Synthesis of *N*-perfluoroalkanesulfonyl aromatic imines

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Abstract

N-Sulfinyl perfluoroalkanesulfonamides, R_fSO_2NSO, prepared by refluxing perfluoroalkanesulfonamides with thionyl chloride, react easily with aromatic aldehydes giving *N*-perfluoroalkanesulfonyl aromatic imines, $R_fSO_2N{=}CHAr$, through elimination of sulfur dioxide.

Introduction

Imine, which have a polar carbon–nitrogen double bond, have much potential in organic synthesis. They can serve as useful intermediates and undergo many organic transformations [1, 2]. Recently, some methods for the preparation of *N*-alkanesulfonyl imines have been reported [3, 4]; however, *N*-perfluoroalkanesulfonyl imines and their derivatives are little known. The only known compound is $CF_3SO_2N{=}CHC_6H_5$ which was prepared by the reaction of CF_3SO_2NCO with C_6H_5CHO [5]. Recently, in our laboratory, several new derivatives of perfluoroalkanesulfonyl amides, i.e. $R_fSO_2N{=}Y$, have been prepared by the reaction of R_fSO_2NSO with $Y{=}O$ ($Y{=}CR^1R^2$, SR^1R^2, PCl_3) [6]. In a similar manner, a series of *N*-perfluoroalkanesulfonyl aromatic imines have been prepared in moderate yield (Scheme 1):

$$\underset{(1)}{R_fSO_2NH_2} + \underset{(excess)}{SOCl_2} \xrightarrow{\text{reflux}} \underset{(2)}{R_fSO_2NSO}$$

$$\underset{(2)}{R_fSO_2NSO} + \underset{(3)}{ArCHO} \xrightarrow[\text{r.t.–80 °C, 6–12 h}]{C_6H_6} \underset{(\mathbf{4aa–de})}{R_fSO_2N{=}CHAr}$$

$R_f = CF_3$ (**2a**), $I(CF_2)_2O(CF_2)_2$ (**2b**), $Cl(CF_2)_2O(CF_2)_2$ (**2c**), $H(CF_2)_2O(CF_2)_2$ (**2d**); $Ar = C_6H_5$ (**3a**), *p*-$CH_3C_6H_4$ (**3b**), *p*-$CH_3OC_6H_4$ (**3c**), *m*-BrC_6H_4 (**3d**), *p*-$NO_2C_6H_4$ (**3e**).

Scheme 1.

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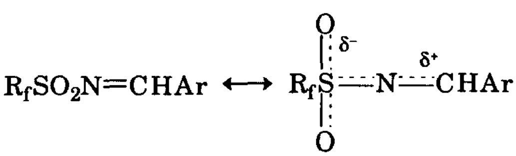
Results and discussion

All the products were moisture sensitive, being decomposed to the corresponding perfluoroalkanesulfonyl amides and aldehydes during purification using column chromatography:

$$R_fSO_2N{=}CHAr \xrightarrow[\text{r.t.}]{\text{moisture}} R_fSO_2NH_2 + ArCHO$$

The pure products were only obtained by means of several vacuum distillations. This contrasts with the behavior of the alkanesulfonyl imines which required refluxing in HCl solution for hydrolysis to occur to the sulfonamides [7]. It is noteworthy that the chemical shifts of the ethylene hydrogen, $-N{=}CH-$, in compounds **4** (except for **4ce**, **4de**) are located at 8.5–9.5 ppm. The extreme downfield shift indicates that the hydrogen is bonded to a partially positively charged carbon atom arising from influence of the strong electron-withdrawing group R_fSO_2-. Recently, Yagupolskii and coworkers have established the value of the constant σ_I for the $CF_3SO_2N{=}$ group as being 1.37, which is larger than that for CF_3SO_2- ($\sigma_I = 1.05$) [8, 9]. Thus compounds **4** may be formulated with charge delocalization:



For the compounds **4ce** and **4de**, which have the $-NO_2$ group in the phenyl position, the chemical shifts of the ethylene proton are 6.30 and 6.33 ppm, respectively.

Attempts to extend this reaction to trichloroacetaldehyde and hexafluoroacetone have failed.

Experimental

Melting points were measured on a Thiele apparatus, and all melting points and boiling points were uncorrected. Solvents were purified before use. ^1H NMR and ^{19}F NMR spectra were recorded on a Varian 360L spectrometer with Me_4Si and TFA as internal and external standards, respectively. IR spectra were obtained with an IR-440 Shimadzu spectrophotometer. Low-resolution mass spectra were obtained on a Finnigan GC–MS 4021 instrument.

