ELSEVIER

Journal of Fluorine Chemistry 89 (1998) 91–95

JOURNAL OF FLUORINE CHEMISTRY

A new SF_5-containing solid ether–bis(β-pentafluorothio-β-fluorosulfonyl-ethyl)ether

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Received 29 July 1997; accepted 22 October 1997

Dedicated to the memory of Prof. Alan F. Clifford

Abstract

The reaction of pentafluorothio(fluorosulfonyl)ketene with formaldehyde has yielded the novel solid ether $[SF_5CH(SO_2F)CH_2]_2O$, **1**. The crystal structure has been determined: crystal class tetragonal I4; $a=b=11.069(2)$ Å, $c=6.0780(1)$ Å; $\alpha=\beta=\gamma=90°$; $V=744.7(2)$ Å^3; $Z=2$. Hydrogen bonding (C–H···O) is believed responsible for the solid state nature of this material.

Keywords: Bis(pentafluorothio, fluorosulfonyl)ether; X-ray structure

1. Introduction

A number of covalent fluorinated ethers containing the pentafluorothio group are known, e.g., $SF_5CH{=}CHOCH_3$, $SF_5CH_2CH(OCH_3)_2$ [1], $SF_5CHClCH_2OCF_3$, SF_5CFCl-CF_2OCF_3 [2]. It is possible also to include SF_5O compounds in this group although they are not true ethers (with C–O–C structure), e.g., $SF_5OC_6H_5$ [3] and $SF_5OCH_2CCl_2F$, $SF_5OCH_2CH_2F$ [4,5], $(SF_5)_2O$, $(SF_5O)_2SF_4$, CF_3OSF_4-OSF_5 and SF_5OCF_3 [6,7]. Without exception, the true ethers are C_2–β-S-compounds.

In all of the above systems, the parent SF_5-organic ethers are covalent liquids. It was quite unexpected to find that the SF_5 containing ether produced from the reaction of $SF_5(SO_2F)C{=}C{=}O$ and formaldehyde was a solid. In order to understand the solid-state properties of this compound, a crystallographic analysis was undertaken.

2. Results and discussion

When $SF_5(SO_2F)C{=}C{=}O$ and trioxane (as a source of formaldehyde) are heated together for 2 h at 155°C, under anaerobic conditions, a colorless liquid is produced. This material, when stored at −12°C in a glass container for several weeks, produces a white crystalline solid. The latter solid was isolated, recrystallized, and analyzed. Analytical results indicate this material to contain SO_2F and SF_5 (^{19}F NMR spectroscopy) in the ratio 1:1, two types of hydrogen in the ratio 1:2, of which one hydrogen was in a low-field position. Elemental analysis indicated it to have an empirical composition close to the formula $C_2H_3F_6O_{5/2}S_2$. In order to determine the structure of this material, an X-ray structure analysis

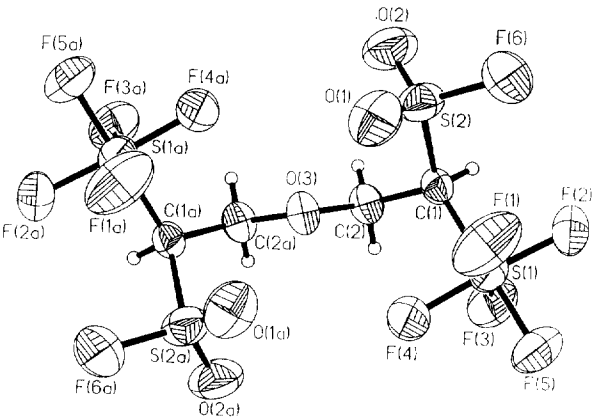

Fig. 1. Thermal ellipsoid view of $[SF_5CH(SO_2F)CH_2]_2O$, **1**.

