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## Halogeno and pseudohalogeno difluoromethanesulfonylfluorides<sup>1</sup>

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#### Abstract

New substituted cyano- and isocyanatodifluoromethanesulfonylfluorides were synthesized and their properties compared with halogenodifluoromethanesulfonylfluorides. NMR parameters are related to the electronegativity and covalent radii of substitutents. © 1997 Elsevier Science S.A.

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#### 1. Introduction

Although the first difluoromethanesulfonylfluorides containing functional groups were synthesized in 1960 [1,2], interest in these compounds has not yet diminished [3].

Previously we have described halogen substituted diffuoromethanesulfonylfluorides  $XCF_2SO_2F$  where X = Cl, Br, I [4]. This paper is devoted to the synthesis of pseudohalogen substituted diffuoromethanesulfonylfluorides  $XCF_2SO_2F$ , where  $X = N \equiv C-$  and O = C = N-, and to comparing their physical properties with halogen substituted diffuoromethanesulfonylfluorides. Perfluoroalkylisocyanates containing a fluorosulfonyl group have not previously been reported.

#### 2. Results and discussion

Cyanodifluoromethanesulfonylfluoride (3) was prepared with high yield from carbamoyldifluoromethanesulfonylfluoride (2) on heating with  $P_2O_5$ . Preparation of (2) needs chloroformyldifluoromethanesulfonylfluoride (1) because fluoroformyldifluoromethanesulfonylfluoride like  $\beta$ -sultones [5] reacts with ammonia non-selectively even at low temperature yielding a mixture of amides. Minor amounts of difluoromethanesulfonylfluoride (4) are produced following hydrolysis and decarboxylation of carbamoyldifluoromethanesulfonylfluoride (2).

$$\begin{array}{ccccccc} CI & NH_3 & H_2N \\ O \stackrel{\sim}{\sim} CCF_2SO_2F & \longrightarrow & O \\ \hline (1) & (2) & (3) & (4) \end{array}$$

Reaction of nitrile (3) with methanol and aniline proceeds under mild conditions at the cyanogroup only.

$$N \equiv C-CF_2SO_2F$$
(3)
$$CH_3OH HN_{CCF_2SO_2F}$$

$$C_{H_3}OH HN_{CCF_2SO_2F}$$

$$C_{6}H_{5}NH_{2} HN_{CCF_2SO_2F}$$

$$C_{6}H_{5}NH H$$
(6)

Nitrile (3) interacts with 2-(mercapto)aniline to produce benzothiazolyl-2-difluoromethanesulfonylfluoride (7). The same compound is obtained when 2-(mercapto)aniline reacts with chloroformyldifluoromethanesulfonylfluoride (1). Benzothiazolyl-2-difluoromethanesulfonylfluoride (7) reacts with sodium azide in methanol to produce benzothiazolyl-2-difluoromethanesulfonylazide (8).

$$N \equiv C - CF_2 SO_2 F \xrightarrow{A \circ OH} SH \xrightarrow{NH_2} NH_2 \xrightarrow{NaN_3} F \xrightarrow{S} SH \xrightarrow{NaN_3} CF_2 SO_2 F \xrightarrow{NaN_3} (7) (8)$$

Isocyanatodifluoromethanesulfonylfluoride (10) was prepared in good yield from azidocarbonyldifluoromethanesulfonylfluoride (9), which was obtained by reaction of sodium azide with chloroformyldifluoromethanesulfonylfluoride (1).

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<sup>&</sup>lt;sup>1</sup> Dedicated to Professor Alois Haas on his 65th birthday.

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XCF <sub>2</sub> SO <sub>2</sub> F	$\delta \underline{FSO}_2$	$\delta \underline{C} F_2$	$\delta \underline{C}F_2$	$J_{C-F}$	${}^{2}J_{C-F}$	${}^{3}J_{\mathrm{F-F}}$	x	R <sub>cov</sub>
HCF <sub>2</sub> SO <sub>2</sub> F	37.7	- 119.9	113.0	285.0	39.1	3.4	2.1	0.37
ICF <sub>2</sub> SO <sub>2</sub> F	24.96	-56.02	87.7	351.8	37.8	2.0	2.5	1.333
BrCF <sub>2</sub> SO <sub>2</sub> F	29.5	- 56.7	115.1	342.8	44.05	5.5	2.8	1.142
CICF <sub>2</sub> SO <sub>2</sub> F	32.0	- 59.0	123.7	329.8	47.63	8.8	3.0	0.994
O=C=NCF <sub>2</sub> SO <sub>2</sub> F <sup>a</sup>	33.2	-70.0	114.2	295.0	45.0	12.7	3.0	0.62
CF <sub>3</sub> SO <sub>2</sub> F <sup>b</sup>	37.9	- 73.3	118.4	318.0	54.9	18.3	4.0	0.709
$N = CCF_2SO_2F^{\circ}$	39.0	-92.0	105.6	289.0	46.0	6.6	2.5	0.60
FSO <sub>2</sub> CF <sub>2</sub> SO <sub>2</sub> F <sup>d</sup>	47.6	- 96.8	116.5	334.2	40.6	6.45		1.030

