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Halogeno and pseudohalogeno difluoromethanesulfonylfluorides [1]

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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 substituents. © 1997 Elsevier Science S.A.

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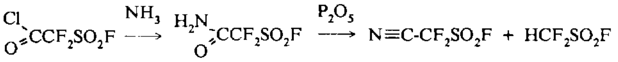
1. Introduction

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 difluoromethanesulfonylfluorides XCF_2SO_2F where X = Cl, Br, I [4]. This paper is devoted to the synthesis of pseudohalogen substituted difluoromethanesulfonylfluorides XCF_2SO_2F, where X = N≡C– and O=C=N–, and to comparing their physical properties with halogen substituted difluoromethanesulfonylfluorides. Perfluoroalkylisocyanates containing a fluorosulfonyl group have not previously been reported.

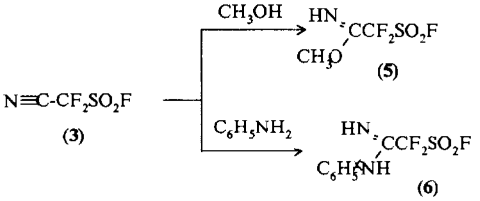
2. Results and discussion

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 β-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**).

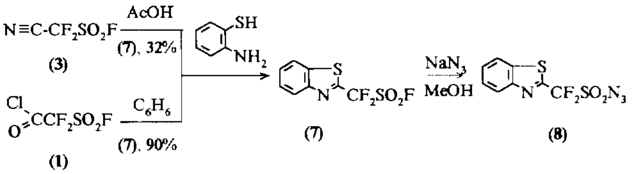


(1) (2) (3) (4)

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



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**).



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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[1] Dedicated to Professor Alois Haas on his 65th birthday.

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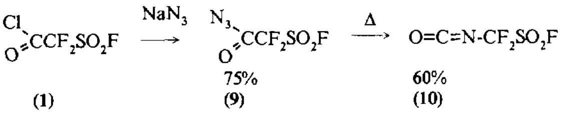
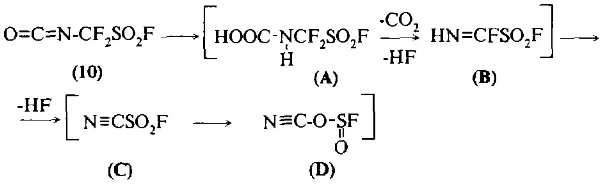
Table 1
^{19}F and ^{13}C NMR data of XCF_2SO_2F, (δ ppm, J Hz, acetone-d_6), electronegativity χ and covalent radius R_{cov} of X

XCF_2SO_2F	$\delta \underline{F}SO_2$	$\delta C\underline{F}_2$	$\delta \underline{C}F_2$	$^1J_{C-F}$	$^2J_{C-F}$	$^3J_{F-F}$	χ	R_{cov}
HCF_2SO_2F	37.7	−119.9	113.0	285.0	39.1	3.4	2.1	0.37
ICF_2SO_2F	24.96	−56.02	87.7	351.8	37.8	2.0	2.5	1.333
$BrCF_2SO_2F$	29.5	−56.7	115.1	342.8	44.05	5.5	2.8	1.142
$ClCF_2SO_2F$	32.0	−59.0	123.7	329.8	47.63	8.8	3.0	0.994
$O{=}C{=}NCF_2SO_2F$ [a]	33.2	−70.0	114.2	295.0	45.0	12.7	3.0	0.62
CF_3SO_2F [b]	37.9	−73.3	118.4	318.0	54.9	18.3	4.0	0.709
$N{\equiv}CCF_2SO_2F$ [c]	39.0	−92.0	105.6	289.0	46.0	6.6	2.5	0.60
$FSO_2CF_2SO_2F$ [d]	47.6	−96.8	116.5	334.2	40.6	6.45	—	1.030

[a] δ N=$\underline{C}$=O 137.9 ppm (s).
[b] Measured in CCl_3F [6].
[c] δ N≡$\underline{C}$ 106.4 ppm (t, $^2J_{C-F} = 39.3$ Hz).
[d] Measured in $CDCl_3$ [3].



