

Polyfluoroalkyl *N*-(Trifluoromethylsulfonyl)amidosulfites, Number One Stable NH-Containing Amidosulfites

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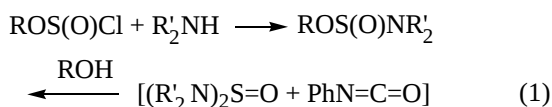
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Abstract—We prepared for the first time NH-containing amidosulfites, polyfluoroalkyl *N*-(trifluoro-methylsulfonyl)amidosulfites $\text{CF}_3\text{SO}_2\text{NHS}(\text{O})\text{OR}_F$, by reaction of *N*-sulfinyl-trifluoromethanesulfonamide $\text{CF}_3\text{SO}_2\text{N}=\text{S}=\text{O}$ with alcohols R_FOH . Amidosulfites were formed also in reaction of chlorosulfites $\text{R}_F\text{OS}(\text{O})\text{Cl}$ with trifluoromethanesulfonamide, with its sodium salt, and *N*-trimethylsilyl derivative.

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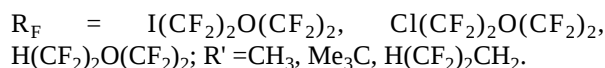
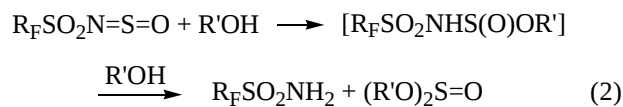
Organic derivatives of sulfurous acid, like dialkyl sulfites $(\text{RO})_2\text{S}=\text{O}$, chlorosulfites $\text{ROS}(\text{O})\text{Cl}$ (intermediates in alcohols chlorination with thionyl chloride), and *N*-sulfinylamines $\text{RN}=\text{S}=\text{O}$, are well known and extensively used as very reactive synthons [1–11]. In contrast, amidosulfites $\text{ROS}(\text{O})\text{NHR}'$ are unstable intermediates whose formation has been only presumed, for instance, in addition reactions of alcohols ROH to substituted *N*-sulfinylamines $\text{R}'\text{N}=\text{S}=\text{O}$ [12, 13]. Only cyclic amidosulfites $\text{ROS}(\text{O})\text{NR}'$ were stable, first obtained by Etlis et al [14] (and not in [15] as claimed Deyrup and Moyer). Under acid conditions the amidosulfites readily hydrolyzed with SO_2 liberation [14, 16, 17]. As to acyclic amidosulfites, only *N,N*-dialkyl amidosulfites $\text{ROS}(\text{O})\text{NMe}_2$ prepared either by aminolysis of chloro-sulfites $\text{ROS}(\text{O})\text{Cl}$ [18], or from tetraalkyl diamidosulfites and phenyl isocyanate [19, 20].



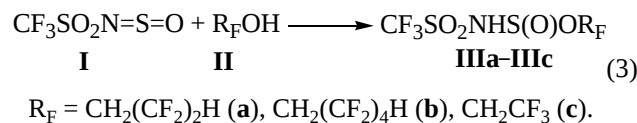
Many among the compounds decomposed on heating with SO_2 elimination and formation of tertiary amines [20]. Amidosulfites containing an NH group were not described.

Among *N*-functionally substituted *N*-sulfinylamines the best understood are *N*-sulfinylsulfonamides $\text{RSO}_2\text{N}=\text{S}=\text{O}$ formed at treating with thionyl chloride of aromatic [10, 11] or perfluoroalkyl-substituted sulfon-

amides [12, 13]. *N*-Sulfinylperfluoroalkanesulfonamides $\text{R}_F\text{SO}_2\text{N}=\text{S}=\text{O}$ are very reactive. At treating the substances with aromatic aldehydes [21, 22], dimethylformamide [22], and carboxylic acids [23] SO_2 liberated and formed products of general formula $\text{R}_F\text{SO}_2\text{N}=\text{Y}$ [$\text{Y} = \text{Ar}$, CHNMe_2 , and $\text{C}(\text{OH})\text{R}'$ respectively]. In the latter case the prototropic tautomerization led to the formation of mixed amides of carboxylic and sulfonic acids $\text{R}_F\text{SO}_2\text{NHC}(\text{O})\text{R}'$. With anilines ArNH_2 transamination occurred giving amides $\text{R}_F\text{SO}_2\text{NH}_2$ and *N*-sulfinylanilines $\text{ArN}=\text{S}=\text{O}$ [12], and the treatment with alkene oxides gave rise to *N*-perfluoroalkanesulfonyl-substituted cyclic amidosulfites [24]. Adducts like $\text{R}_F\text{SO}_2\text{NHS}(\text{O})\text{X}$ were successfully prepared only with PH- and CH-acids [$\text{X} = \text{P}(\text{O})(\text{OMe})_2$, $\text{CH}(\text{CHCOOEt})_2$] [12]. The attempts to stop the reaction with proton-donor reagents ROH (water, alcohols, acids, amines) at the stage of adducts $\text{R}_F\text{SO}_2\text{NHS}(\text{O})\text{OR}$ formation were doomed to failure. The reaction with alcohols gave rise to dialkyl sulfites and perfluoroalkanesulfonamides, and it was stated in [12] that all attempts to isolate the intermediate amidosulfites $\text{R}_F\text{SO}_2\text{NHS}(\text{O})\text{OR}$ were unsuccessful.



