1,2-Bis[trifluorosulfur(IV)]tetrafluoroethane $F_3S–CF_2–CF_2–SF_3$: A Bifunctional Molecule with Two Fluoroamphoteric Sulfur Centers☆

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The title compound $(–CF_2–SF_3)_2$ (**2**) is prepared from $(–CF_2–SCl)_2$ (**1**) and F_2 at –90 °C in 83 % yield. Reaction of **2** with CsF and TASF yields $Cs[(–CF_2–SF_3)_2F]$ (**8**), TAS $[(–CF_2SF_3)_2F]$ (**9**) and $(TAS)_2[(–CF_2–SF_4)_2]$ (**10**). Fluoride-ion abstraction yields $[(–CF_2SF_2)_2F]$ $[AsF_6]$ (**6**), BF_3-catalysed solvolysis in SO_2 gives $[–CF_2–S(O)F]_2$ (**4**), and CsF-catalysed oxidation with F_2 leads to the previously reported $(–CF_2–SF_5)_2$ (**11**). Ab initio calculations of the molecular structures of **2** and the related methane derivative $F_2C(SF_3)_2$ are reported.

Introduction

α,ω-Bis(trifluorosulfur)perfluoroalkanes, $SF_3-(CF_2)_n-SF_3$, should show a rich and interesting chemistry as a result of the bifunctionality and high reactivity of the SF_3 groups. The only compound of this class known to date is $F_2C(SF_3)_2$, which is prepared by the direct fluorination of CS_2[1][2][3]. As well as the chemistry of this compound and its reaction product $CF_2[S(O)F]_2$[4], the gas-phase structure of bis(trifluorosulfur)difluoromethane has been studied by electron diffraction[5]. There is an intramolecular interaction between the two SF_3 groups in the gas phase; one of the axial fluorine atoms of the pseudo-trigonal bipyramidal sulfur atom interacts equatorially with the other sulfur center and vice versa.

We thought it would be interesting to observe the effect that increasing the length of the perfluoroalkane chain would have on the interaction between the sulfur centers, the stability and the reactivity. We report here the synthesis of 1,2-bis(trifluorosulfur)tetrafluoroethane and illustrate the diverse reaction possibilities with some examples. The structures of $SF_3(CF_2)_nSF_3$ ($n = 1, 2$) calculated by ab initio methods are compared to that of $CF_2(SF_3)_2$[5] determined by electron diffraction.

Results and Discussion

Synthesis of 1,2-Bis(trifluorosulfur)-1,1,2,2-tetrafluoroethane ($F_3S-CF_2-CF_2-SF_3$)

The bis(trifluorosulfur)ethane derivative **2** was prepared in high yield by low-temperature fluorination of the corresponding chlorosulfenyl derivative **1**[6].

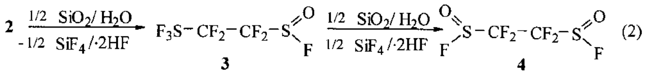
$$\underset{\textbf{1}}{ClS–CF_2–CF_2–SCl} + 3\,F_2 \xrightarrow{-\,90^\circ C} \underset{\textbf{2}}{F_3S–CF_2–CF_2–SF_3} + Cl_2 \qquad (1)$$

Fluorine was expanded through a metal vacuum line under reduced pressure into a cooled nickel reactor containing compound **1** as a thin film on the inner surface. Decomposition products and the resulting chlorine were periodically removed on reaching a pressure of approximately 100 mbar. The reaction was taken as complete when no more fluorine uptake was observed, i.e. a subsequent oxidation of compound **2** to the respective sulfur(VI) derivative **11** does not occur under these conditions.

Compound **2** was prepared by this reaction on a preparative scale with a yield of 83%. **2** is a colourless, hydrolysis-sensitive liquid, as is the corresponding methane derivative $CF_2(SF_3)_2$.