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



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 χ 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 $^2J_{C-F}$ 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 $^1J_{C-F}$, as well as ^{19}F chemical shifts δ $\underline{F}SO_2$, δ $C\underline{F}_2$. For $^3J_{F-F}$, 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 σ_i of the X substituent, does not improve it noticeably and we can see that a relationship between inductive effect σ_i of the X substituent and NMR parameters does not exist.

Thus, simple linear regressions may be used for estimation of $^1J_{C-F}$ and $^3J_{F-F}$ values only. Observed and predicted values of $^1J_{C-F}$ and $^3J_{F-F}$ for XCF_2SO_2F are shown in Figs. 1 and 2. Other NMR spectral parameters show poor simple linear correlation.

Using the electronegativity χ and covalent radius R_{cov} as independent variables and $^3J_{F-F}$ 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 variable				Multiple correlation	
	Electronegativity χ		Covalent radius R_{cov}			
	r	p	r	p	R	p
$\delta \underline{F}SO_2$	0.500	0.300	**0.922**	**0.005**	0.924	0.021
$\delta C\underline{F}_2$	0.741	0.079	**0.924**	**0.005**	0.939	0.014
$\delta \underline{C}F_2$	−0.530	0.267	488	0.315	0.629	0.365
$^1J_{C-F}$	0.474	0.331	**0.970**	**0.0005**	0.971	0.003
$^2J_{C-F}$	**0.926**	**0.004**	−0.624	0.171	0.930	0.018
$^3J_{F-F}$	**0.984**	0.001	**−0.909**	**0.067**	0.986	0.0001

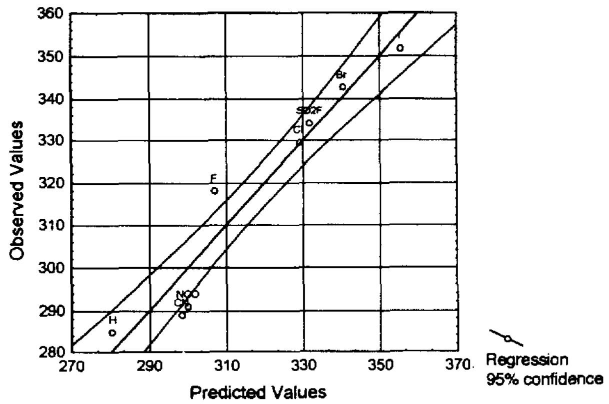


Fig. 1. Observed and predicted Values of $^1J_{C-F}$ from the simple regression $^1J_{C-F}=251(\pm 8)+78(\pm 9)R_{cov}$; $S_o=7.5$, $r=0.964$, $p=0.0001$, $N=8$.

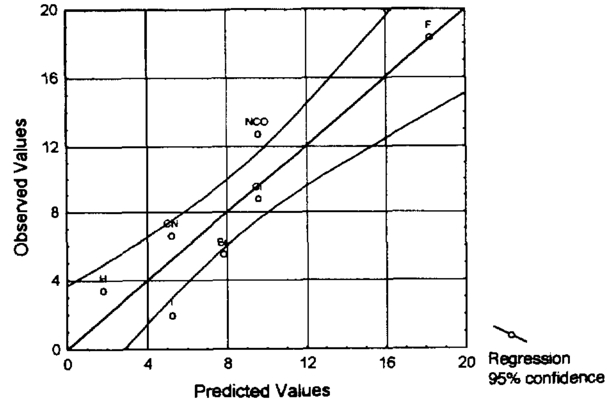


Fig. 2. Observed and predicted values of $^3J_{F-F}$ from the simple regression $^3J_{F-F}=-16.4(\pm 4.9)+0.91(\pm 0.18)\chi$; $S_o=2.5$, $r=0.917$, $p=0.002$, $N=7$.