We found that the reaction of equimolar amounts of *N*-sulfinyltrifluoromethanesulfonamide $\text{CF}_3\text{SO}_2\text{N}=\text{S}=\text{O}$ (**I**) and fluorinated alcohols $\text{R}_\text{F}\text{OH}$ (**II**) led to the formation of *N*-[(polyfluoro-alkoxy)sulfinyl]trifluoromethanesulfonamides **IIIa–IIIc**.

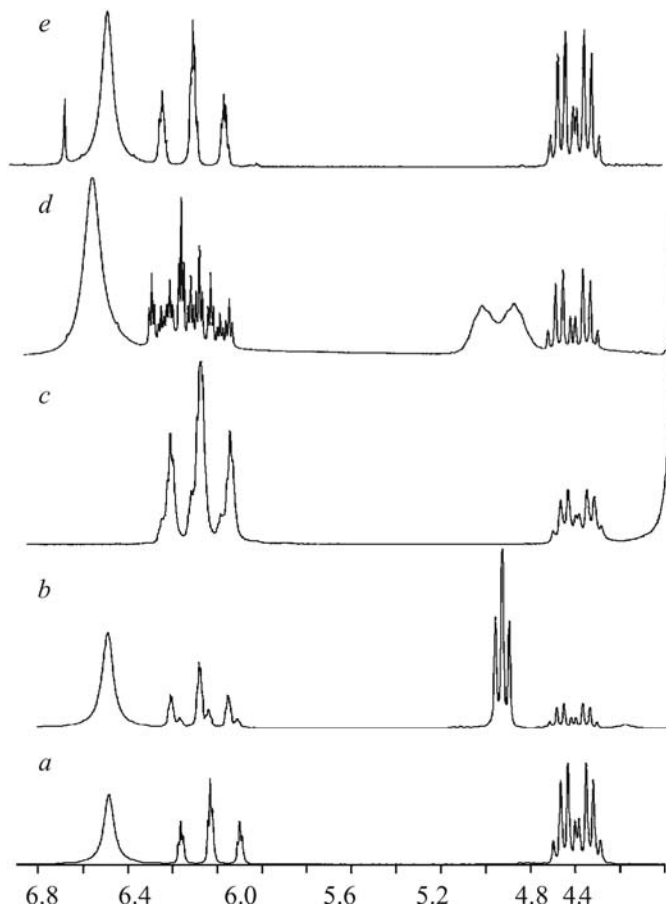
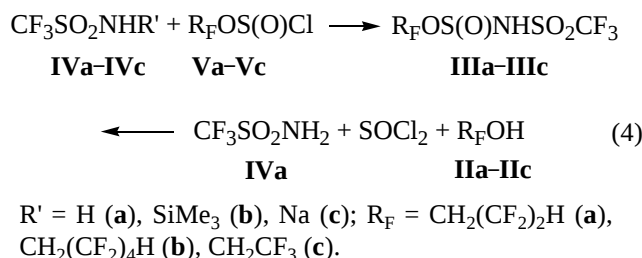


The structure of compounds **IIIa–IIIc** was unambiguously proved by the presence in their ^1H NMR spectra of signals belonging to diastereotopic protons of the CH_2 group in the radical R_F that appear as two *AB* quartets (due to coincidence of coupling constants $^2J_{\text{HH}}$ and $^3J_{\text{HF}}$ for compounds **IIIa** and **IIIb**) or as two doublets of quartets (for compound **IIIc**) in the region 4.3–4.7 ppm with a constant $^2J(\text{H}^{\text{A}}\text{H}^{\text{B}}) \sim 13$ Hz. The observed spectral pattern is caused by the presence in these molecules of a chiral center (sulfur atom). This picture coincides with that described for their structural analogs $\text{CH}_3\text{CH}_2\text{OS}(\text{O})\text{CF}_3$ and $\text{CF}_3\text{CH}_2\text{OS}(\text{O})\text{CF}_3$ [3, 4, 25].

