

Formation and structure of $\overline{\text{S}(\text{O})\text{CF}_2\text{S}(\text{O})\text{O}}$, the most simple perfluoroalkane bis(sulfinic acid) anhydride

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Abstract

Difluoromethane bis(sulfinic acid) $\text{F}_2\text{C}(\text{S}(\text{O})\text{OH})_2$ (**3**) was isolated from the hydrolysis of $\text{F}_2\text{C}(\text{S}(\text{O})\text{F})_2$ (**1**) by moist air. Single crystals of the corresponding anhydride $\overline{\text{S}(\text{O})\text{CF}_2\text{S}(\text{O})\text{O}}$ (**2**) were obtained after $\text{Cs}^+[\text{F}_2\text{C}(\text{SF}_3)_2\text{F}]^-$ (**4**) was stored in a glass vessel for several weeks. The crystal structure of **2** and preliminary results for **3** are reported. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

α,ω -Bis(trifluorosulfur)perfluoroalkanes $\text{F}_3\text{S}(\text{CF}_2)_n\text{SF}_3$ are a very interesting class of compounds because of the high reactivity of the SF_3 -group and because of their bifunctionality. Due to the lack of readily available starting materials, only the first two members ($n = 1$ [1–3], 2 [4]) of this series are known. The methane derivative $\text{F}_2\text{C}(\text{SF}_3)_2$ was first observed in 1953 by Clifford et al. [1] as a byproduct in the electrochemical fluorination of carbon disulfide. Later, it was shown that this compound can be prepared in high purity by direct fluorination of CS_2 in a ‘four zone reactor’ [2]. On a preparative scale it is accessible by a low temperature, low pressure reaction from the same starting materials.

Oxidative additions to the SF_3 -groups [3] and controlled BF_3 -catalysed solvolysis in liquid SO_2 to give $\text{F}_2\text{C}(\text{S}(\text{O})\text{F})_2$ have been described [5]. The chemistry of the sulfinyl halide with nitrogen nucleophiles has been investigated in detail. While in these reactions the expected products (e.g., $\text{F}_2\text{C}(\text{S}(\text{O})\text{NMe}_2)_2$ and $\text{MeNS}(\text{O})\text{CF}_2\text{SO}$) are isolated in good yield, extensive decomposition was found on direct hydrolysis of the bis(sulfinyl fluoride) [5].

In the present paper we report an improved synthesis for difluoromethane bis(sulfinic acid) and the isolation and structure determination of the corresponding anhydride.

2. Results and discussion

On a 1-g scale, yields up to 60% of the acid **3** were obtained when moist air was allowed to expand into an evacuated glass vessel containing **1** at -78°C and kept at this temperature for 3 weeks. In this reaction no detectable amounts of the anhydride **2**, expected as an intermediate, were found.

Single crystals of the anhydride were isolated, after salt **4** [6] was stored in a glass flask for several weeks at 8°C . All attempts to prepare the anhydride on a preparative scale failed whether by dehydration of the acid or by reaction of the sulfinyl fluoride with $\text{Me}_3\text{SiOSiMe}_3$.

2.1. Difluoromethane bis(sulfinic acid) $\text{CF}_2(\text{S}(\text{O})\text{OH})_2$ (**3**)

Acid **3** forms colourless crystals (mp. 81°C (dec)). In the mass spectrum, peaks for the dimeric species were detected suggesting intermolecular interactions. Further evidence for intermolecular interactions were obtained from preliminary X-ray diffraction studies. Crystals formed by sublimation at 30°C were of poor quality and showed high disorder. From our preliminary data, solid-state interactions, as shown by Fig. 1, are suggested.

2.2. Difluoromethane bis(sulfinic acid) anhydride $\overline{\text{F}_2\text{CS}(\text{O})\text{OSO}}$ (**2**)

Anhydride **2** forms colourless crystals which were manipulated under extremely anhydrous conditions at temperatures below 10°C . Due to the low yield, only X-ray investigations