In an analogous way to $CF_2(SF_3)_2$, which was described in the Introduction, α,ω-bis(trifluorosulfur)perfluoroalkanes display intramolecular donor-acceptor properties as a result of the acid-base amphoteric behaviour of the SF_3 groups, a phenomenon that leads to a chemical stabilization of the SF_3 groups. Evidence for such an interaction was also obtained by NMR spectroscopy. The ^{19}F-NMR spectra of SF_4 and CF_3SF_3 show only one signal for the sulfur-bonded fluorine atoms as a result of Berry pseudorotation at room temperature. However, the fluorine atoms do become non-equivalent at −20°C. In the ^{19}F-NMR spectrum of **2** [and also of $CF_2(SF_3)_2$], no inequivalence of the sulfur-bonded fluorine atoms is observed even at −80°C. We assume that, in addition to Berry pseudorotation, fast intramolecular fluorine exchange between the two SF_3 groups is responsible for this behaviour.

NMR measurements of **2** and $CF_2(SF_3)_2$ at −30°C show that **2** is less stable to hydrolysis than $CF_2(SF_3)_2$ and forms the sulfinyl products $F_3S-CF_2-CF_2-S(O)F$ (**3**) and $[-CF_2-S(O)F]_2$ (**4**), while $F_2C(SF_3)_2$ is stable under these conditions.



$$2 \xrightarrow[-1/2\ SiF_4/-2HF]{1/2\ SiO_2/H_2O} F_3S-CF_2-CF_2-S(=O)F \xrightarrow[1/2\ SiF_4/-2HF]{1/2\ SiO_2/H_2O} F(O=)S-CF_2-CF_2-S(=O)F \qquad (2)$$

3 **4**

While **4** can be synthesized simply by BF_3-catalysed solvolysis of **2** in SO_2, **3** has only been observed as an intermediate (see Eq. 2). The ^{19}F-NMR spectrum of **3** shows a complex AA′BB′MX$_3$ splitting pattern with $\delta(SF_3) = +8.0$ (s, br.), $\delta[S(O)F] = -13.1$ (m), $\delta(CF_2SF_3) = -102.2$ and $\delta[CF_2S(O)F] = -118.1$ (m).

The intramolecular interaction between the two SF_3 groups in **2** appears to be weaker than in $CF_2(SF_3)_2$ and the reactivity higher as a result of the longer perfluoroalkane chain. Evidence for this hypothesis through structural analysis of **2** has not yet been obtained.

Reaction of $(-CF_2SF_3)_2$ with BF_3 and AsF_5 in SO_2: Synthesis of $[-CF_2S(O)F]_2$ and $[(-CF_2SF_2)_2F][AsF_6]$

Perfluoroalkanesulfinyl fluorides can be obtained by two synthetic routes: (i) from perfluoroalkenes and SOF_2[7] or SO_2[8] and (ii) by hydrolysis of perfluoroalkylsulfur trifluorides[7]. The second route is particularly unsatisfactory due to the difficulty in controlling the reaction. As a result of our attempt to synthesize sulfonium salts $R_FSF_2^+BF_4^-$ from the corresponding perfluoroalkylsulfur trifluorides by fluoride abstraction using BF_3 in SO_2, we observed the quantitative formation of $R_FS(O)F$[4]. On addition of BF_3 to a solution of **2** in SO_2 at −40°C, a colourless solid precipitated. This precipitate disappeared on slow warming to room temperature and was not observed again on cooling.

$$2 + BF_3 \xrightarrow[SO_2]{-40°C} [(-F_2C-SF_2)_2F]^+[BF_4]^- \xrightarrow[-2\,SOF_2]{+2\,SO_2} [-CF_2-S(O)F]_2 + BF_3 \qquad (3)$$

5 **4**

It is likely that the colourless precipitate is salt **5**. As discussed previously[4], the FSO_2^- ions resulting from the SO_2/BF_4^- equilibrium attack the cations of **5** leading to the formation of **4**. Compound **4** is isolated as a colourless liquid in > 90% yield.