Table 1 <sup>19</sup>F and <sup>13</sup>C NMR data of XCF<sub>2</sub>SO<sub>2</sub>F, ( $\delta$  ppm, J Hz, acetone- $d_6$ ), electronegativity  $\chi$  and covalent radius  $R_{cov}$  of X

<sup>a</sup>  $\delta N = C = O 137.9 \text{ ppm}(s).$ 

<sup>b</sup> Measured in CCl<sub>3</sub>F [6].

<sup>c</sup> δ N≡C 106.4 ppm (t,  ${}^{2}J_{C-F}$  = 39.3 Hz).

<sup>d</sup> Measured in CDCl<sub>3</sub> [3].

Isocyanatodifluoromethanesulfonylfluoride is extremely sensitive to moisture. Autocatalytic fragmentation is observed with water.

$$O=C=N-CF_2SO_2F \longrightarrow \left[HOOC-NCF_2SO_2F \xrightarrow{-CO_2} HN=CFSO_2F\right] \longrightarrow$$

$$(10) \qquad (A) \qquad (B)$$

$$\xrightarrow{-HF} \left[N=CSO_2F \longrightarrow N\equiv C-O-SF \right]$$

$$(C) \qquad (D)$$

The presence of intermediates A–D was determined by IR and NMR spectrometry after standing pure 10 for 12 days.

Chemical shifts and coupling constants of pseudohalogenodifluoromethanesulfonylfluorides and halogenodifluoromethanesulfonylfluorides [4] together with spectral data of trifluoromethanesulfonylfluoride, measured by Newmark and Chung [6], and bis(fluorosulfonyl)difluoromethane, measured by Waterfeld et al. [3], are given in Table 1.

It is known that coupling constants and chemical shifts are sensitive to the electronegativity and Van der Waals value of substituents [7,8]. Therefore it was interesting to compare NMR spectra data with the covalent radius  $R_{cov}$  and the electronegativity  $\chi$  of the first substituent atom. Their values were from [9]. For statistical analysis a multiple regression technique was used [10]. Coefficients of multiple and partial correlation (R and r) as well as corresponding probabilities (p) are shown in Table 2.

As may be seen from Table 2, a relationship exists between the  ${}^{2}J_{C-F}$  coupling constant and the electronegativity of the X substituent. The size of the first substituted atom is not significant. At the same time an opposite effect is observed for coupling constants  ${}^{1}J_{C-F}$ , as well as  ${}^{19}$ F chemical shifts  $\delta$ <u>FSO<sub>2</sub></u>,  $\delta$  C<u>F</u><sub>2</sub>. For  ${}^{3}J_{F-F}$ , contributions from the electronegativity and the atomic size are the same. Inclusion into the multiple regression equation of a new independent variable, the inductive effect  $\sigma_i$  of the X substituent, does not improve it noticeably and we can see that a relationship between inductive effect  $\sigma_i$  of the X substituent and NMR parameters does not exist.

Thus, simple linear regressions may be used for estimation of  ${}^{1}J_{C-F}$  and  ${}^{3}J_{F-F}$  values only. Observed and predicted values of  ${}^{1}J_{C-F}$  and  ${}^{3}J_{F-F}$  for XCF<sub>2</sub>SO<sub>2</sub>F are shown in Figs. 1 and 2. Other NMR spectral parameters show poor simple linear correlation.