The relative stability of amidosulfites **III** cannot be directly ascribed to the higher acidity of the polyfluorinated alcohols compared to their nonfluorinated analogs, for the reaction of even more acidic substances, for instance, carboxylic acids, with *N*-sulfinylperfluoroalkanesulfonamides $\text{R}_\text{F}\text{SO}_2\text{N}=\text{S}=\text{O}$ proceeds with sulfur dioxide elimination and results in *N*-perfluoroalkanesulfonamides $\text{R}_\text{F}\text{SO}_2\text{NHCOR}$ [23].

We also investigated the alternative procedures for preparation of amidosulfites **III** by reaction (4) of *N*-substituted trifluoromethanesulfonamide $\text{CF}_3\text{SO}_2\text{NHR}'$ (**IV**) with chlorosulfites of polyfluorinated alcohols $\text{R}_\text{F}\text{OS}(\text{O})\text{Cl}$ (**V**) or by a three-component reaction involving trifluoromethanesulfonamide **IVa**, thionyl chloride, and polyfluorinated alcohols **II**.

In all cases on mixing the components at room temperature or at slight heating, as in reaction (3), amidosulfites **III** were obtained. Their formation was



^1H NMR spectra of reaction mixtures in CD_3CN : (a) **I** + **IIa**; (b) **IVa** + **Va**; (c) $\text{CF}_3\text{SO}_2\text{NHNa}$ + **Va**; (d) $\text{CF}_3\text{SO}_2\text{NHSiMe}_3$ + **Va**; (e) **IIa** + **IVa** + SOCl_2 .

confirmed by the presence in the ^1H NMR spectra of the same multiplet of the diastereotopic protons of the CH_2 group (see the figure), and also by comparison with the published data on the chemical shifts and coupling constants in the ^1H , ^{13}C , and ^{19}F NMR spectra of the initial compounds and probable reaction products, like $\text{R}_\text{F}\text{OS}(\text{O})\text{Cl}$ [5, 9] and $(\text{R}_\text{F}\text{O})_2\text{S}=\text{O}$ [12].

Compounds **III** are readily hydrolyzed giving trifluoromethanesulfonamide **IVa**, alcohol $\text{R}_\text{F}\text{OH}$, and SO_2 .

EXPERIMENTAL

NMR spectra were registered on a spectrometer Bruker DPX-400 [operating frequencies 400 (^1H), 100 (^{13}C), and 376 MHz (^{19}F)], internal reference HMDS, chemical shifts are reported with respect to TMS (^1H , ^{13}C) and CCl_3F (^{19}F).

Chlorosulfites of polyfluorinated alcohols **V** were obtained by procedure [9]. All reactions were carried out under an argon atmosphere.

3-[(Chlorosulfinyl)oxy]-1,1,2,2-tetrafluoropropane (Va). Yield 75%, bp 22–23°C (2 mm Hg), n_D^{19} 1.3860 {bp 61°C (40 mm Hg), n_D^{20} 1.3704 [5]}. ^1H NMR spectrum (CDCl_3), δ , ppm: 4.56 d.t (1H, H^A , $^2J_{\text{HH}}$ 11.8, $^3J_{\text{HF}}$ 11.8 Hz), 4.81 d.t (1H, H^B , $^2J_{\text{HH}}$ 11.8, $^3J_{\text{HF}}$ 11.8 Hz), 5.92 t (1H, CHF_2 , $^2J_{\text{HF}}$ 52.9 Hz). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 59.20 t (CH_2 , $^2J_{\text{CF}}$ 30.0 Hz), 109.15 t.t (CHF_2 , $^1J_{\text{CF}}$ 250.7, $^2J_{\text{CF}}$ 36.6 Hz), 113.48 t.t (CF_2 , $^1J_{\text{CF}}$ 250.6, $^2J_{\text{CF}}$ 28.8 Hz). ^{19}F NMR spectrum (CD_3CN), δ , ppm: –122.41 s (2F, CF_2), –136.83 d.d (2F, CHF_2 , J 53.4, 12.05 Hz).

