$\overline{\mathrm{F_2C{-}N{\cdots}S(F){\cdots}N{-}CF_2}}{}^-$, a Cyclic Bis(imino)fluorosulfinate from an Unexpected Rearrangement

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The first cyclic bis(imino)fluorosulfinate $S(NMe_2)_3^+$ $\overline{\mathrm{F_2C{-}N{\cdots}S(F){\cdots}N{-}CF_2}}{}^-$ **2** is obtained by fluoride ion addition to $NC{-}CF_2{-}NSF_2$, $(F_2SN{-}CF_2)_2$ or $\overline{\mathrm{F_2C{-}N{=}S{=}N{-}CF_2}}$; the X-ray structure of **2** is reported.

Recently we have shown that fluoride ion can be added, by TASF $[(Me_2N)_3S^+Me_3SiF_2^-]$,[1] to sulfur difluoride imides R_FNSF_2 to give the corresponding sulfur trifluoride amide anions $R_FNSF_3^-$ (R_F = perfluoralkyl, SF_5, FSO_2).[2] On the other hand, as F^- is known to catalyse additions to CN bonds, $R_FCF{=}N^-$ anions might be formed as intermediates. It was of interest to us how F^- would interact with systems in which both functional groups are present, *i.e.* $NC{-}CF_2{-}NSF_2$.[3] NMR experiments show that attack of F^- at the sulfur centre is the primary step in this reaction (Scheme 1).

For **1** two unresolved signals in the SF region at δ 61.5 and 56.2‡ in the intensity ratio 2:1 are observed together with $\delta(CF_2)$ at −43.1. This primary product rearranges quantitatively within 2 hours at −30 °C to a final product showing a quintet at δ 88.5 and a doublet at δ −80.8 (J = 33.3 Hz, intensity ratio 1:4) (Scheme 2).

These NMR data are consistent with structure **2**, if rapid inversion at the sulfur occurs. This rearrangement under attack of the nitrile group is very unusual, since the CN group is rather unreactive towards $S^{IV}{-}F$ species. CF_3CN, for example reacts with SF_4 only at temperatures above 150 °C to give $CF_3CF_2NSF_2$;[3] even under these conditions with excess nitrile no sulfur diimide formation is reported.

Compound **2** is also obtained when $(F_2SNCF_2)_2$ reacts with TASF in a 1:2 molar ratio and when F^- is added to the cyclic sulfur diimide $\overline{\mathrm{F_2C{-}N{=}S{=}N{-}CF_2}}$[4] (Scheme 3).

Only a few acyclic bis(imino)fluorosulfinates $RNS(F)NR^-$ have been described in the literature [R = $PhSO_2$,[5] FSO_2, $(CF_3)_2CF$,[6] C_2F_5, CF_3[7]] and no structure determinations have been reported. Single crystals of **2** were obtained by diffusion of diethyl ether into an almost saturated solution of **2** in MeCN at −30 °C. The structure of the anion of **2** is presented in Fig. 1.†

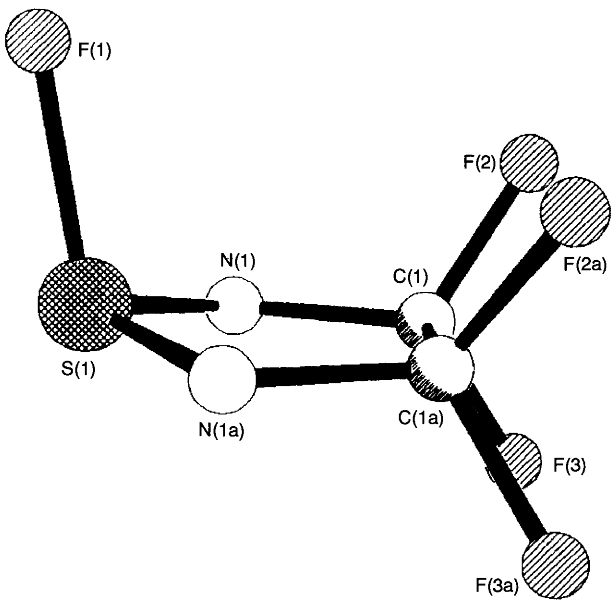
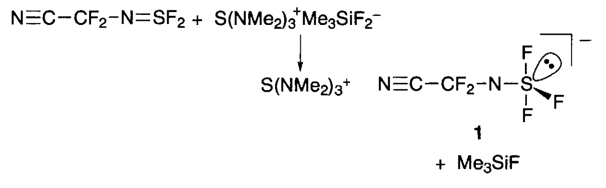
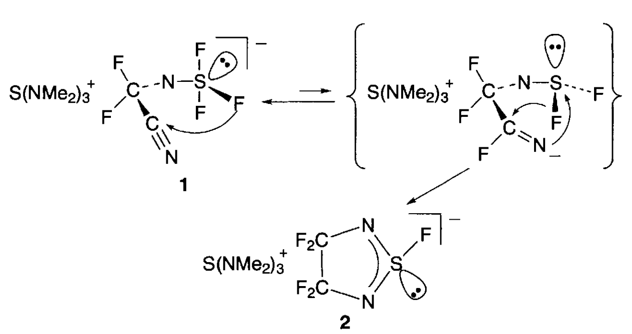