Perfluoroalkanesulfonyl amides (**1**) were prepared according to literature methods [10].

$Cl(CF_2)_2O(CF_2)_2SO_2NH_2$ (**1b**): m.p., 51 °C. Analysis: Found: C, 14.08; H, 0.60; N, 3.95; F, 45.08%. $C_4H_2ClF_8O_3S$ requires: C, 14.48; H, 0.60; N, 4.22; F, 45.85%. ^1H NMR, $(CD_3)_2CO$, 60 MHz, δ: 3.45 (s, 2H) ppm. ^{19}F NMR, 54.67 MHz, δ: 2.0 (s, $ClCF_2$); 5.4 (m, OCF_2); 10.7 (m, CF_2O); 41.0 (s, CF_2S) ppm. IR (cm^{-1}); 3366 (s); 3290 (s); 1693 (m); 1387 (s); 1349 (s); 1308 (s); 1180–1130 (vs); 1010 (m); 971 (s); 926 (m); 746 (m); 617 (s); 554 (m); 498 (s). MS *m/z*: 332/334 (M^+H, 1.89/0.64); 264 ($C_4F_8SO_2^+$, 13.41); 135/137 ($ClC_2F_4^+$, 63.21/21.09); 85/87 ($ClCF_2^+$, 100/32.69); 64 (SO_2^+, 31.64); 59 ($CSNH^+$, 43.10).

N-Sulfinyl perfluoroalkanesulfonyl amides (**2**) were prepared as follows. A solution of **1b** (16.6 g, 0.05 mol) and thionyl chloride (18 g, 0.15 mol) was refluxed for 48 h, excess $SOCl_2$ was distilled out and vacuum distillation gave **2b** (13.3 g), yield 70%. Compounds **2a** and **2c** were prepared similarly.

$Cl(CF_2)_2O(CF_2)_2SO_2NSO$ (**2b**): b.p., 58 °C/1 Torr. Analysis: Found: C, 12.81; N, 3.82; F, 40.10%. $C_4ClF_8NO_4S_2$ requires: C, 12.72; N, 3.71; F, 40.26%. ^{19}F NMR δ: 1.6 (s, $ClCF_2$); 5.3 (m, OCF_2); 10.7 (m, CF_2O); 40.0 (s, SCF_2) ppm. IR (cm^{-1}): 1418 (s); 1361 (s); 1321 (s); 1282 (s); 1240–1120 (vs); 980 (s); 782 (m); 760 (m); 660 (m); 632 (m). MS *m/z*: 378/380 (M^+H, 1.50/0.50); 264 ($^+(CF_2)_2O(CF_2)_2SO$, 10.20); 135/137 ($ClCF_2CF_2^+$, 48.2/14.1); 85/87 ($ClCF_2^+$, 33.0/9.5); 64 (SO_2^+, 27.77); 58 (CSN^+, 41.11); 48 (SO^+, 6.63); 44 (CS^+, 100).

$H(CF_2)_2O(CF_2)_2SO_2NO$ (**2c**): b.p., 56 °C/1 Torr. Analysis: Found: C, 14.01; H, 0.46; N, 4.08; F, 44.01%. $C_4HF_8NO_4S_2$ requires: C, 13.99; H, 0.30; N, 4.08; F, 44.31%. ^1H NMR δ: 6.05 (t, 1H, $^2J_{HF}=55$ Hz) ppm. ^{19}F NMR δ: 62.1 (d, HCF_2); 5.1 (m, OCF_2); 12.5 (m, CF_2O); 40.7 (s, CF_2S) ppm. IR (cm^{-1}): 2923 (w); 1423 (w); 1390 (s); 1287 (s); 1202 (vs); 1125 (s); 1100 (s); 980 (s); 928 (m); 612 (m); 550 (m). MS *m/z*: 344 (M^+H, 4.84); 343 (M^+, 28.87); 278 (M^+-H-SO_2, 16.68); 226 ($^+CF_2CF_2SO_2NSO$, 3.48); 180 ($^+OC_2F_4SO_2$, 25.34); 162 ($^+C_2F_4SON$, 11.92); 110 (SO_2NS^+, 36.44); 100 ($C_2F_4^+$, 22.91); 80 (SOS^+, 14.31); 65 ($^+SO_2H$ or HCF_2N^+, 100); 64 (SO_2^+, 32.84).