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0022-1139/98/$19.00
PII S0022-1139(98)00091-8

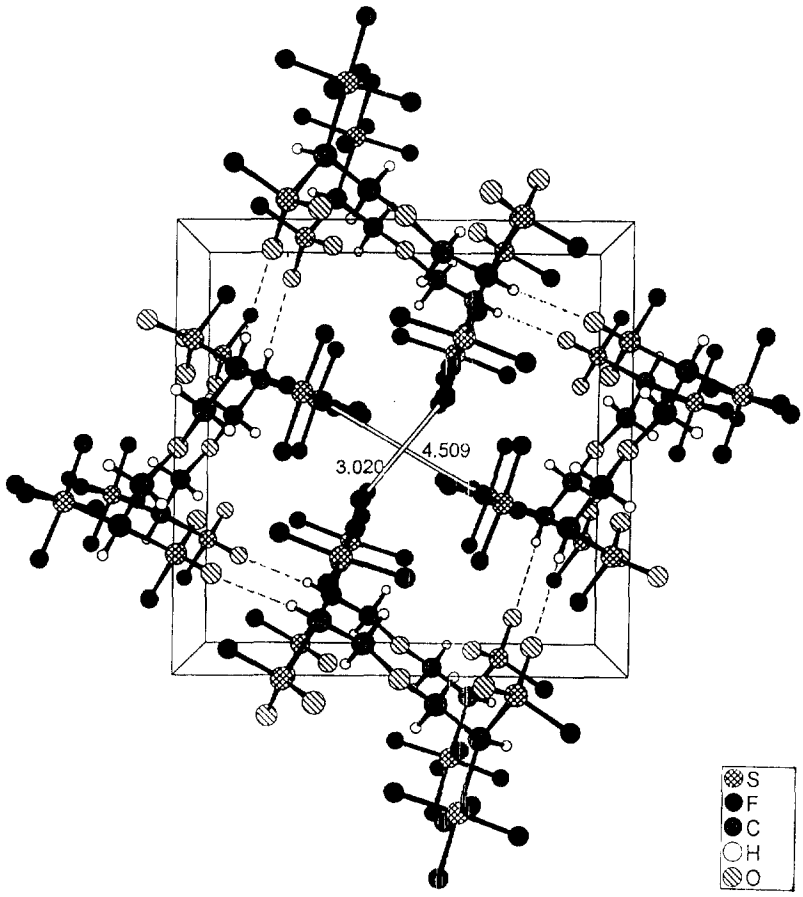

Fig. 2. Unit cell for **1** showing hydrogen bonds (dashed lines) and intermolecular fluorine distances.

Table 1
Crystal data for $[SF_5CH(SO_2F)CH_2]_2O$, **1**

Formula	$C_4H_6F_{12}O_5S_4$
$a=b$	11.069(2) Å
c	6.0780(10) Å
$\alpha=\beta=\gamma$	90°
V	744.7(2) Å^3
Z	2
F.W.	490.33
Space group	$I\bar{4}$
T	293(2) K
λ	0.71069 Å
ρ_{calc}	2.187 Mg m^{-3}
Absorption coefficient	0.794 mm^{-1}
Final R indices	$R1=0.344$, $wR2=0.836$
R indices (all data)	$R1=0.0395$, $wR2=0.0878$

Table 2
Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [Å$^2\times 10^3$] for **1**

	x	y	z	U(eq)
S(1)	3744(1)	2691(1)	2381(3)	58(1)
F(1)	3543(4)	2239(3)	4750(6)	100(1)
C(1)	3253(4)	1276(4)	1045(8)	40(1)
O(1)	3278(4)	−165(3)	4574(6)	74(1)
F(2)	2428(3)	3200(3)	2301(7)	84(1)
C(2)	4186(4)	671(4)	−409(7)	45(1)
S(2)	2542(1)	163(1)	2760(2)	62(1)
O(2)	2164(4)	−753(4)	1353(8)	85(1)
F(3)	3987(3)	3233(3)	10(7)	92(1)
O(3)	5000	0	890(7)	44(1)
F(4)	5088(3)	2269(3)	2456(8)	93(1)
F(5)	4144(3)	3938(3)	3341(8)	102(2)
F(6)	1464(3)	848(3)	3602(8)	101(1)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

was carried out. Fig. 1 shows that the solid is an ether containing β-SF_5 and SO_2F groups. The molecule $[SF_5(SO_2F)CHCH_2]_2O$ has nearly C_2-symmetry (it is slightly distorted) with the C_2-axis lying in the C–O–C plane. The SF_5-groups are thus on opposite sides of the plane (Fig. 2). The arrangement, perhaps due to mutual steric repulsion of the two SF_5-groups, has interesting consequences for the arrangement of the molecules in the lattice. In Table 1, the pertinent crystallographic data are listed while in Table 2, the non-hydrogen atomic coordinates and isotropic thermal parameters are found; selected bond lengths and angles are presented in Table 3.