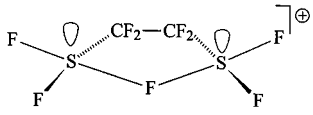
The ^{19}F-NMR spectrum of compound **4** shows two AA′BB′XX′ spin patterns (see Experimental Section), demonstrating the presence of two isomers in a 1:1 ratio, which can be assigned to the *meso* and D,L compounds as a result of the two chiral sulfinyl centers.

If reaction (3) is performed with AsF_5 as a Lewis acid, the salt **6** is isolated in almost quantitative yield.

$$2 + AsF_5 \longrightarrow [(-F_2C-SF_2)_2F]^+[AsF_6]^- \xrightarrow{AsF_5}\!\!\!\!\!\!\!\!/\;\; [(-F_2C-SF_2)_2]^{2+}[AsF_6^-]_2 \qquad (4)$$

6 **7**

The formation of the dicationic compound **7** is not observed, even with a large excess of AsF_5. We assume that the abstraction is prevented due to the mutual interaction of both sulfonium centers. In the ^{19}F-NMR spectrum of **6** only one signal is observed for the *C*- and *S*-bonded fluorine atoms, even at low temperature [$\delta(CF) = -98.3$ (s), $\delta(SF) = -37.2$ (s, br.)]. This equivalence suggests a fast intramolecular fluoride exchange between the two sulfonium centers via a cyclic transition state in which the sulfur centers have pseudo-trigonal bipyramidal coordination through bridging over axially bonded fluoride. Single crystals of **6** suitable for an X-ray-structural analysis have not been obtained to date. In comparison with other sulfonium salts $R_FSF_2^+AsF_6^-$ ($R_F = CF_3, C_2F_5, C_3F_7$)[9][10][11], **6** is not very stable; **6** can only be stored satisfactorily at room temperature in Kel-F or Teflon vessels.



Reactions of $F_3SCF_2CF_2SF_3$ with Fluoride Ions

$R_FSF_4^-$ anions can be prepared by fluoride-ion addition to R_FSF_3 derivatives [$R_F = CF_3, (CF_3)_2CF$][12]. Spectroscopic studies show that the sulfur atom has a pseudo-octahedral geometry in these complexes, with the four fluorine atoms in the basal and the perfluoroalkyl groups in the apical positions. These anions correspond to the transition state of a nucleophilic S_N2 substitution at pseudo-pentacoordinated sulfur.

As we showed recently, fluoride-ion addition to $F_2C(SF_3)_2$ leads to a stable four-membered cyclic anion with a symmetrical S−F−S′ bridge[13]. Similarly, fluoride-ion addition to **2** with CsF and TASF [$(Me_2N)_3S^+Me_3SiF_2^-$] leads to the stable salts **8** and **9**.

$$2 + CsF \longrightarrow Cs^+[(-CF_2-SF_3)_2F]^- \qquad (5)$$

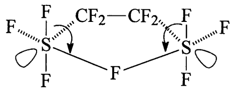
8

$$2 + TASF \longrightarrow TAS^+[(-CF_2-SF_3)_2F]^- + 2\,Me_3SiF \qquad (6)$$

9

In contrast to the neutral starting material **2**, the salts **8** and **9** are much more stable. They can be stored in glass vessels at room temperature under an inert atmosphere for several weeks. The attack by nucleophiles (e.g. H_2O) is impeded through anion formation.

The ^{19}F-NMR spectra of the salts **8** and **9** each show two signals, and these have been assigned to the sulfur- and carbon-bonded fluorine atoms, respectively. Although only broad singlets are observed for the Cs salt **8** [$\delta(CF) = -96.0$ (s), $\delta(SF) = +12.0$ (s, br.)], the S*F* signal in the TAS salt **9** [$\delta(CF) = -95.6$ (s, br.), $\delta(SF) = +12.5$ (quint)] is split into a quintuplet ($^3J = 15.6$ Hz). The equivalence of all S*F* and C*F* atoms deduced from the ^{19}F-NMR spectra can be explained by a fast intramolecular exchange between the two sulfur centers and a rotation around the C−S bonds.



