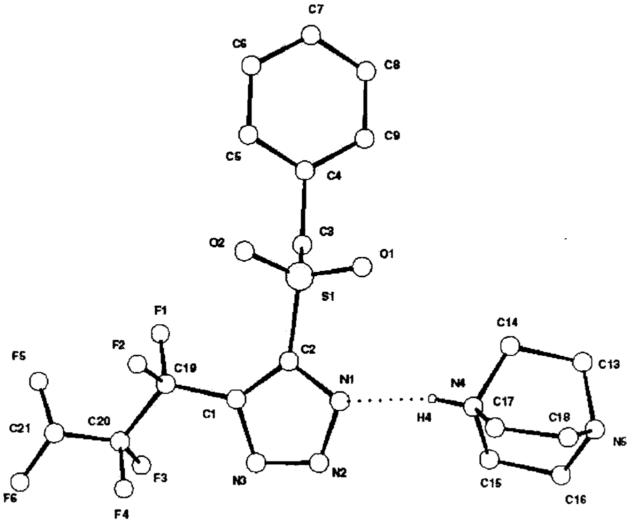


Fig. 1. Overall view of the cation and anion in compound **3d**.

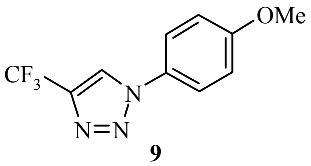
The central triazole heterocycle $N_{(1-3)}C_{(1)}C_{(2)}$ is planar (the deviation of the atoms from the mean-square plane does not exceed 0.002 Å) and the benzene ring $C_{(4-9)}$ forms dihedral angle of 21.1° with this plane. The bond lengths and bond angles in the heterocycle $N_{(1-3)}C_{(1)}C_{(2)}$ are close to the corresponding values found for the molecules **9** [9] and **10** [10]. The geometric parameters for the SO_2CH_2Ph group are standard [11, 12].

TABLE 1. Basic Bond Lengths *d* and Bond Angles ω in the Salt **3d**

Bond	*d*, Å	Angle	ω, deg.
$S_{(1)}$–$O_{(1)}$	1.432(5)	$O_{(1)}$–$S_{(1)}$–$O_{(2)}$	117.3(3)
$S_{(1)}$–$O_{(2)}$	1.417(6)	$O_{(1)}$–$S_{(1)}$–$C_{(2)}$	107.4(3)
$S_{(1)}$–$C_{(2)}$	1.749(5)	$O_{(2)}$–$S_{(1)}$–$C_{(2)}$	108.5(3)
$S_{(1)}$–$C_{(3)}$	1.774(7)	$O_{(1)}$–$S_{(1)}$–$C_{(3)}$	108.5(4)
$N_{(1)}$–$N_{(2)}$	1.334(7)	$O_{(2)}$–$S_{(1)}$–$C_{(3)}$	110.3(3)
$N_{(1)}$–$C_{(2)}$	1.334(8)	$C_{(2)}$–$S_{(1)}$–$C_{(3)}$	104.0(3)
$N_{(2)}$–$N_{(3)}$	1.321(8)	$N_{(2)}$–$N_{(1)}$–$C_{(2)}$	107.8(5)
$N_{(3)}$–$C_{(1)}$	1.351(9)	$N_{(1)}$–$N_{(2)}$–$N_{(3)}$	110.2(5)
$N_{(4)}$–$C_{(14)}$	1.490(8)	$N_{(2)}$–$N_{(3)}$–$C_{(1)}$	106.9(6)
$N_{(4)}$–$C_{(15)}$	1.494(9)	$C_{(14)}$–$N_{(4)}$–$C_{(15)}$	108.1(6)
$N_{(4)}$–$C_{(17)}$	1.486(9)	$C_{(14)}$–$N_{(4)}$–$C_{(17)}$	108.7(6)
$N_{(5)}$–$C_{(13)}$	1.464(9)	$C_{(15)}$–$N_{(4)}$–$C_{(17)}$	109.8(6)
$N_{(5)}$–$C_{(16)}$	1.474(8)	$C_{(13)}$–$N_{(5)}$–$C_{(16)}$	108.3(5)
$N_{(5)}$–$C_{(18)}$	1.447(9)	$C_{(13)}$–$N_{(5)}$–$C_{(18)}$	109.3(6)
$C_{(1)}$–$C_{(2)}$	1.368(9)	$C_{(16)}$–$N_{(5)}$–$C_{(18)}$	109.2(6)
$C_{(1)}$–$C_{(19)}$	1.477(11)	$N_{(3)}$–$C_{(1)}$–$C_{(2)}$	107.9(6)
$C_{(3)}$–$C_{(4)}$	1.508(9)	$N_{(3)}$–$C_{(1)}$–$C_{(19)}$	119.5(7)
		$C_{(2)}$–$C_{(1)}$–$C_{(19)}$	131.9(7)
		$S_{(1)}$–$C_{(2)}$–$N_{(1)}$	119.5(5)
		$S_{(1)}$–$C_{(2)}$–$C_{(1)}$	133.4(5)
		$N_{(1)}$–$C_{(2)}$–$C_{(1)}$	107.2(5)
		$S_{(1)}$–$C_{(3)}$–$C_{(4)}$	111.5(4)