The following general procedure was used for the synthesis of compounds **4***. A solution of phenyl aldehyde (**3a**, 2.1 g, 0.02 mol) in dry benzene (10 ml) was added dropwise to a solution of **2a** (3.9 g, 0.02 mol) and benzene (10 ml) in a 50 ml three-necked flask equipped with a reflux condenser, dry tube and magnetic stirring bar. The reaction mixture was stirred for 12 h at 80 °C. The benzene was evaporated and the residue distilled under vacuum giving **4aa** (2.7 g). The pure product was obtained by vacuum distillation twice. Other *N*-perfluoroalkanesulfonyl aromatic imines were prepared similarly.

$I(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_5$ (**4ba**): ^1H NMR δ: 9.25 (s, =CH); 8.00 (m, 2ArH); 7.70 (m, 3ArH) ppm. ^{19}F NMR δ: −10.0 (s, ICF_2); 4.9 (m, OCF_2); 9.2 (m, CF_2O); 39.2 (s, CF_2S) ppm. IR (cm^{-1}): 3058 (w); 1590 (s); 1560 (s); 1450 (m); 1368 (s); 1300 (m); 1180–1110 (vs); 990 (m); 970 (m); 856 (m); 810 (s); 760 (m); 510 (m); 500 (s). MS *m/z*: 512 (M^+H, 47.63); 511 (M^+, 20.33); 384 (M^+-I, 3.69); 336 (M^+-I-SO, 1.21); 177 (ICF_2^+, 36.64); 168 ($^+SO_2N{=}CHC_6H_5$, 100); 152 ($^+SON{=}CHC_6H_5$, 32.11); 127 (I^+, 3.63); 104 ($^+N{=}CHC_6H_5$, 83.64); 77 (C_6H_5, 36.51).

$Cl(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_5$ (**4ca**): ^1H NMR δ: 9.31 (s, =CH); 8.03 (m, 2ArH); 7.71 (m, 3ArH) ppm. ^{19}F NMR δ: −2.0 (s, $ClCF_2$); 5.3 (m, oCF_2); 11.0 (m, CF_2O); 40.0 (s, CF_2S) ppm. IR (cm^{-1}): 3069 (w); 1593 (s); 1563

*Details regarding these compounds are given in Table 1.

TABLE 1

Preparation of compounds **4**

Reactants 2	Reactants 3	Product 4	Temp. (°C)	Time (h)	Yield (%)	M.p. (°C) or b.p. (°C/Torr)	Elemental analysis Found (Required) C	H	N	F
2a	**3a**	**4aa**	80	12	58	86–88/1[a]				
2b	**3a**	**4ba**	80	12	62	127/1	25.61 (25.83)	1.03 (1.17)	2.81 (2.74)	29.43 (29.75)
2c	**3a**	**4ca**	r.t.	8	63	122–125/1	31.26 (31.46)	1.36 (1.43)	3.44 (3.34)	37.31 (37.80)
2d	**3a**	**4da**	r.t.	8	62	118–120/1	34.12 (34.28)	1.77 (1.82)	3.80 (3.64)	39.56 (39.38)
2b	**3b**	**4bb**	r.t.	6	60	45	27.02 (27.40)	1.35 (1.52)	2.60 (2.67)	29.54 (29.00)
2c	**3b**	**4cb**	r.t.	6	60	43	32.97 (33.22)	1.78 (1.85)	3.20 (3.23)	35.08 (35.06)
2b	**3c**	**4bc**	r.t.	6	62	47–49	26.28 (26.62)	1.33 (1.48)	2.87 (2.59)	28.80 (28.10)
2c	**3c**	**4cc**	r.t.	6	58	43	31.91 (32.03)	1.61 (1.78)	3.00 (3.11)	39.58 (38.81)
2d	**3c**	**4dc**	r.t.	6	60	40–42	34.67 (34.67)	2.07 (2.16)	3.38 (3.37)	37.26 (36.61)
2c	**3d**	**4cd**	r.t.	6	71	48–50	26.94 (26.50)	1.27 (1.00)	2.66 (2.81)	30.60 (30.52)
2d	**3d**	**4dd**	r.t.	6	72	42–45	27.60 (28.51)	1.18 (1.29)	3.20 (3.02)	33.25 (32.00)
2c	**3e**	**4ce**	r.t.	6	72	77	27.31 (28.41)	1.18 (1.07)	5.73 (6.03)	32.71 (32.70)
2d	**3e**	**4de**	r.t.	6	74	71–73	30.23 (30.69)	1.57 (1.40)	6.34 (6.51)	35.44 (35.44)

[a]Product **4aa** is a known compound (see ref. 5).