Although it was not possible to add a second fluoride ion to $CF_2(SF_3)_2$, the reaction of **2** with an excess of TASF led quantitatively to **10**, a salt containing a dianion with two pseudo-octahedrally coordinated sulfur centers.

$$\mathbf{2} + 2\,\text{TASF} \longrightarrow \underset{\mathbf{10}}{(\text{TAS}^+)_2[(-CF_2-SF_4)_2]^{2-}} + 2\,Me_3SiF \qquad (7)$$

These reactions show, on the one hand, that the interaction between the two sulfur centers in α,ω-bis(trifluorosulfur) derivatives of the type $F_3S-(CF_2-)_nSF_3$ seems to decrease with increasing chain length and, on the other hand, that the S−F−S′ bridge in **8** and **9** can only be broken by using "naked" or nearly naked, highly reactive fluoride ions such as those in TASF. The colourless stable salt **10** (mp 132°C, decomp.) was characterized by elemental analysis and IR spectroscopy (Experimental Section). Due to the high charge on the anion of **10** it is very insoluble in acetonitrile, the most convenient solvent for reactions with TASF, and, as a result, neither NMR-spectroscopic investigation nor recrystallization of the salt was possible.

CsF-Catalysed Oxidative Fluorination of $SF_3-CF_2-CF_2-SF_3$ to $SF_5-CF_2-CF_2-SF_5$ (11)

CsF-catalysed oxidative fluorinations have found wide use in fluorine chemistry. The oxidation is made easier through intermediate anion formation, as shown by numerous examples in the chemical behaviour of the elements of groups 15−18. Compound **2** can be oxidized to the corresponding sulfur(VI) oxidation state in a way similar to the conversion of $CF_2(SF_3)_2$ to $CF_2(SF_5)_2$[3].

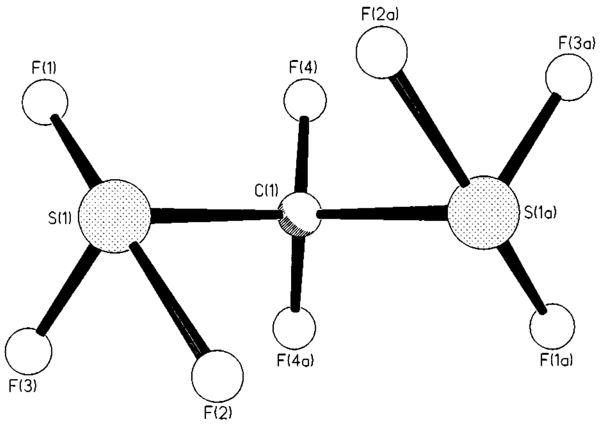
$$\mathbf{2} + 2\,F_2 \xrightarrow[-196° \longrightarrow \text{r.t.}]{\text{CsF}} \underset{\mathbf{11}}{F_5S-CF_2-CF_2-SF_5}\ (21.5\ \%) \qquad (8)$$

11 was first observed as a by-product in the electrofluorination of 3-oxapentane-1,5-dithiol[14]. The ^{19}F-chemical shifts of the fluorine atoms of our product differ only slightly from the literature values. For the *C*-bonded fluorine atoms we observe a nonuplet of triplets, since $^3J(CF-SF_4) = {}^4J(CF-SF_4) = 14.6$ Hz and $^3J(CF-SF_{apical}) = {}^4J(CF-SF_{apical}) = 3.0$ Hz. The fine splitting of the A and B_4 parts of the SF_5 groups ($^2J = 152.3$ Hz) indicates a spin system of type $AA'B_4B_4'X_2X_2'$. From the splitting of the ^{13}C signal (δ = 119.9, ttq) we determined the following coupling constants: $^1J(C-F) = 314.2$ Hz, $^2J(C-F) = 35.5$ Hz and $^2J(C-SF_4) = 28.4$ Hz.