5-[(Chlorosulfinyl)oxy]-1,1,2,2,3,3,4,4-octafluoropentane (Vb). Yield 87%, bp 40–42°C (2 mm Hg), n_D^{18} 1.3680 {bp 64°C (5 mm Hg), n_D^{20} 1.3630 [9], bp 98.5–99°C (50 mm Hg), n_D^{20} 1.3580 [5]}. ^1H NMR spectrum (CDCl_3), δ , ppm: 4.86–4.89 m (2H, CH_2), 6.06 t (1H, CHF_2 , $^3J_{\text{HF}}$ 51.96 Hz). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 59.14 t (CH_2 , $^2J_{\text{CF}}$ 27.5 Hz), 107.59 t.t (CHF_2 , $^1J_{\text{CF}}$ 254.4, $^2J_{\text{CF}}$ 31.3 Hz), 110.08 t.t (CF_2 , $^1J_{\text{CF}}$ 264.14, $^2J_{\text{CF}}$ 30.1 Hz), 110.71 t.t (CF_2 , $^1J_{\text{CF}}$ 264.45, $^2J_{\text{CF}}$ 33.3 Hz), 113.87 t.t (CF_2 , $^1J_{\text{CF}}$ 258.9, $^2J_{\text{CF}}$ 31.3 Hz). ^{19}F NMR spectrum (CD_3CN), δ , ppm: –137.31 d (2F, CHF_2 , $^2J_{\text{HF}}$ 52.2 Hz), –129.83 s (2F, CHF_2CF_2), –125.10 s (2F, CH_2CF_2), –119.67 quintet (2F, $\text{CF}_2\text{CF}_2\text{CF}_2$, $^3J_{\text{FF}}$ 11.8 Hz).

2-[(Chlorosulfinyl)oxy]-1,1,1-trifluoroethane (Vc). Yield 40%, bp 92–96°C. ^1H NMR spectrum (CDCl_3), δ , ppm: 4.65 d (2H, CH_2 , $^2J_{\text{HF}}$ 67.5 Hz). ^{13}C NMR spectrum (CDCl_3), δ , ppm: 59.84 q (CH_2 , $^2J_{\text{CF}}$ 38.8 Hz), 122.12 q (CF_3 , $^1J_{\text{CF}}$ 277.3 Hz). ^{19}F NMR spectrum (CDCl_3), δ , ppm: –73.88 t (3F, CF_3CH_2 , $^3J_{\text{HF}}$ 8.0 Hz).

N-[(2,2,3,3-Tetrafluoropropoxy)sulfinyl]trifluoromethanesulfonamide (IIIa). *a.* To 0.195 g (1 mmol) of compound **I** was added at vigorous stirring while cooling with ice (5°C) 0.132 g (1 mmol) of 2,2,3,3-tetrafluoropropanol (**IIa**), the mixture was stirred at room temperature for 6 h, left standing at this temperature for 16 h, and then it was evaporated to dryness. Yield 0.46 g (70%), colorless crystals that sublime with decomposition at 70°C. ^1H NMR spectrum (CD_3CN), δ , ppm: 4.41 d.t (1H, H^A , $^2J_{\text{HH}}$ 13.1, $^3J_{\text{HF}}$ 13.1 Hz), 4.53 d.t (1H, H^B , $^2J_{\text{HH}}$ 13.2, $^3J_{\text{HF}}$ 13.2 Hz), 6.17 t.t (CHF_2 , $^2J_{\text{HF}}$ 52.3, $^3J_{\text{HF}}$ 4.6 Hz), 6.62 br.s (1H, NH). ^{13}C NMR spectrum ($\text{CD}_3\text{CN} + \text{CDCl}_3$), δ , ppm: 58.38 t (CH_2 , $^2J_{\text{CF}}$ 29.1 Hz), 109.74 t.t (CHF_2 , $^1J_{\text{CF}}$ 250.3, $^2J_{\text{CF}}$ 35.3 Hz), 114.56 t.t (CF_2 , $^1J_{\text{CF}}$ 250.5, $^2J_{\text{CF}}$ 27.6 Hz), 120.17 q (CF_3SO_2 , $^1J_{\text{CF}}$ 319.4 Hz). ^{19}F NMR spectrum ($\text{CD}_3\text{CN} + \text{CDCl}_3$), δ , ppm: –80.41 s (3F, CF_3SO_2), –125.38 m (2F, CF_2), –139.36 d (2F, CHF_2 , $^2J_{\text{HF}}$ 52.2 Hz). Found, %: C 13.94;

H 1.09; N 4.01. $\text{C}_4\text{H}_4\text{F}_7\text{N}_1\text{O}_4\text{S}_2$. Calculated, %: C 14.68; H 1.23; N 4.28.

b. To a solution of 0.745 g (5 mmol) of compound **IVa** in 2 ml of CD_3CN was added at stirring and cooling to 5°C 1.07 g (5 mmol) of sulfinylchloride **Va**. Signals in the ^1H NMR spectrum of the reaction mixture after stirring for 1.5 h at room temperature coincided with the signals of amidosulfite **IIIa** prepared by procedure *a* (see the figure, *b*).