(s); 1451 (m); 1364 (s); 1306 (m); 1180–1110 (vs); 997 (m); 970 (m); 864 (m); 813 (s); 760 (m); 648 (m); 526 (m); 508 (s). MS *m/z*: 420/422 (M^+H, 47.66/18.97); 384 (M^+-Cl, 5.83); 336 ($M^+-Cl-SO$, 1.35); 320 ($M^+-Cl-SO_2$, 1.52); 168 ($^+SO_2NCHC_6H_5$, 100); 152 ($^+SONCHC_6H_5$, 32.11); 119 ($C_2F_3^+$, 26.91); 104 ($^+NCHC_6H_5$, 88.23); 85/87 ($ClCF_2^+$, 16.49/4.64); 77 ($C_6H_5^+$, 86.74).

$H(CF_2)_2O(CF_2)_2SO_2N=CHC_6H_5$ (**4da**): ^1H NMR δ: 8.53 (s, =CH); 7.33 (m, 2ArH); 7.00 (m, 3ArH); 5.35 (t, HCF_2, $^2J_{HF}=55$ Hz) ppm. ^{19}F NMR δ: 62.1 (d, HCF_2); 5.0 (m, OCF_2); 12.6 (m, CF_2O); 41.0 (s, CF_2S) ppm. IR (cm^{-1}): 3030 (m); 1624 (m); 1590 (m); 1380 (vs); 1328 (s); 1290 (s); 1200 (vs); 1128 (s); 928 (s); 930 (m); 855 (m); 610 (m). MS *m/z*: 386 (M^+H, 41.60); 366 (M^+-F, 1.46); 302 (M^+-F-SO_2, 2.49); 168 ($M^+-H(CF_2)_2O(CF_2)_2$, 7.64); 154 ($C_6H_5CH=SO_2^+$, 12.64); 152 ($C_6H_5CH=NSO^+$, 17.80); 104 ($C_6H_5CH=N^+$, 75.91); 101 ($HCF_2CF_2^+$, 25.39); 77 ($C_6H_5^+$, 100); 64 (SO_2^+, 4.77); 51 (HCF_2^+, 34.70).

$I(CF_2)_2O(CF_2)_2SO_2N=CHC_2)_2SO_2N=CHC_6H_4Me$-*p* (**4bb**): ^1H NMR δ: 2.30 (s, CH_3); 7.0–7.2 (m, 2ArH); 7.5–7.7 (m, 2ArH); 8.85 (s, =CH) ppm. ^{19}F

NMR δ: -10.0 (s, ICF_2); 5.0 (m, OCF_2); 9.2 (m, CF_2O); 39.5 (s, CF_2S) ppm. IR (cm^{-1}): 3025 (m); 2990 (m); 1662 (m); 1592 (m); 1530 (m); 1375 (s); 1320 (s); 1280 (s); 1160–1100 (vs); 1080 (m); 990 (m); 900 (s); 800 (m); 750 (m). MS *m/z*: 526 (M^+H, 33.47); 463 (M^+-SON, 2.22); 461 (M^+-SO_2, 2.37); 398 (M^+-I, 1.56); 227 ($IC_2F_4^+$, 18.70); 182 ($M^+-I(CF_2)_2O(CF_2)_2$, 10.04); 180 ($^+OCF_2CF_2SO_2$, 13.20); 177 (ICF_2^+, 14.64); 121 ($^+C_6H_4CH{=}S$, 31.01); 118 ($CH_3C_6H_4CH{=}N^+$, 6.92); 100 ($C_2F_4^+$, 17.06); 64 (SO_2^+, 100).

$Cl(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_4Me$-*p* (**4cb**): ^1H NMR δ: 2.35 (s, CH_3); 7.25–7.35 (m, 2ArH); 7.70–7.85 (m, 2ArH); 9.85 (s, $=CH$) ppm. ^{19}F NMR δ: 0.67 (s, $ClCF_2$); 8.00 (m, OCF_2); 13.0 (m, CF_2O); 43.3 (s, CF_2S) ppm. IR (cm^{-1}): 3030 (m); 2993 (w); 1590 (m); 1532 (m); 1460 (m); 1380 (s); 1325 (s); 1282 (s); 1165–1110 (vs); 1072 (m); 980 (m); 900 (s); 808 (m); 746 (m); 650 (m); 505 (s). MS *m/z*: 434/436 (M^+H, 75.19/35.73); 418/420 (M^+-O, 1.85/0.75); 398 (M^+-Cl, 5.25); 350 ($M^+-Cl-SO$, 2.19); 334 ($M^+-Cl-SO_2$, 1.74); 182 ($M^+-ClC_2F_4OC_2F_4$, 100); 166 ($M^+-ClC_2F_4-O$, 34.93); 118 ($CH_3C_6H_4CH{=}N^+$, 72.95); 107 ($CH_3C_6H_4O^+$, 23.65); 85/87 ($ClCF_2^+$, 3.37/0.73); 65 ($C_5H_5^+$, 9.76).