Using the electronegativity  $\chi$  and covalent radius  $R_{cov}$  as independent variables and  ${}^{3}J_{F-F}$  coupling constant as a dependent variable, the value of electronegativity for the S

Table 2

Statistical analysis data of the multilinear correlation of the NMR parameters with electronegativity and Van der Waals effects of the X substituent

Dependent variable	Independent van	Multiple correlation				
	Electronegativity $\chi$		Covalent radius R <sub>cov</sub>			
	r	p	r	p	R	p
δFSO <sub>2</sub>	0.500	0.300	0.922	0.005	0.924	0.021
$\delta \overline{C}F_{2}$	0.741	0.079	0.924	0.005	0.939	0.014
$\delta C \overline{F_2}$	-0.530	0.267	488	0.315	0.629	0.365
	0.474	0.331	0.970	0.0005	0.971	0.003
$J_{C-F}^{C-F}$	0.926	0.004	-0.624	0.171	0.930	0.018
${}^{3}J_{\mathrm{F}-\mathrm{F}}$	0.984	0.001	- 0.909	0.067	0.986	0.0001



Fig. 1. Observed and predicted Values of  ${}^{1}J_{C-F}$  from the simple regression  ${}^{1}J_{C-F} = 251(\pm 8) + 78(\pm 9)R_{cov}$ ;  $S_{o} = 7.5$ , r = 0.964, p = 0.0001, N = 8.



Fig. 2. Observed and predicted values of  ${}^{3}J_{F-F}$  from the simple regression  ${}^{3}J_{F-F} = -16.4(\pm 4.9) + 0.91(\pm 0.18)\chi; \quad S_{0} = 2.5, \quad r = 0.917, \quad p = 0.002, \quad N = 7.$ 



Fig. 3. Observed and predicted values of electronegativity  $\chi$  from the multiple regression  $\chi = 1.44(\pm 0.09) + 0.61(\pm 0.08)R_{\rm cov} + 0.114$  $(\pm 0.005)^3 J_{\rm F-F}$ ;  $S_0 = 0.06$ , r = 0.997, p = 0.0004, N = 6 (the -NCO substituent is not included).

atom in SO<sub>2</sub>F and SO<sub>2</sub>CF<sub>3</sub> groups may be estimated from the regression equation given in Fig. 3 as  $2.80 \pm 0.06$  and  $2.76 \pm 0.06$  respectively. For comparison, the value of electronegativity for the SCF<sub>3</sub> group is equal to 2.7 [11].

#### 3. Experimental details

<sup>1</sup>H and <sup>19</sup>F NMR spectra were measured with a Bruker WP-200 (at 200.13 and 188.28 MHz respectively) NMR spectrometer using HMDS and CFCl<sub>3</sub> as internal standards, and acetone- $d_6$  as solvent. <sup>19</sup>F and <sup>13</sup>C NMR spectra were measured with a Varian VXR-300 NMR spectrometer (<sup>19</sup>F at 282.22 MHz and <sup>13</sup>C at 75.43 MHz) using acetone- $d_6$  as solvent. <sup>19</sup>F and <sup>13</sup>C NMR chemical shifts are reported relative to internal CFCl<sub>3</sub> and TMS respectively. All boiling and melting points are reported uncorrected.

Fluoro- and chloroformyldifluoromethanesulfonylfluoride were prepared according to literature methods [1,2,12].

#### 3.1. Carbamoyldifluoromethanesulfonylfluoride (2)

To solution of 19.6 g (0.1 mol) chloroformyldifluoromethanesulfonylfluoride (1) [12] in 150 ml dry ether was bubbled 4500 ml of dry ammonia whilst stirring vigorously and cooling to -40 to -20 °C. The precipitate was filtered off, and ether evaporated. The residue was crystallized from chloroform-benzene; m.p. 54–55 °C. Yield 16.3 g (92%).

IR spectra (film): 820 (S–F), 1100–1190 (C–F), 1240 (SO<sub>2</sub> as), 1440 (SO<sub>2</sub> s), 1600–1610 (N–H), 1720 (C=O) cm<sup>-1</sup>.

<sup>19</sup>F NMR spectra: 40.3 (t, 1F, SO<sub>2</sub>F), -103.0 (d, 2F, CF<sub>2</sub>) ppm,  ${}^{3}J_{F-F}$ =4.5 Hz. Analysis: C 13.54; H 1.16; N 7.9. C<sub>2</sub>H<sub>2</sub>F<sub>3</sub>NO<sub>3</sub>S calculated: C 13.57; H 1.14; N 7.9%.

#### 3.2. Cyanodifluoromethanesulfonylfluoride (3)

8.9 g (50 mmol) of carbamoyldifluoromethanesulfonylfluoride (**2**) was mixed with 20 g (140 mmol) of P<sub>2</sub>O<sub>5</sub> and slowly heated to 130 °C, collecting the product in a trap cooled to -80 °C. The product was distilled, collecting the fraction b.p. 24.0–24.5 °C/760 mmHg. Yield 6.4 g (80%) of (**3**),  $d_4^{20} = 1.46$ ,  $n_D^{20} = 1.3150$ .  $MR_D = 21.01$  (found),  $MR_D = 21.12$  (calculated).