TABLE 2. Atomic Coordinates and Equivalent Isotropic Thermal Parameters U_{eq} in the Structure of Compound **3d**

Atom	x	y	z	U_{eq}, Å^2
$S_{(1)}$	0.29075(11)	0.2138(3)	0.56210(6)	0.0547
$O_{(1)}$	0.3692(3)	0.108(1)	0.53573(18)	0.0757
$O_{(2)}$	0.2679(4)	0.4311(9)	0.5461(2)	0.0817
$N_{(1)}$	0.3916(4)	0.094(1)	0.6496(2)	0.0569
$N_{(2)}$	0.3974(4)	0.1229(12)	0.7026(2)	0.0716
$N_{(3)}$	0.3289(5)	0.2587(12)	0.7184(2)	0.0732
$N_{(4)}$	0.5322(4)	-0.210(1)	0.62170(19)	0.0487
$N_{(5)}$	0.6456(4)	-0.5321(9)	0.6147(2)	0.0561
$C_{(1)}$	0.2781(5)	0.3181(13)	0.6739(3)	0.0667
$C_{(2)}$	0.3180(4)	0.2147(12)	0.6309(2)	0.0483
$C_{(3)}$	0.1870(5)	0.0434(13)	0.5564(3)	0.0634
$C_{(4)}$	0.1466(4)	0.0416(13)	0.4998(2)	0.0545
$C_{(5)}$	0.0869(4)	0.2075(13)	0.4819(3)	0.0611
$C_{(6)}$	0.0496(5)	0.2019(17)	0.4293(3)	0.0778
$C_{(7)}$	0.0735(6)	0.0308(18)	0.3964(3)	0.0798
$C_{(8)}$	0.1325(6)	-0.1299(16)	0.4145(3)	0.0808
$C_{(9)}$	0.1702(5)	-0.1289(13)	0.4651(3)	0.0652
$C_{(13)}$	0.5730(5)	-0.5405(13)	0.5713(3)	0.0635
$C_{(14)}$	0.5075(5)	-0.3418(13)	0.5729(3)	0.0641
$C_{(15)}$	0.5218(5)	-0.3553(14)	0.6696(3)	0.0670
C(16)	0.5949(6)	-0.5372(13)	0.6663(3)	0.0661
$C_{(17)}$	0.6339(6)	-0.1342(14)	0.6180(4)	0.0871
$C_{(18)}$	0.6996(5)	-0.3295(12)	0.6110(3)	0.0690
$C_{(19)}$	0.2043(8)	0.4923(18)	0.6776(4)	0.1196
$C_{(20)}$	0.1817(9)	0.5765(19)	0.7338(5)	0.1331
$C_{(21)}$	0.1330(11)	0.769(2)	0.7380(5)	0.4113
$F_{(1)}$	0.1270(5)	0.4283(19)	0.6501(4)	0.2115
$F_{(2)}$	0.2353(7)	0.6915(13)	0.6541(3)	0.1832
$F_{(3)}$	0.1479(6)	0.3970(15)	0.7616(3)	0.1821
$F_{(4)}$	0.2600(8)	0.6538(15)	0.7585(4)	0.2001
$F_{(5)}$	0.0608(12)	0.757(4)	0.7085(5)	0.3784
$F_{(6)}$	0.1082(13)	0.810(2)	0.7869(4)	0.2863
$H_{(4)}$	0.485(6)	-0.118(13)	0.626(3)	0.07(2)



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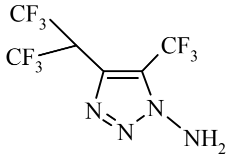

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In the crystal of compound **3d** the cation and anion are bonded *via* an extremely strong [13] $N_{(1)}\cdots H_{(4)}$–$N_{(4)}$ hydrogen bond. The basic geometrical parameters for this bond are $N_{(1)}\cdots N_{(4)}$ 2.783 (8), $N_{(1)}\cdots H_{(4)}$ 1.92 (8), $N_{(4)}$–$H_{(4)}$ 0.87 (8) Å and $N_{(1)}$–$H_{(4)}$–$N_{(4)}$ 168 (5)°.