$I(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_4OMe$-*p* (**4bc**): ^1H NMR δ: 3.20 (s, OCH_3); 6.95–7.15 (m, 2ArH); 7.75–7.95 (m, 2ArH); 9.85 (s, $=CH$) ppm. ^{19}F NMR δ: -8.0 (s, ICF_2); 4.5 (m, CF_2O); 8.9 (m, OCF_2); 40.0 (s, CF_2S) ppm. MS *m/z*: 542 (M^+H, 71.16); 541 (M^+H, 43.65); 415 (M^+H-I, 18.65); 414 (M^+-I, 8.18); 227 ($IC_2F_4^+$, 3.15); 198 ($M^+-IC_2F_4OC_2F_4$, 94.47); 182 ($M^+-IC_2F_4OC_2F_4-O$, 28.67); 134 ($MeOC_6H_4{=}N^+$, 100); 107 ($MeOC_6H_4^+$, 26.08); 92 ($C_6H_4O^+$, 26.81); 64 (SO_2^+, 20.34).

$Cl(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_4OMe$-*p* (**4cc**): ^1H NMR δ: 2.83 (s, OCH_3); 6.65–6.75 (m, 2ArH); 7.10–7.30 (m, 2ArH); 9.78 (s, $=CH$) ppm. ^{19}F NMR δ: -1.3 (s, $ClCF_2$); 6.8 (m, OCF_2); 11.0 (m, CF_2O); 41 (s, CF_2S) ppm. MS *m/z*: 450/452 (M^+H, 1.51/0.63); 434/436 (M^+H-O, 100/34.34); 418/420 (M^+-OCH_3, 4.04/1.14); 389 (M^+-Cl-O, 12.99); 182 ($M^+-ClC_2F_4OC_2F_4-O$, 92.60); 166 ($MeOC_6H_4CH{=}NS$, 17.89); 135/137 ($ClC_2F_4^+$, 5.85/1.86); 107 ($MeOC_6H_4^+$, 9.78); 100 ($C_2F_4^+$, 5.87); 91 ($C_7H_7^+$, 49.54); 65 ($C_5H_5^+$, 24.86).

$H(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_4OMe$-*p* (**4dc**): ^1H NMR δ: 3.80 (s, OCH_3); 6.32 (t, HCF_2, $^2J_{HF}=54$ Hz); 6.80–7.20 (m, 2ArH); 7.80–8.20 (m, 2ArH); 9.02 (s, $=CH$) ppm. ^{19}F NMR δ: 61.7 (d, HCF_2); 4.9 (m, OCF_2); 12.2 (m, CF_2O); 40.2 (s, CF_2S) ppm. IR (cm^{-1}): 3020 (w); 2900 (w); 2850 (w); 1590 (s); 1550 (s); 1510 (s); 1428 (m); 1360 (s); 1322 (s); 1271 (s); 1160–1100 (vs); 990 (m); 842 (m); 808 (m); 770 (m); 630 (m); 508 (m).

$Cl(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_4Br$-*m* (**4cd**): ^1H NMR δ: 7.23–7.73 (m, 4ArH); 8.83 (s, $=CH$) ppm. ^{19}F NMR δ: -0.7 (s, $ClCF_2$); 7.5 (m, OCF_2); 12.3 (m, CF_2O); 42.3 (s, CF_2S) ppm. IR (cm^{-1}): 3030 (w); 1580 (m); 1360 (s); 1322 (m); 1284 (s); 1220–1120 (vs); 958 (s); 775 (m); 600 (s); 485 (m). MS *m/z*: 489/500/502 (M^+H, 100/73.66/20.19); 462/464 (M^+-Cl, 6.83/7.76); 246/248 ($BrC_6H_4CH{=}NSO_2^+$, 59.38/56.62); 230/232 ($BrC_6H_4CH{=}NSO^+$, 13.49/16.05); 182/184 ($BrC_6H_4CH{=}N^+$, 49.92/43.30); 155/

157 ($BrC_6H_4^+$, 33.24/30.21); 135/137 ($ClC_2F_4^+$, 16.82/6.10); 100 ($C_2F_4^+$, 8.68); 76 ($^+CSO_2$, 27.64).