Structure and Bonding in $F_3S(CF_2)_nSF_3$ (*n* = 1, 2)

The gas-phase structure of the methane derivative $F_2C(SF_3)_2$ has been determined by electron diffraction[5]. However, our attempts to determine the structure of the ethane derivative **2** have been fruitless to date due to the extreme moisture sensitivity of this species. Figure 1 shows the RHF/6-311+G*-calculated[15] structure for $F_2C(SF_3)_2$, with the experimentally determined bond lengths and angles given for comparison. The conformation as well as the angles and distances are in good agreement. The experimentally observed interaction between the two SF_3 groups is also clearly seen in the calculated structure. The calculated distance between the axial fluoride F(2) and the neighbouring sulfur center S(1a) [or F(2a)−S(1)] of 263 pm lies well below the sum of the van der Waals radii of S and F (320 pm). The experimentally found value is 266 pm. The averaged S−F bond lengths of 163.6 pm (calculated) and 163.0(3) pm (experimental) are identical, although the individual values differ substantially.

Figure 1. Fully optimized structure of $F_3S-CF_2-SF_3$[a]



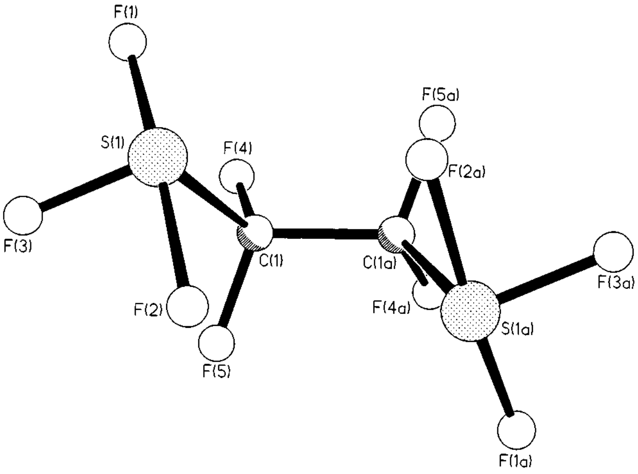
[a] Calculated [and experimental[5]] bond lengths [pm] and bond angles [°]: C(1)−S(1) 187.6 [188.8(7)], C(1)−F(4) 129.1 [131.8(5)], S(1)−F(1) 164.1 [166.4(4)], S(1)−F(2) 172.0 [166.6(4)], S(1)−F(3) 154.7 [156.2(6)], S(1)···F(2a) 263 [266]; S(1)−C(1)−S(1a) 108.6 [108.2(5)], F(4)−C(1)−F(4a) 110.1 [109.8(18)], F(4)−C(1)−S(1) 111.8 [109.7(5)], F(4a)−C(1)−S(1) 107.2, F(1)−S(1)−F(2) 167.7 [173.1(15)], F(1)−S(1)−F(3) 87.6 [88.1(13)], F(2)−S(1)−F(3) 85.8 [88.1(3)], F(1)−S(1)−C(1) 89.0 [89.1(8)], F(2)−S(1)−C(1) 82.0 [85.1(8)], F(3)−S(1)−C(1) 101.2 [97.2(11)].

An average S−F bond length and the difference $\Delta = (S-F_a) - (S-F_e)$ were obtained experimentally, equally large $S-F_a$ distances were assumed. From these data the bond lengths $S-F_a$ and $S-F_e$ were derived. However, it is expected that the interaction of the axial 3c-4e$^-$ bond system with the neighbouring centers will lead to a stretching of the bridging SF and a corresponding shortening of the non-bridging fluoride. For example, this phenomenon is observed in the structure of SF_3-SF[16]. In this case the two $S-F_a$ bonds of the pseudo-pentacoordinated sulfur center differ by approximately 10 pm, and a difference of 7.9 pm was calculated for $F_2C(SF_3)_2$ (172.0 and 164.1 pm).