EXPERIMENTAL

^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on a Varian VXR-300 spectrometer at working frequencies of 299.943, 282.203, and 75.43 MHz respectively. The internal standards were tetramethylsilane and hexafluorobenzene (-162.9 ppm relative to CCl_3F). Monitoring of the reaction course was carried out by

^{19}F NMR spectroscopic method. IR spectra were taken on UR-20 instrument. The ionization constants were determined by spectroscopic method and by pH-titration at λ = 227 nm using SF-16 and Specord UV-vis spectrophotometers and an EV-74 pH meter [14]. Both methods gave the same result. The ionization constant value at 20°C and ionic strength of 0.1 (KCl) was 2.00 ± 0.03. The anion form of compound **8b** has weak light absorption maxima at λ = 212 and 217 nm ($\varepsilon = 1.5 \times 10^4$) and the molecular form – at $\lambda < 212$ nm in the UV spectrum. Both forms have four low intensity absorption maxima in the region of 250-270 nm.

2-Azido-1-benzylsulfonyl-3,3-difluoroprop-1-ene (4a). Suspension of sulfone **1a** (0.54 g, 2 mmol), triethylamine (0.28 ml, 2 mmol), and sodium azide (0.15 g, 2.3 mmol) in benzene (10 ml) was refluxed for 3 min, cooled, and washed with water (2 × 5 ml). After drying with $CaCl_2$ the solvent was evaporated and the remaining oily material was dissolved in mixture of hexane and ether (4:1, 20 ml) and then left for 12 h at -20°C. The precipitated crystals were filtered off to give compound **4a** (0.31 g, 56%); mp 87-89°C. IR spectrum (KBr), ν, cm^{-1}: 2170 (N_3), ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 7.32-7.45 (5H, m, C_6H_5); 6.10 (1H, t, $^2J_{HF} = 53.1$, HCF_2); 5.77 (1H, t, $^4J_{HF}$ (*trans*) = 1.0, CH=); 4.42 (2H, s, CH_2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): -117.71 (2F, d, $^2J_{FH} = 53.1$, CF_2H). Found, %: S 11.45; N 15.38. $C_{10}H_9F_2N_3O_2S$. Calculated, %: S 11.73; N 15.38.

2-Azido-1-benzylsulfonyl-3,3,4,4,5,5-hexafluoropent-1-ene (4b). A. The compound **4b** is obtained similarly to compound **4a** from sulfone **1b** (0.74 g, 2 mmol), triethylamine (0.28 ml, 2 mmol), and sodium azide (0.15 g, 2.3 mmol) in benzene (10 ml). Refluxing time 15 min. After evaporation of benzene a slowly crystallizing oil was obtained. Yield 0.65 g (87%).

B. Solution of trimethylsilyl azide (0.23 g, 2 mmol) in benzene (5 ml) was added dropwise to solution of vinyl fluoride **2b** (0.7 g, 2 mmol) in benzene (15 ml) and the mixture was held for 8 h at 40°C. The solvent was evaporated to give a residue of compound **4b** in quantitative yield. IR spectrum (thin layer), ν, cm^{-1}: 2150 (N_3). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 7.40 (5H, m, C_6H_5); 6.05 (1H, s, CH=); 6.01 (1H, tt, $^2J_{HF} = 52.0$, $^3J_{HF} = 5.4$, HCF_2); 4.45 (2H, s, CH_2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): -114.58 (2F, s, CF_2); -129.98 (2F, s, CF_2); -137.48 (2F, d, $^2J_{FH} = 52.0$, CF_2H). Found, %: S 8.56; N 11.21. $C_{12}H_9F_6N_3O_2S$. Calculated, %: S 8.59; N 11.26.