c. To 1.11 g (5 mmol) of *N*-trimethylsilyltrifluoromethanesulfonamide (**IVb**) was added at stirring 1.07 g (5 mmol) of sulfinylchloride **Va**. Signals in the ^1H NMR spectrum of the reaction mixture after stirring for 1 h at room temperature coincided with the signals of amidosulfite **IIIa** prepared by procedure *a* (see the figure, *c*).

d. A mixture of 0.40 g (2.3 mmol) of trifluoromethanesulfonamide sodium salt (**IVc**), 0.56 g (2.6 mmol) of sulfinylchloride **Va**, and 2 ml of CD_3CN was stirred at room temperature for 1 h, then heated at 80°C for 10 min. Signals in the ^1H NMR spectrum of the reaction mixture registered after cooling coincided with the signals of amidosulfite **IIIa** prepared by procedure *a* (see the figure, *d*).

e. A mixture of 0.149 g (1 mmol) of trifluoromethanesulfonamide (**IVa**), 0.132 g (1 mmol) of 2,2,3,3-tetrafluoropropanol (**IIa**), and 0.118 g (1 mmol) of thionyl chloride in 2 ml of benzene was stirred at room temperature for 4 h. On evaporating benzene in a vacuum in the ^1H NMR spectrum of the residue signals were observed coinciding with the signals of amidosulfite **IIIa** prepared by procedure *a* (see the figure, *e*).

N-[(2,2,3,3,4,4,5,5-Octafluoropentyloxy)sulfinyl]trifluoromethanesulfonamide (IIIb) was prepared similarly to compound **IIIa** by procedure *a*. ^1H NMR spectrum ($\text{CD}_3\text{CN} + \text{CDCl}_3$), δ , ppm: 4.63 d.t (1H, H^A , $^2J_{\text{HH}}$ 13.6, $^3J_{\text{HF}}$ 13.6 Hz), 4.50 d.t (1H, H^B , $^2J_{\text{HH}}$ 13.3, $^3J_{\text{HF}}$ 13.3 Hz), 6.34 t.t (CHF_2 , $^2J_{\text{HF}}$ 51.5, $^3J_{\text{HF}}$ 6.7 Hz), 6.53 br.s (1H, NH). ^{13}C NMR spectrum ($\text{CD}_3\text{CN} + \text{CDCl}_3$), δ , ppm: 58.88 t (CH_2 , $^2J_{\text{CF}}$ 26.8 Hz), 109.03 t.t (C^5F_2 , $^1J_{\text{CF}}$ 253.2, $^2J_{\text{CF}}$ 31.1 Hz), 115.59 t.t (C^2F_2 , $^1J_{\text{CF}}$ 256.7, $^2J_{\text{CF}}$ 31.3 Hz), 120.78 q (CF_3SO_2 , $^1J_{\text{CF}}$ 319.4 Hz). We failed to identify the signals of atoms C^3 and C^4 because of their low intensity. ^{19}F NMR spectrum (CD_3CN), δ , ppm: –80.52 s.c (3F, CF_3SO_2), –120.20 quintet (2F, C^3F_2 , $^3J_{\text{FF}}$ 12.3 Hz), –125.47 s (2F, C^2F_2), –130.48 s (2F, C^4F_2), –138.74 d (2F, CHF_2 , $^2J_{\text{HF}}$ 51.6 Hz).

N-[(2,2,2-Trifluoroethoxy)sulfinyl]trifluoromethanesulfonamide (IIIc) was prepared similarly to compound **IIIa** by procedure *a*. ^1H NMR spectrum (CD_3CN), δ , ppm: 4.48 d.q (1H, H^A , $^2J_{\text{HH}}$ 12.8, $^3J_{\text{HF}}$ 8.4 Hz), 4.56 d.q (1H, H^B , $^2J_{\text{HH}}$ 12.8, $^3J_{\text{HF}}$ 8.4 Hz), 6.63 br.s (1H, NH). ^{13}C NMR spectrum (CD_3CN), δ , ppm: 59.61 q (CH_2 , $^2J_{\text{CF}}$ 37.3 Hz), 120.91 q (CF_3SO_2 , $^1J_{\text{CF}}$ 318.5 Hz), 124.23 q (CF_3CH_2 , $^1J_{\text{CF}}$ 276.7 Hz). ^{19}F NMR spectrum (CD_3CN), δ , ppm: -80.65 s (1F, CF_3SO_2), -74.78 t (1F, CF_3CH_2 , $^3J_{\text{HF}}$ 8.6 Hz).

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