The influence of the interaction between the two SF_3 groups on the geometrical configuration of the substituents at the sulfur centers is minimal. Through the lengthening of the one axial S−F bond we would expect a distortion of the pseudo-trigonal bipyramid towards a pseudo-tetrahedron and through the interaction of this bridging fluoride with the neighbouring sulfur center we would expect an increase in sulfur coordination towards a pseudo-octahedron. These interactions have little influence, as shown by a comparison with the experimentally determined structure of CF_3SF_3[17]. Deviations from ideal pseudo-trigonal bipyramidal geometry can be explained by the influence of the lone pair of electrons in accordance with VSEPR theory[18].

The RHF/6-311 + G*-calculated[15] structure of $F_3S-CF_2-CF_2-SF_3$ (**2**) with bond lengths and angles is shown in Figure 2. Interaction of the two SF_3 groups is also clearly seen here. The distances between the non-bonded atoms S(1)F(2a) and S(1a)F(2) of 283 pm are also significantly longer than those in the methane derivative. This is in agreement with the conclusions drawn from the experimental results, i.e. that the interaction of the SF_3 groups leads to a stabilization and that the lesser interaction in **2**, compared to that in $F_2C(SF_3)_2$, is responsible for its higher reactivity towards nucleophiles.

Figure 2. Fully optimized structure of compound **2**[a]



[a] Calculated bond lengths [pm] and bond angles [°]: C(1)−C(1a) 155.8, C(1)−S(1) 188.9, C(1)−F(4) 130.2, C(1)−F(5) 130.6, S(1)−F(1) 164.3, S(1)−F(2) 170.2, S(1)−F(3) 155.0, S(1)···F(2a) 283; F(1)−S(1)−F(2) 170.9, F(1)−S(1)−F(3) 88.1, F(1)−S(1)−C(1) 89.9, F(2)−S(1)−F(3) 86.7, F(2)−S(1)−C(1) 83.6, F(3)−S(1)−C(1) 99.2, S(1)−C(1)−C(1a) 115.4, S(1)−C(1)−F(4) 110.0.

As expected, the S−C and averaged S−F bonds, as well as the bond angles in the $C-SF_3$ groups of **2** and $CF_2(SF_3)_2$, differ only slightly. The weaker interaction of the two SF_3 groups in **2** corresponds to the lesser stretching of the axial S−F bonds [170.2 pm compared to 172.0 pm in $CF_2(SF_3)_2$] towards bridging fluorides S(1)F(2a) and S(1a)F(2). The terminal S−F bonds are only slightly longer.

Conclusions

In α,ω-bis(trifluorosulfur)perfluoroalkanes, $F_3S(CF_2)_n$-SF_3 (n = 1, 2), the intramolecular interaction between the two SF_3 groups decreases with increasing chain length, as shown unequivocally by experimental results and ab initio calculations. In both cases fluoride-ion addition and abstraction gives intramolecular fluoride-bridged anions and cations. With excess "naked" fluoride (e.g. from TASF) only the ethane derivative forms a dianion on ring cleavage. The synthesis of dications, even with a large excess of a strong fluoro Lewis acid (e.g. AsF_5), was unsuccessful. It will be interesting to perform further investigations to assess the chain length necessary in order that the SF_3 groups have no influence on each other.

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Experimental Section

All reactions were performed with rigorous exclusion of moisture in thick-walled glass reactors with Teflon valves, or in nickel vessels previously passivated with ClF_5. Work involving aggressive gases was undertaken in a metal vacuum manifold. Volatile reagents were condensed in vacuum lines and solids transferred in a glove box under argon or nitrogen. The starting materials $(-CF_2-SCl)_2$[6], TASF[19] and AsF_5[20] were prepared using literature methods. − IR: Biorad FTS-7-FT-IR. − MS: Finnigan MAT 8222, EI 70 eV. − NMR: Bruker AC 80 and WH 360. − Elemental analyses were performed by the Mikroanalytisches Labor Beller (Göttingen).