$H(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_4Br$-*m* (**4dd**): ^{1}N NMR δ: 5.63 (t, HCF_2); 6.93–7.50 (m, 4ArH); 8.95 (s, =CH) ppm. ^{19}F NMR δ: 61.7 (d, HCF_2); 4.5 (m, OCF_2); 11.9 (m, CF_2O); 39.3 (s, CF_2S) ppm. IR (cm^{-1}): 3030 (w); 2990 (w); 1590 (s); 1540 (m); 1460 (m); 1370 (s); 1330 (m); 1280 (s); 1200–1100 (vs); 980 (m); 850 (m); 810 (s); 790 (s); 670 (s); 635 (m); 522 (s). MS *m/z*: 464/466 (M^+H, 0.59/0.52); 400/402 (M^+-SO_2, 2.30/2.10); 298 ($HC_4F_8SO_2N^+$, 13.18); 278 ($C_4F_8SO_2N^+$, 4.03); 232 ($C_4F_8S^+$, 1.16); 187/189 ($BrC_6H_4S^+$, 64.42/1.88); 185/187 ($BrC_6H_4NO^+$, 54.78/64.42); 101 ($HC_2F_4^+$, 24.59); 80 (SO_3^+, 47.51); 64 (SO_2^+, 100); 51 (HCF_2^+, 20.59).

$Cl(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_4NO_2$-*p* (**4ce**): ^{1}H NMR δ: 6.30 (s, =CH); 7.80–7.95 (m, 2ArH); 8.26–8.40 (m, 2ArH) ppm. ^{19}F NMR δ: −1.3 (s, $ClCF_2$); 6.7 (m, OCF_2); 11.7 (m, CF_2O); 41.6 (s, CF_2S) ppm. IR (cm^{-1}): 3100 (w); 1705 (s); 1600 (w); 1531 (s); 1387 (s); 1347 (s); 1309 (s); 1200–1130 (vs); 970 (s); 850 (m); 818 (m); 740 (m); 616 (m). MS *m/z*: 465/467 (M^+H, 2.65/1.54); 400/402 (M^+-SO_2, 0.48/0.23); 332/334 ($M^+-C_2F_4S$, 22.01/8.87); 248 ($C_4F_8SO^+$, 4.93); 180 ($NO_2C_6H_4CNS^+$, 8.20); 150 ($M^+H-ClC_2F_4OC_2F_4SO_2$, 30.31); 135/137 ($ClC_2F_4^+$, 36.92/7.63); 100 ($C_2F_4^+$, 24.75); 85/87 ($ClCF_2^+$, 29.28/10.55); 80 (SO_3^+, 92.03); 64 (SO_2^+, 100); 46 (NO_2^+, 10.07).

$H(CF_2)_2O(CF_2)_2SO_2N{=}CHC_6H_4NO_2$-*p* (**4de**): ^{1}H NMR δ: 5.60 (t, HCF_2); 6.33 (s, =CH); 7.83–7.95 (m, 2ArH); 8.30–8.42 (m, 2ArH) ppm. ^{19}F NMR δ: 62.0 (d, HCF_2); 5.1 (m, OCF_2); 12.5 (m, CF_2O); 40.8 (s, CF_2S) ppm. IR (cm^{-1}): 3090 (w); 1700 (s); 1600 (w); 1532 (s); 1380 (s); 1345 (s); 1305 (s); 1200–1125 (vs); 973 (s); 848 (m); 810 (m); 738 (m); 615 (m); 500 (m). MS *m/z*: 431 (M^+H, 3.42); 430 (M^+, 1.05); 366 (M^+-SO_2, 0.58); 248 ($C_4F_8S^+$, 6.93); 196 ($NO_2C_6H_4CNSO^+$, 9.37); 180 ($NO_2C_6H_4CNS^+$, 8.18); 122 ($NO_2C_6H_4^+$, 1.47); 100 ($C_2F_4^+$, 28.37); 80 (SO_3^+, 93.64); 64 (SO_2^+, 100); 51 (HCF_2^+, 36.34); 46 (NO_2^+, 10.84).

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