Fig. 1 Structure of the $\overline{\mathrm{F_2C{-}N{\cdots}S(F){\cdots}N{-}CF_2}}$ anion; bond distances (pm) and bond angles (°): S(1)–F(1) 170.2(2), S(1)–N(1) 153.6(2), N(1)–C(1) 137.7(3), C(1)–F(2) 135.0(2), C(1)–F(3) 136.7(2), C(1)–C(1a) 153.4(4), N(1)–S(1)–N(1a) 104.9(2), N(1)–S(1)–F(1) 103.6(1), C(1)–N(1)–S(1) 107.6(2), F(2)–C(1)–F(3) 103.0(2), F(2)–C(1)–N(1) 112.7(2), F(3)–C(1)–N(1) 110.6(2), F(2)–C(1)–C(1a) 110.7(2), F(3)–C(1)–C(1a) 110.6(1), N(1)–C(1)–C(1a) 109.1(1)

In the anion the five-membered heterocycle adopts an envelope conformation. The pseudo-tetrahedrally coordinated sulfur atom lies *ca.* 21 pm above the N(1)–N(1a)–C(1)–C(1a) plane. The S–F bond [170.2(2) pm] is appreciably longer than found in other tetrahedrally coordinated sulfur(IV) derivatives [*e.g.* 163.3(14) pm in $\overline{\mathrm{NC(F)NC(F)NSF}}$[8]]. The S–N bond lengths [153.6(2) pm] are not affected by this anion formation, and are similar to those observed in acyclic sulfur diimides.[9] These RN=S=NR derivatives are usually found in the *Z*/*E*-conformation with an N–S–N angle of ≈115°.[10] in sulfur diimides with *Z*/*Z*-conformation this angle widens to ≈125–130°.[11] In **2** an N–S–N angle of 104.9(2)° is found, suggesting appreciable ring strain. Despite this, according to MNDO calculations, the cyclic anion of **2** is more stable by *ca.* 350 kJ mol^{-1} than the acyclic isomer $NC{-}CF_2{-}NSF_3^-$.



Scheme 1



Scheme 2

$$(F_2SNCF_2)_2 + 2\,S(NMe_2)_3^+\,Me_3SiF_2^- \longrightarrow \mathbf{2} + S(NMe_2)_3^+SF_5^- + 2\,Me_3SiF$$

$$\overline{\mathrm{F_2C{-}N{=}S{=}N{-}CF_2}} + S(NMe_2)_3^+\,Me_3SiF_2^- \longrightarrow \mathbf{2} + Me_3SiF$$

Scheme 3

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Footnotes

† *Crystal data for* $S(NMe_2)_3^+$ $F_2\overline{C{-}N{\cdots}S(F){\cdots}N{-}C}F_2^-$: orthorhombic, space group *Pnma*, a = 1281.2(3), b = 1202.2(2), c = 993.2(2) pm, U = 1.5298(5) nm^3, Z = 4, D_c = 1.491 g cm^{-3}, μ = 0.398 mm^{-1}, $F(000)$ = 712, crystal dimensions 0.8 × 0.5 × 0.5 mm. 7477 Reflections collected with $2.59 < \theta < 27.49°$, 1840 unique (R_{int} = 0.0601) used in the structural analysis. The data set was collected on a Siemens P4 diffractometer using Mo-Kα radiation (λ = 71.073 pm) at 173 K. The structure was solved by direct methods. All non-H atoms were refined anisotropically. The refinement (101 parameters) converged with $wR2$ = 0.1005 ($R1$ = 0.0386) and final difference electron density maxima of 315 e nm^{-3} and minima of −368 e nm^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ NMR, standards: all NMR shifts are reported as positive to high frequency of $CFCl_3$.

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11 See, for instance: D. G. Anderson, H. E. Robertson, D. W. H. Rankin and J. D. Woollins, *J. Chem. Soc., Dalton Trans.*, 1989, 859; A. Gieren, H. Betz, T. Hübner, V. Lamm, M. Herberhold and K. Guldner, *Z. Anorg. Allg. Chem.*, 1984, **513**, 160.