$F_3S-CF_2-CF_2-SF_3$ (**2**): In a vacuum line, 3.0 g of F_2 (79 mmol) from a reservoir was added to 5.2 g of $(-CF_2-SCl)_2$ (**1**, 22 mmol), previously condensed onto the inner surface of a 1-l nickel vessel, over a period of 10 h at −90°C. The resulting chlorine and decomposition products were removed as soon as the pressure exceeded 100 mbar. The reaction was complete when uptake of fluorine was no longer observed. Fractional condensation at 10^{-3} mbar (−78 and −196°C) led to 5.1 g of **2** as a colourless solid in the −78°C trap, yield 83%. − IR (gas, cm^{-1}): ν = 1280 m, 1261 m, 1222 vs, 1149 m, 932 s, 850 vs, 680 vs, 637 m, 583 m, 564 s, 521 m, 455 w. − ^{19}F NMR: δ = −100.5 (s, CF), 8.0 (s, br., SF). − EI MS; *m*/*z* (%): 259(1) [M^+], 189(5) [$M^+ - SF_3$], 119(100) [$CF_3CF_2^+$].

$FS(O)CF_2-CF_2S(O)F$ (**4**): 3.0 g of **2** (10.8 mmol), approximately 10 ml of SO_2 and 0.2 g of BF_3 (2.9 mmol) were condensed into a glass reactor fitted with a Teflon valve at −196°C. A colourless solid formed on warming the mixture to −40°C, and this solid disappeared on stirring for 3 h at ambient temperature. BF_3 was then removed by condensation onto 5 g of NaF and subsequent stirring at ambient temperature for 6 h. Fractional condensation under vacuum (−78 and −196°C) resulted in 2.3 g of **4** in the −78°C trap, yield 91%. − IR (gas, cm^{-1}): ν = 1281 sh, 1255 vs, 1234 s, 1184 s, 1129 s, 745 s, 603 w, 481 w. − ^{19}F NMR ($CDCl_3$/$CFCl_3$, 307 K): Two AA′BB′XX′ spin patterns were observed in the ratio 1:1; δ = −17.75 (m, SF), −18.1 (m, SF), −119.5 (m, CF_2, center point of the AA′BB′ part). − ^{13}C NMR: δ = 117.0 (dddddd, $^1J_{CF}$ = 309.6 Hz, $^1J_{CF}$ = 306.0 Hz, $^2J_{CCF}$ = 32.5 Hz, $^2J_{CCF}$ = 32.0 Hz, $^2J_{C\text{-}SF}$ = 16.4 Hz, $^3J_{C\text{-}SF}$ = 2.0 Hz). − EI MS; *m*/*z* (%): 167(24) [M^+ − SOF], 148(2) [$CF_2CF_2SO^+$], 67(100) [SOF^+]. − $C_2F_6O_2S_2$ (234.1): calcd. F 48.7, S 37.4; found F 48.7, S 37.3.

$[(-CF_2-SF_2)F]AsF_6$ (**7**): 1.9 g of **2** (6.8 mmol), 2.0 g of AsF_5 (11.8 mmol) and approximately 10 ml of SO_2 as solvent were condensed into a glass reactor fitted with a Teflon valve at −196°C. The mixture was stirred for 1 h at −40°C and the volatile materials were subsequently removed at this temperature under dynamic vacuum. 3.0 g of **7** (quantitative) remained as a colourless solid, mp. 97°C. − IR: Due to the sensitivity of the compound we have been unable to obtain satisfactory IR spectra. − ^{19}F NMR: δ = −37.2 (s, br., SF), −57.2 (s, br., AsF), −98.3 (s, CF). − $C_2AsF_{15}S_2$ (448.0): calcd. As 16.7, F 63.6; found As 17.4, F 61.8.