IR spectra (gas): 820 (S–F), 1120–1170 (C–F), 1244 (SO<sub>2</sub> s), 1464 (SO<sub>2</sub> as), 2275 (C $\equiv$ N) cm<sup>-1</sup>.

Analysis: N 8.9. C<sub>2</sub>F<sub>3</sub>NO<sub>2</sub>S calculated: N 8.8%.

Additionally by distilling the bottoms at 50–52 °C/760 mmHg difluoromethanesulfonylfluoride (4) was collected. Yield 0.67 g (10%),  $n_D^{20} = 1.31$ ,  $d_4^{20} = 1.58$  [13].

<sup>1</sup>H NMR spectra: 6.35 (t, 1H, CH) ppm,  ${}^{3}J_{H-F} = 52$  Hz.

#### 3.3. Azidocarbonyldifluoromethanesulfonylfluoride (9)

5.88 g (40 mmol) of chloroformyldifluoromethanesulfonylfluoride (1) in 10 ml of *p*-xylene was added dropwise to 1.95 g (40 mmol) of sodium azide. The mixture was stirred vigorously for 1 h, then poured on ice and washed with water to remove the rest of 1. The lower layer was separated, dried over Na<sub>2</sub>SO<sub>4</sub> and distilled in vacuo, b.p. 70–71 °C/ 90 mmHg. Yield 4.52 g (75%), *T*(decomp.) = 90 °C,  $d_4^{20} = 1.65$ ,  $n_D^{20} = 1.6428$ ,  $MR_D = 29.40$  (found),  $MR_D = 29.20$ (calculated).

Analysis: F 22.93.  $C_2F_3N_3O_3S$  calculated: F 22.93%.

IR spectra (film): 810 (S–F), 875 (C–S), 1070, 1190 (C– F), 1240 (S=O, sym), 1460 (S=O, as), 1780 (C=O), 2200 (N=N=N), 2240 (N<sub>2</sub>+), cm<sup>-1</sup>.

<sup>19</sup>F NMR spectra: -103.4 (d, CF<sub>2</sub>, 2F), 41.8 (t, SO<sub>2</sub>F, 1F) ppm,  ${}^{3}J_{F-F} = 5.2$  Hz.

#### 3.4. Isocyanatodifluoromethanesulfonylfluoride (10)

To a Kleisenflask, equipped with the thermometer, 5 ml of xylene was heated to 75 °C. 3.22 g of azidocarbonyldifluoromethanesulfonylfluoride (9) was added dropwise. The temperature was then raised to 110 °C. During the heating formation of gaseous N<sub>2</sub> was observed. 1.2 g of the product were collected, and then fractionated on a column. The fraction, boiling at 68–68.5 °C was collected. Yield 1.9 g (60%).

Analysis: F 33.0; 33.10. C<sub>2</sub>F<sub>3</sub>NO<sub>3</sub>S calculated: 32.95%.

IR spectra (film): 805 (S-F), 870 (C-S), 1095, 1160 (C-F), 1250-1280 (S=O, s), 1340 (C-N), 1470 (S=O, as), 1590 (C=N),  $2280 (N=C=O) \text{ cm}^{-1}$ .

#### 3.5. 2-(Benzothiazolyl)difluoromethanesulfonylfluoride (7)

Method A. 1.25 g (10 mmol) of 2-mercaptoaniline and 1.6 g (10 mmol) cyanodifluoromethanesulfonylfluoride (**3**) were heated and stirred in 10 ml of acetic acid at 50 °C for 120 h. Acetic acid was removed. The residue was washed with water then extracted with benzene. After removing benzene the product was crystallized from hexane; m.p. 54–55 °C. Yield 0.75 g (32%).

IR spectra (KBr): 820 (S–F), 1120–1160 (C–F), 1260 (S=O, s), 1400 (S=O, as), 1500 (C=N), 3010–3100 (C–H) cm<sup>-1</sup>.

<sup>1</sup>H NMR spectra: 8.42–8.30 (m, 2H), 7.76–7.82 (m, 2H) ppm.

<sup>19</sup>F NMR spectra: F 37.9 (t, 1F, SO<sub>2</sub>F), -91.7 (d, 2F, CF<sub>2</sub>) ppm,  ${}^{3}J_{F-F} = 4.9$ .

Analysis: C 40.9; H 1.7; N 6.0.  $C_8H_4F_3NO_2S_2$  calculated: C 40.87; H 1.71; N 5.95%.