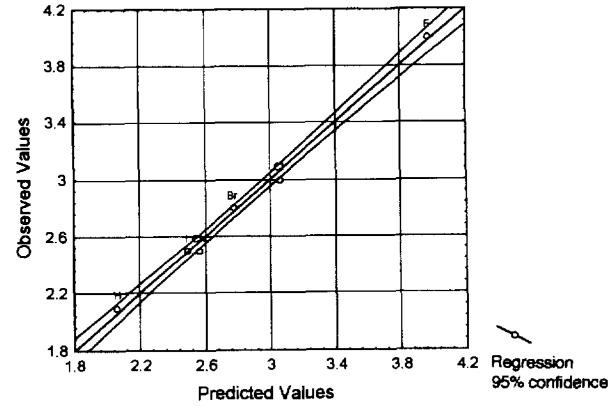


Fig. 3. Observed and predicted values of electronegativity χ from the multiple regression $\chi=1.44(\pm 0.09)+0.61(\pm 0.08)R_{cov}+0.114(\pm 0.005)^3J_{F-F}$; $S_o=0.06$, $r=0.997$, $p=0.0004$, $N=6$ (the –NCO substituent is not included).

atom in SO_2F and SO_2CF_3 groups may be estimated from the regression equation given in Fig. 3 as 2.80±0.06 and 2.76±0.06 respectively. For comparison, the value of electronegativity for the SCF_3 group is equal to 2.7 [11].

3. Experimental details

^1H and ^{19}F NMR spectra were measured with a Bruker WP-200 (at 200.13 and 188.28 MHz respectively) NMR spectrometer using HMDS and $CFCl_3$ as internal standards, and acetone-d_6 as solvent. ^{19}F and ^{13}C NMR spectra were measured with a Varian VXR-300 NMR spectrometer (^{19}F at 282.22 MHz and ^{13}C at 75.43 MHz) using acetone-d_6 as solvent. ^{19}F and ^{13}C NMR chemical shifts are reported relative to internal $CFCl_3$ 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_2 as), 1440 (SO_2 s), 1600–1610 (N–H), 1720 (C=O) cm^{-1}.

^{19}F NMR spectra: 40.3 (t, 1F, SO_2F), −103.0 (d, 2F, CF_2) ppm, $^3J_{F-F}=4.5$ Hz. Analysis: C 13.54; H 1.16; N 7.9. $C_2H_2F_3NO_3S$ 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_2O_5 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_2 s), 1464 (SO_2 as), 2275 (C≡N) cm^{-1}.

Analysis: N 8.9. $C_2F_3NO_2S$ 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].

^1H NMR spectra: 6.35 (t, 1H, CH) ppm, $^3J_{H-F}=52$ 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_2SO_4 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_2+), cm^{-1}.

^{19}F NMR spectra: −103.4 (d, CF_2, 2F), 41.8 (t, SO_2F, 1F) ppm, $^3J_{F-F} = 5.2$ 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_2 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. $C_2F_3NO_3S$ 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) 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^{-1}.

^1H NMR spectra: 8.42–8.30 (m, 2H), 7.76–7.82 (m, 2H) ppm.

^{19}F NMR spectra: F 37.9 (t, 1F, SO_2F), −91.7 (d, 2F, CF_2) ppm, $^3J_{F-F} = 4.9$.

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_3), 2275 (N_2^+), 3010–3130 (C–H) cm^{-1}.

^1H NMR spectra: 8.38–8.24 (m, 2H), 7.82–7.68 (m 2H) ppm.

^{19}F NMR spectra: −94.5 (s, 2F, CF_2) 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. $C_3H_4F_3NO_3S$ 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_3), 3100 (N–H) cm^{-1}.

^{19}F NMR spectra: −106.2 (d, 2F, CF_2), $^3J_{F-F} = 5,7$ Hz; 38.9 (t, 1F, SO_2F) ppm, $^3J_{F-F} = 5.7$ Hz.

^1H NMR spectra: 4.13 (s, CH_3), 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^{-1}.

^{19}F NMR spectra: −102.5 (d, 2F, CF_2) $^3J_{F-F} = 5.9$ Hz; 40.7 (t, 1F, SO_2F) ppm, $^3J_{F-F} = 5.9$ Hz.

^1H NMR spectra: 7.78–7.87 (m, 5H, C_6H_5), 4.9 (s, 1H, $N\underline{H}C_6H_5$), 9.7 (broad s, 1H, =NH) ppm.

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