1,4-Diazabicyclo[2.2.2]octane Salt of 4-Benzylsulfonyl-5-difluoromethyl-ν-triazole (3b) and 4-Benzylsulfonyl-5-difluoromethyl-ν-triazole (8a). Solution of trimethylsilyl azide (0.28 ml, 2.1 mmol) in benzene (2 ml) was added to solution of sulfone **1a** (0.54 g, 2 mmol) and 1,4-diazabicyclo[2.2.2]octane (0.45 g, 4 mmol) in benzene (10 ml) which was heated to 80°C. After cooling to 20°C the mixture was stirred for 8 h. The solvent was slowly evaporated to give an oily crystalline material which was rapidly washed with cold water (5 ml) to give compound **3b** (0.28 g, 36%); mp 133-135°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 11.28 (1H, br, NH); 7.21-7.32 (3H, m, C_6H_5); 7.02-7.10 (2H, m, C_6H_5); 6.87 (1H, tt, $^2J_{HF} = 55.0$, HCF_2); 4.45 (2H, s, CH_2SO_2); 3.04 (12H, s, NCH_2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): -112.10 (2F, d, $^2J_{HF} = 55.0$, CF_2H). Found, %: S 8.41; N 17.82. $C_{16}H_{21}F_2N_5O_2S$. Calculated, %: S 8.32; N 18.17.

Solution of silver nitrate (0.6 g) was added to the aqueous mother liquors from the washings of compound **3b** and the precipitated silver salt **7a** was filtered off, washed on the filter with water (2 × 5 ml), and dissolved in acetonitrile (30 ml). The solution was filtered through Celite and concentrated HCl (1 ml) was added. The precipitated silver chloride was filtered off and acetonitrile was evaporated in vacuo. Benzene (10 ml) was added to the residue and the organic layer was separated, dried over calcium chloride, and evaporated. The residue contained compound **8a** (0.26 g, 47%); mp 143-145°C (hexane–ether, 3:2). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): 12.35 (1H, br, NH); 7.31-7.36 (3H, m, C_6H_5); 7.10-7.19 (2H, m, C_6H_5); 6.73 (1H, tt, $^2J_{HF} = 53.0$, HCF_2); 4.57 (2H, s, CH_2). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm, *J* (Hz): -116.20 (2F, d, $^2J_{HF} = 53.0$, CF_2H). Found, %: S 11.63; N 15.63. $C_{10}H_9F_2N_3O_2S$. Calculated, %: S 11.73; N 15.38.

1,4-Diazabicyclo[2.2.2]octane Salt of 4-Benzylsulfonyl-5-(ω-H-hexafluoropropyl)-ν-triazole (3d). A. Solution of trimethylsilyl azide (0.28 ml, 2.1 mmol) was added to solution of sulfone **2b** (0.74 g, 2 mmol) and 1,4-diazabicyclo[2.2.2[octane (0.45 g, 4 mmol) in benzene (10 ml) which was heated to 80°C. After cooling to 20°C the precipitate was filtered off to give compound **3d** (0.94 g, 97%).

B. Suspension of sulfone **1b** (0.74 g, 2 mmol), triethylamine (0.28 g, 2 mmol), and sodium azide (0.15 g, 2.3 mmol) in benzene (15 ml) was stirred for 16 h at 20°C. The precipitate was filtered off and solution of 1,4-diazabicyclo[2.2.2]octane (0.24 g, 2.1 mmol) in benzene (5 ml) was added to the mother liquor. The mixture was stirred for a further 30 min and the precipitated compound **3d** was filtered off. Yield 0.86 g (89%); mp 210-212°C (water). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, J (Hz): 10.11 (1H, br, NH); 7.22-7.34 (3H, m, C$_6$H$_5$); 7.02-7.10 (2H, m, C$_6$H$_5$); 6.63 (1H, tt, $^2J_{HF}$ = 52.2, $^3J_{HF}$ = 6.0, HCF$_2$); 4.50 (2H, s, CH$_2$SO$_2$); 2.99 (12H, s, NCH$_2$). ^{19}F NMR spectrum (CDCl$_3$), δ, ppm, J (Hz): -106.07 (2H, s, CF$_2$); -132.61 (2F, s, CF$_2$); -138.64 (2F, d, $^2J_{HF}$ = 52.2, CF$_2$H). ^{13}C NMR spectrum (DMSO), δ, ppm, J (Hz): 142.92 (s, C$_{(4)}$); 134.27 (t, $^2J_{CF}$ = 29.7, C$_{(5)}$); 132.07 and 129.05 (2C, C$_{(o)}$ and C$_{(m)}$, C$_6$H$_5$); 129.51 and 129.06 (2C, C$_{(p)}$ and C$_{(i)}$, C$_6$H$_5$); 114.37 (tt, J_{CF} = 248.5, $^2J_{CF}$ = 28.4, $\underline{CF_2}$–C$_{(5)}$); 112.01 (tm, J_{CF} = 260.8, $\underline{CF_2}$–CF$_2$–C$_{(5)}$); 109.89 (tt, J_{CF} = 250.5, $^2J_{CF}$ = 28.8, CF$_2$H); 62.40 (s, CH$_2$SO$_2$); 44.97 (s, CH$_2$N). Found, %: S 6.46; N 14.25. $C_{18}H_{21}F_6N_5O_2S$. Calculated, %: S 6.60; N 14.43.