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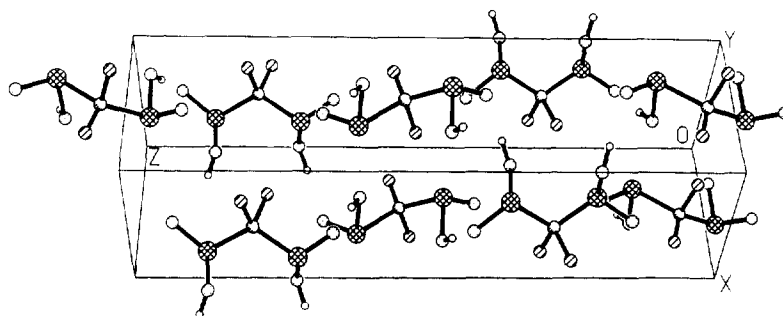
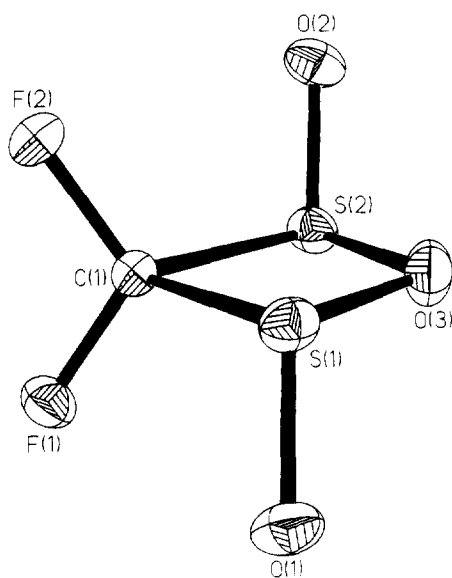
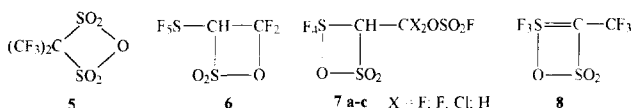
Fig. 1. Suggested structure of $F_2C(S(O)OH)_2$ in the solid state.

Fig. 2. Molecular structure of $F_2CS(O)OSO$ showing thermal ellipsoids at 50% probability (Bond distances [pm] and bond angles [$^\circ$]: $S(1)-O(1)$ 145.9(2), $S(1)-O(3)$ 167.9(2), $S(1)-C(1)$ 189.4(4), $S(2)-O(2)$ 146.2(2), $S(2)-O(3)$ 167.1(3), $S(2)-C(1)$ 189.2(3), $C(1)-F(1)$ 131.4(4), $C(1)-F(2)$ 132.5(3), $O(1)-S(1)-O(3)$ 107.6(1), $O(1)-S(1)-C(1)$ 105.2(2), $O(3)-S(1)-C(1)$ 80.4(1), $O(2)-S(2)-O(3)$ 107.4(1), $O(2)-S(2)-C(1)$ 105.8(1), $O(3)-S(2)-C(1)$ 80.7(1), $S(1)-O(3)-S(2)$ 107.7(1), $S(1)-C(1)-S(2)$ 91.2(1), $S(1)-C(1)-F(1)$ 112.0(2), $S(2)-C(1)-F(1)$ 115.1(2), $S(1)-C(1)-F(2)$ 114.6(2), $S(2)-C(1)-F(2)$ 111.6(2), $F(1)-C(1)-F(2)$ 111.1(2).

were possible. The structure determination shows a planar four-membered 1,2-dioxo-1,2 λ^4 , 4 λ^4 -oxadithietane with the exocyclic oxygen substituents *trans* to each other (Fig. 2). For the related 1,2 λ^4 ,4 λ^4 -azadithietane $CF_2S(O)N(Me)SO$, the structure of the *cis*-derivative is reported, but NMR investigations of the bulk material also showed the presence of the *trans*-isomer [5]. For **2**, a second isomer may also exist.



Numerous four-membered, sulfur-containing heterocycles are described in the literature. Whilst, e.g., dithietanes (C_2S_2 -systems) with sulfur in almost all possible oxidation states and coordination numbers have been isolated [7–11], only a

Table 1

Selected bond angles and bond lengths in $CF_2-S(O)-XS(O)$ [$X = CF_2$ [6], NCH_3 [5], $O(2)$]

	$X = CF_2$	NCH_3	$O(2)$
$\angle SCS$ [$^\circ$]	100.6(2)	94.1(1)	91.2(1)
$\angle CSX$ [$^\circ$]	79.4(2)	78.4(1)	80.7(1)
		78.0(1)	80.4(1)
S–C [pm]	188.0(3)	187.9(2)/187.3(2)	189.4(4)/189.2(3)
S–X [pm]	189.0(4)	169.3(2)/168.0(2)	167.1(3)/167.9(2)

few 1,2,4-oxadithietanes are known, exclusively with sulfur in the (VI) oxidation state. Knunyants and co-workers [12,13] prepared bis(trifluoromethyl)methane bis(sulfonic acid)anhydride **5**, Gard and co-workers [14] **6**, and Seppelt and co-workers [15] reported **6–8** and determined the structures of **7a** and **8**.