It is profitable to compare bond lengths and angles with values of related systems. For the following compounds, such quantities were determined previously: $F_5S(SO_2F)CHC$-

Table 3
Bond lengths (Å) and angles (°) for **1**

S(1)–F(1)	1.541(4)	S(1)–F(4)	1.560(3)
S(1)–F(2)	1.562(3)	S(1)–F(5)	1.562(3)
S(1)–F(3)	1.584(4)	S(1)–C(1)	1.847(4)
C(1)–C(2)	1.516(6)	C(1)–S(2)	1.795(4)
O(1)–S(2)	1.418(4)	C(2)–O(3)	1.409(5)
S(2)–O(2)	1.391(4)	S(2)–F(6)	1.504(4)
O(3)–C(2)[a]	1.409(5)		
F(1)–S(1)–F(4)	90.7(3)	F(1)–S(1)–F(2)	90.7(2)
F(4)–S(1)–F(2)	176.3(2)	F(1)–S(1)–F(5)	88.8(2)
F(4)–S(1)–F(5)	89.1(2)	F(2)–S(1)–F(5)	87.6(2)
F(1)–S(1)–F(3)	176.3(2)	F(4)–S(1)–F(3)	88.8(2)
F(2)–S(1)–F(3)	89.6(2)	F(5)–S(1)–F(3)	87.6(2)
F(1)–S(1)–C(1)	95.3(2)	F(4)–S(1)–C(1)	92.2(2)
F(2)–S(1)–C(1)	91.0(2)	F(5)–S(1)–C(1)	175.7(2)
F(3)–S(1)–C(1)	88.4(2)	C(2)–C(1)–S(2)	109.5(3)
C(2)–C(1)–S(1)	115.5(3)	S(2)–C(1)–S(1)	117.1(3)
O(3)–C(2)–C(1)	110.0(4)	O(2)–S(2)–O(1)	117.6(3)
O(2)–S(2)–F(6)	109.8(3)	O(1)–S(2)–F(6)	108.7(3)
O(2)–S(2)–C(1)	105.9(3)	O(1)–S(2)–C(1)	112.0(2)
F(6)–S(2)–C(1)	101.5(2)	C(2)–O(3)–C(2)[a]	111.9(4)

[a] Symmetry transformations used to generate equivalent atoms: $-x+1, -y, z$.

$(O)N(C_2H_5)_2$ (**2**) [8]; $(F_5SCH_2CHO)_3$ (= a trioxane) (**3**) [9]; $F_5S(SO_2F)CC(O)OCH_3 \cdot NHR_3$ (**4**)[2]; FO_2SCH-FCOOH (**5**) [11]. Some pertinent values are listed below [pm].

	2	3	4	5	Ether 1
$S(1)O_2F$					
S–O(1)	139.6	–	142.0	138.1	141.8
S–O(2)	140.2	–	139.9	139.3	139.1
S–F	152.2	–	157.2	149.3	150.4
$S(O_2F)$–C_1	180.1	–	167.8	178.9	179.5
$S(2)F_5$					
S–F(average)	154.8	156.8	158.3	–	156.2
$S(F_5)$–C_1	185.6	178.9	177.3	–	184.7
C(1)–C(2)	154.4	151.0	144.0	152.2	151.6