Method B. 3.9 g (20 mmol) of chloroformyldifluoromethanesulfonylfluoride (3) in 50 ml of dry chloroform was added dropwise to 5 g (40 mmol) of 2-mercaptoaniline in 50 ml of dry chloroform. The mixture was stirred and the temperature was raised to 60 °C for 1 h. 2-Mercaptoaniline hydrochloride was filtered off. After removing solvent the residue was crystallized from hexane. Yield 4.0 g (85%).

#### 3.6. 2-(Benzothiazolyl)difluoromethanesulfonylazide (10)

0.7 g (10 mmol) of sodium azide was added to 2.35 g (10 mmol) 2-(benzthiazolyl) difluoromethanesulfonylfluoride (9) in 10 ml of methanol and the reaction mixture was stirred for 1 h. Sodium fluoride was filtered off. Methanol was evaporated in vacuo. The residue was crystallized from benzene; m.p. 64.5–65 °C. Yield 2.3 g (89%).

Analysis: C 33.0; H 1.38; N 19.4.  $C_8H_4F_2N_4O_2S_2$  calculated: C 33.1; H 1.38; N 19.3%.

IR spectra (KBr): 1115–1150 (C–F), 1260 (S=O, s), 1400 (S=O, as), 1500 (C=N), 2180 (N<sub>3</sub>), 2275 (N<sub>2</sub><sup>+</sup>), 3010–3130 (C–H) cm<sup>-1</sup>.

<sup>1</sup>H NMR spectra: 8.38–8.24 (m, 2H), 7.82–7.68 (m 2H) ppm.

 $^{19}$ F NMR spectra: -94.5 (s, 2F, CF<sub>2</sub>) ppm.

### 3.7. Methoxyimidoyldifluoromethanesulfonylfluoride (5)

0.96 g (6 mmol) of cyanodifluoromethanesulfonylfluoride(3) was added dropwise at 0 °C to 3 ml of absolute methanol in 2 ml of diglyme. The mixture was stood for 12 h.

Methanol was evaporated, and the residue was distilled in vacuo at 88-91 °C/130 mmHg. Yield 0.36 g (35%).

Analysis: C 19.0; H 2.20; N 7.0. C<sub>3</sub>H<sub>4</sub>F<sub>3</sub>NO<sub>3</sub>S calculated: C 18.8; H 2.11; N 7.3%.

IR spectra (film): 780 (S–F), 829 (C–S), 1026, 1159, 1209 (C–F), 1243 (S=O, s), 1462 (S=O, as), 1610–1670 (C=NH), 2990 (CH<sub>3</sub>), 3100 (N–H) cm<sup>-1</sup>.

<sup>19</sup>F NMR spectra: -106.2 (d, 2F, CF<sub>2</sub>), <sup>3</sup> $J_{F-F}$ =5,7 Hz; 38.9 (t, 1F, SO<sub>2</sub>F) ppm, <sup>3</sup> $J_{F-F}$ =5.7 Hz.

<sup>1</sup>H NMR spectra: 4.13 (s, CH<sub>3</sub>), 9.8 (s, broad, NH) ppm.

# 3.8. *Phenylaminoimidoyldifluoromethanesulfonylfluoride* (6)

0.96 g (6 mmol) of cyanodifluoromethanesulfonylfluoride (3) was added dropwise at 0 °C to 1.1 g (6 mmol) of aniline in 2 ml of diglyme. The mixture was stood for 12 h, poured on ice and extracted with ether, the ether evaporated and the residue crystallized from chloroform-benzene; m.p. 98–101 °C. Yield 0.3 g (35%).

Analysis: C 38.3; H 3.00; N 10.8.  $C_8H_7F_3N_2O_2S$  calculated: C 38.1; H 2.80; N 11.1%.

IR spectra (KBr): 780 (S–F), 840 (C–S), 1090–1130 (C– F), 1246 (S=O, s), 1465 (S=O, as), 1610–1670 (C=N), 3050 (C–H, Ar), 3100 (N–H), cm<sup>-1</sup>.

<sup>19</sup>F NMR spectra: -102.5 (d, 2F, CF<sub>2</sub>) <sup>3</sup> $J_{F-F}$ =5.9 Hz; 40.7 (t, 1F, SO<sub>2</sub>F) ppm, <sup>3</sup> $J_{F-F}$ =5.9 Hz.

<sup>1</sup>H NMR spectra: 7.78–7.87 (m, 5H,  $C_6H_5$ ), 4.9 (s, 1H, NH $C_6H_5$ ), 9.7 (broad s, 1H, =NH) ppm.

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