In Table 1, selected bond lengths and bond angles of **2** are compared with those for the azadithietane $CF_2S(O)N(Me)SO$ and the dithietane $CF_2-S(O)-CF_2-SO$. In the systems $F_2CS(O)XS(O)$ ($X = F_2C$, NCH_3 , O) the intraannular angle at the sulfur ($78.0(1)^\circ$ – $80.7(1)^\circ$) is rather rigid and almost independent of X , while the SCS-angles range from $91.2(1)^\circ$ (for $X = O$) to $100.6(2)^\circ$ ($X = CF_2$).

In the sulfur(VI) derivatives, **7a** and **8**, the intraannular angles at the tetracoordinated SO_2 -centres ($86.5(1)^\circ$ and $84.8(3)^\circ$ for **7a** and **8**, respectively) are significantly larger than those at the sulfinyl centres of $CF_2-S(O)-X-S(O)$ (Table 1) in agreement with the VSEPR-model. Due to orbital contraction, the intraannular SC- and SO-bonds around the SO_2 group in **7a** are shorter by about 10 and 7 pm, respectively, than those around the sulfinyl centres in the $CF_2S(O)XS(O)$ -systems.

3. Experimental

$CF_2(S(O)F)_2$ (**1**) [5] and $Cs(F_2C(SF_3)_2F)$ [**6**] were prepared according to literature methods.

3.1. Difluoromethane bis(sulfinic acid) **3**

An evacuated glass trap, containing 1.3 g (7.07 mmol) **1** was opened to moist air for a short time at -78°C , then kept for 3 weeks at this temperature. Fractional condensation (-20 , -78 , -196°C) under vacuum gave 0.8 g unreacted **3** (-78°C) and 0.3 g **3** (-20°C) as a colourless solid in the -20°C trap (mp. 81°C (dec.) yield: 61.3% rel. to reacted **1**).

3.2. Difluoromethane bis(sulfinic acid) anhydride **2**

The anhydride is formed in a slow hydrolysis of **4** [6] at 8° in a glass vessel due to the presence of traces of moisture; **2** sublimes to the top of the vessel as transparent crystals.

4. Structure determination of **2**

Suitable single crystals for X-ray crystallography were obtained by sublimation. Transfer of the crystals from the sublimation vessel under cooling and in an inert gas atmosphere are necessary because **2** is sensitive towards hydrolysis. The crystal for the structure determination was selected under a polarisation microscope in cooled Nujol and the measurements were performed at -120°C . Details of the structure analysis are given below and in Fig. 2 with bond lengths and bond angles.

Crystal data: $\text{CF}_2\text{O}_3\text{S}_2$, $M = 162.1$, trigonal, space group $P3_2$; $a = 5.730(2)$, $c = 11.795(6)$, $V = 335.4(3) \text{ \AA}^3$; $Z = 3$, $D_4 = 2.408 \text{ Mg/m}^3$; $\lambda(\text{Mo K}\alpha) = 0.71073 \text{ \AA}$; $\mu = 1.141$

Table 2

The atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> (eq)
S(1)	1357(1)	1646(1)	5000	18(1)
S(2)	5310(1)	3623(1)	3421(1)	18(1)
O(1)	2433(3)	2190(4)	6151(2)	23(1)
O(2)	4233(3)	3095(4)	2267(2)	24(1)
O(3)	3338(5)	4361(3)	4206(2)	24(1)
C(1)	3340(5)	326(4)	4212(3)	16(1)
F(1)	4774(3)	-260(3)	4902(2)	21(1)
F(2)	1887(3)	-1702(3)	3512(2)	21(1)

mm^{-1} . Data were collected to $2\theta_{\text{max}} = 55^{\circ}$ on a Siemens P4 diffractometer. Of 3182 collected data, 1032 were unique ($R_{\text{int}} = 0.0649$). The structure was solved by direct methods and refined anisotropically on F [16]. The final wR was 0.0359 for 1001 observed reflections ($F > 4.0\sigma(F)$) and 72 parameters. Final atomic coordinates are presented in Table 2.

Acknowledgements

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