The S–O(1) and S–O(2) bond length of compound **1** are similar to those reported for other FSO_2 systems (compounds **2**, **5**) in which significant intermolecular hydrogen bonding between the oxygens of FSO_2 groups and the methine hydrogen occurs (see Fig. 2 showing intermolecular hydrogen bonding). The presence of highly electronegative SF_5 and SO_2F groups attached to the β-carbon brings about, through induction, increased acidity of the methine hydrogen. The increased charge on the methine hydrogen is responsible for intermolecular hydrogen bonding. The C–H···O distance in the ether is 3.278 Å. This distance is long compared to normal interactions involving O–H and N–H groups (2.3–2.8 Å) but is comparable to the value of 3.2 Å reported for $(HCN)_n$ [12] and to the values found for $SF_5\overline{CHCF_2OSO_2}$ (3.177 Å and 3.230 Å) [13]. There is little doubt that the hydrogen-bonded intermolecular network is responsible for the solid state nature of $[SF_5CH(SO_2F)CH_2]_2O$. It should be noted that the bond distance between the hydrogen on one molecule and the oxygen of another molecule is slightly shorter (233.4 pm) than the sum of the van der Waals radii of oxygen and hydrogen [14]. Robinson has drawn attention to the generality of hydrogen bonding in sulfonyl systems that lead to higher boiling points or melting points [15].

TINTF

The SF_5–C and FSO_2–C bond lengths are in agreement with other covalent molecules containing SF_5 and FSO_2 groups; for the anion **4** these values are significantly smaller. The smaller values for **4** can be explained using an ionic model where increased coulombic interactions due to higher charge density at C_1 favor shorter F_5S–C, FSO_2–C, and C_1–C_2 distances [10]. The sum of the angles at the carbon bearing the sulfur substituents in **2**, **4** and the ether **1**, $<S_1$–C_1–$C_2 + <S_1$–C_1–$S_2 + <S_2$–C_1–C_2, are, respectively, 334.6°, 359.1° and 342.1°. This shows that the amide **2** is more strongly pyramidalized than the ether **1**. On the other hand, the value for the anion of **4** (359.1°) shows that its anion is almost flat while **2** is almost tetrahedral (where the sum would be 328.4°). The arrangement in ether **1** represents an intermediate situation between the neutral amide **2** and the anion in **4**. This may be explained by the cryptoacidic nature of the hydrogen at C_1 which would increase the charge density at C_1. Agreement is found with the ^1H NMR spectrum which places this proton in a rather deshielded position. The rest of the molecule is similar to the values found for diethyl ether [16], e.g., <C–O–C are 111.65° and 112.02° (there are two ether molecules of slightly different structure in an asymmetric unit), while <C–O–C = 111.9(4)° for **1**. Compound **5**, which also is a solid, shows that the atomic arrangement of the fluorosulfonyl unit is largely uninfluenced by other substituents at C_α. This compound is also strongly pyramidalized (sum of the angles of the three substituents, excluding H, at C_α is 330.4°).

In Fig. 2, it is interesting to note that the SF_5 groups are pointing inward thereby creating tunnels, the walls of which are composed of SF_5 groups. The larger tunnels have a distance of 302 pm between the axial fluorine atoms of two opposite SF_5 groups. This distance, minus twice the van der Waals radius of fluorine give an approximate upper limit width of 22 pm. Therefore, these tunnels are too small to absorb other molecules.

The infrared spectrum of the ether **1** has the characteristic absorption band for the SF_5 and SO_2F groups. Cross et al. [17] have reported that compounds containing the SF_5 grouping have strong absorptions in the region 850–920 cm^{-1} (S–F stretching modes) and in the region of 600 cm^{-1} (one of the S–F deformation modes). For ether **1**, the absorption in the 857–877 cm^{-1} is assigned to the S–F stretching modes; the 600 cm^{-1} band to the S–F deformation mode.

[2] This paper mislabelled a fluorine and oxygen. Some important revised values are: S(2)–O(4), 142.0(3) pm; S(2)–F(6), 157.2(2) pm; C(1)–S(2)–O(4), 112.0(2)°; C(1)–S(2)–F(6), 104.5(2)°; O(3)–S(2)–O(4), 118.5(2)°; O(3)–S(2)–F(6), 103.7(2)°. Also, several additional corrected values are: C(2)–O(2), 133.7(4) pm; C(1)–C(2)–O(1), 124.4(3)°; O(1)–C(2)–O(2), 120.3(3)° [10].