$Cs[(-CF_2-SF_3)_2F]$ (**8**): 1.3 g of **2** (4.7 mmol) and 10 ml of CH_3CN were condensed onto 0.6 g of CsF (4.0 mmol), previously dried at 140°C under vacuum. The mixture was stirred for 3 h at −30°C and all volatile products were subsequently removed at this temperature and for a short time at ambient temperature under dynamic vacuum. 1.7 g of **8** (quantitative) was obtained as a colourless non-volatile solid, mp. 105°C (decomp.). − IR (nujol,

cm^{-1}): $\tilde{\nu}$ = 1247 s, 1203 s, 1184 vs, 1168 sh, 1127 m, 1113 sh, 1027s, 902s, 846 m, 778 sh, 741 sh, 722 vs (br.), 655 s. − ^{19}F NMR ($CD_3CN/CFCl_3$, 307 K): δ = +12.0 (s, br., SF), −96.0 (s, br., CF).

TAS[(−CF$_2$−SF$_3$)$_2$F] (**9**): 0.80 g of **2** (2.9 mmol) was condensed on to 0.67 g of TASF (2.4 mmol) in 5 ml of CH_3CN in a glass reactor fitted with a Teflon valve at −196°C. After stirring for 15 min at −40°C, approximately 20 ml of diethyl ether was condensed onto the reaction mixture at −80°C. The resulting oily product was then washed several times with diethyl ether. 1.13 g of **9** (quantitative) remained as a colourless solid after removal of the volatile materials under vacuum, mp 96°C. − IR (nujol, cm^{-1}): ν = 1282 m (br.), 1229 s, 1200 sh, 1168 m, 1153 sh, 1112 w, 1062 w, 1027 m, 970 m, 945 m, 901 s (br.), 766 sh, 736 vs, 722 vs, 605 s (br.), 579 s (br.), 482 m. − ^{19}F NMR (CD_3CN, $CFCl_3$, 173 K): δ = 12.5 (quint, SF, $^3J_{\text{CF-SF}}$ = 15.6 Hz), −95.6 (s, br., CF). − $C_8H_{18}F_{11}N_3S_3$ (461.4): calcd. C 20.8, H 3.93, F 45.3; found C 21.3, H 4.1, F 44.0.

(TAS)$_2$(−CF$_2$SF$_4$)$_2$ (**10**): 0.45 g of **2** (1.6 mmol) was stirred with 0.93 g TASF (3.4 mmol) in approximately 5 ml of CH_3CN at −40°C for 15 min in a way similar to the synthesis of **9**. A colourless solid precipitated and was washed twice with CH_3CN at −40°C. 1.09 g of **9** (quantitative) remained after removal of the volatile materials in vacuo, mp. 132°C (decomp.). − IR (nujol, cm^{-1}); ν = 1282 m, 1197 s, 1169 m, 1152 m, 1132 s, 1113 sh, 1065 m, 1032 m, 968 s, 950 s, 899 s, 768 m, 722 vs, 689 m, 676 w, 617 s, 550 vs (br.), 426 m. − $C_{14}H_{36}F_{12}N_6S_4$ (644.7): calcd. C 26.1, H 5.63, F 35.4; found C 26.7, H 6.39, F 33.7.

SF$_5$−CF$_2$−CF$_2$−SF$_5$ (**11**): 2.2 g of **2** (7.9 mmol) and 0.3 g of F_2 (7.9 mmol) were condensed onto 5.3 g of CsF (35 mmol) in a 1-l nickel reactor. The reaction mixture was allowed to warm up to ambient temperature over 12 h and subsequently left to stand for 48 h at this temperature. Fractional condensation (−78 and −196°C) gave 0.30 g of **11** in the −78°C trap, yield 21% (based on F_2).

☆ Dedicated to Professor Dr. *Walter Siebert* on the occasion of his 60th birthday.

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