4-Benzylsulfonyl-5-(ω-H-hexafluoropropyl)-ν-triazole (8b). Solution of silver nitrate (0.34 g, 2 mmol) in water (3 ml) was added dropwise to solution of the salt **3d** (0.97 g, 2 mmol) in water (40 ml) which was heated at 85-90°C. The precipitated silver salt **7b** was filtered off, washed with water (5 ml), and then dissolved in acetonitrile (25 ml). The solution was filtered through Celite, concentrated hydrochloric acid (2 ml) was added, and the precipitated silver chloride was filtered off. The mother liquor was evaporated, benzene (15 ml) was added to the residue, and the organic layer was dried over calcium chloride and evaporated. The residue contained compound **8b** as an oil which crystallized upon standing. Yield 0.56 g (75%); mp 95-97°C (hexane–ether, 4:1). ^{1}H NMR spectrum (CDCl$_3$), δ, ppm, J (Hz): 13.12 (1H, br, NH); 7.19-7.40 (5H, m, C$_6$H$_5$); 6.26 (1H, tt, $^2J_{HF}$ = 52.2, $^3J_{HF}$ = 6.0, HCF$_2$); 4.63 (2H, s, CH$_2$). ^{19}F NMR spectrum (CDCl$_3$), δ, ppm, J (Hz): -108.03 (2F, s, CF$_2$); -131.25 (2F, s, CF$_2$); -137.98 (2F, d, $^2J_{FH}$ = 52.2, CF$_2$H). ^{13}C NMR spectrum (DMSO), δ, ppm, J (Hz): 145.78 (s, C$_{(4)}$); 136.02 (t, $^2J_{CF}$ = 32.2, C$_{(5)}$); 132.17 and 129.36 (2C, C$_{(o)}$ and C$_{(m)}$, C$_6$H$_5$); 129.68 and 127.93 (2C, C$_{(p)}$ and C$_{(i)}$, C$_6$H$_5$); 112.83 (tt, J_{CF} = 251.5, $^2J_{CF}$ = 31.0, $\underline{CF_2}$–C$_{(5)}$); 112.44 (tm, J_{CF} = 262.0, $\underline{CF_2}$–CF$_2$–C$_{(5)}$); 109.10 (tt, J_{CF} = 251.0, $^2J_{CF}$ = 29.9, CF$_2$H); 62.33 (s, CH$_2$SO$_2$). Found, %: S 8.23; N 11.21. $C_{12}H_9F_6N_3O_2S$. Calculated, %: S 8.59; N 11.26.

X-Ray Diffraction Investigation of the Compound 3d Monocrystal with the linear dimensions of 0.18 × 0.19 × 0.56 mm was carried out at room temperature on an Enraf-Nonius CAD-4 automatic, four-circle diffractometer (CuKα radiation, relative scanning velocity $\theta/2\theta = 1.2$, $\theta_{max} = 60$, sphere segment $0 \leq h \leq 16$, $0 \leq k \leq 7$, $-29 \leq l \leq 29$). In all 3603 reflections were collected, of which 3103 were symmetrically independent (mean R-factor 0.036). Crystals of compound **3d** are monoclinic with unit cell parameters: a = 13.833 (2), b = 6.0914 (9), c = 24.922 (2) Å; α = 90.95 (1)°; V = 2099.6 Å^3; M = 484.45; Z = 4; d_{calc} = 1.54 g/cm^3, μ = 20.75 cm^{-1}, space group $P2_1/c$ (N 14). The structure was solved by a direct method and refined by least-squares method in the full-matrix, anisotropic approximation using the CRYSTALS computer program [15]. Accounting of absorption in the crystal was carried out using the azimuthal scanning method [16]. In the refinement 1812 reflections were used with $I > 5\sigma(I)$ (293 parameters refined, the number of reflections per parameter 6.2, with the Chebyshev weighting scheme [17] for five parameters: 1.97, -0.58, 0.72, -0.71, and -0.29). Approximately 50% of the hydrogen atoms were revealed in the electron density differential synthesis and the remaining hydrogen atoms were located geometrically. All of the hydrogen atoms were included in the calculation with fixed positions and thermal parameters. Only the 4-H atom, involved in the formation of the hydrogen bond, was refined isotropically. The values of the final divergence factors were R = 0.082 and R_W = 0.088. The residual electron density from the Fourier series 0.64 and -0.45 e/Å^3. The atomic coordinates are given in Table 2.

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