Compounds containing $-SO_2F$ functional group exhibit a strong asymmetric ($-SO_2-$) band in the 1400–1470 cm^{-1} region and a strong ($-SO_2-$) symmetric stretching band in the 1200–1300 cm^{-1} range; the strong S–F absorption band of the SO_2F group is usually located near 790 cm^{-1} [18,19]. For the ether **1**, the absorption bands at 1431 cm^{-1} and in the 1202–1222 cm^{-1} region are, respectively, assigned to the SO_2 asymmetric and symmetric vibrations; the S–F stretch is found at 803 cm^{-1}. The C–H absorption bands are found near 3000 cm^{-1}.

The ^{19}F NMR spectrum (AB_4X) shows that the SF_5 fluorine resonances consist of a AB_4 multiplet with B_4 equatorial fluorines split into a doublet (band center at 68.3 ppm) and the A part into a nine-line pattern (line 6 at 76.5 ppm); coupling constant values are $J_{AB}=146.6$ Hz and $J_{BX}=11.7$ Hz. The ^1H NMR spectrum consists of an ABX pattern with $\delta_A=4.45$ ppm and $\delta_B=4.51$ ppm. The methine proton (SF_5CH) is found at 5.98 ppm. This value, as expected, is intermediate between the proton resonances observed $SF_5CH(SO_2F)C(O)F$ (6.18 ppm) and $SF_5CH_2SO_2F$ (5.33 ppm) [20].

While some preliminary work has been done on the liquid that was first isolated (possibly an SF_5 olefin) we have not been able to determine exactly how it is formed or how it is converted into the solid ether **1**. It should be pointed out that $(CF_3)_2C{=}C{=}O$ gives a β-lactone when reacted with formaldehyde [21]. We would expect similar behavior with the SF_5 ketene; however, we did not isolate a β-lactone derivative. Additional work is planned in order to resolve this unusual reaction scheme.

3. Experimental details

3.1. Materials

The ketene was prepared by literature method [21]. Trioxane was obtained from American Tokyo Kasei and used as received.

3.2. General methods

Volatile materials were manipulated in a conventional Pyrex glass vacuum line, equipped with a Heise Bourdon tube gauge and a Televac thermocouple unit. IR spectra were obtained with a Nicolet 20 DX spectrometer. NMR spectra were recorded on a Bruker AMX-400 (400 MHz, H; 375 MHz, F) instrument; CCl_3F and $Si(CH_3)_4$ were used as external standards and by convention, resonances appearing downfield from CCl_3F are assigned positive values while upfield resonances are assigned negative values. A gas chromatography–mass spectrometer (Hewlett Packard HP 5970) with DB 5 (25 m) column was used; temperature program was 50°C for 5 min then 10°C min^{-1} to 280°C. Elemental analysis was performed by Mikroanalytisches Laboratorium, Göttingen, Germany.

The stable $[SF_5CH(SO_2F)CH_2]_2O$ solid formed colorless needles; the size of the crystal used in this study was $0.5\times0.2\times0.2$ mm. The data collection was carried out on a Siemens-Stoe AED 2 diffractometer employing MoK_α radiation ($\lambda=0.710\,69$ Å) and a graphite monochromator. The number of reflections collected was 2164 with 970 independent reflection ($R_{int}=2.24\%$). The structure solution was obtained by direct methods. The goodness of fit was 1.56 and the final difference map showed a residual of 0.47 electrons $Å^{-3}$. The SHELXTL Plus (PC version) program led to resolution of all atomic positions.

3.3. Isolation of $[SF_5CH(SO_2F)CH_2]_2O$

In a 50-ml Carius tube, 0.66 g of $F_5S(SO_2F)C{=}C{=}O$, 2.64 mmol, and 0.08 g of trioxane, 0.89 mmol, were heated in vacuo at 155°C for 2 h. The mixture had darkened and 0.60 g of a colorless liquid was vacuum-transferred; a dark residue was left behind. The volatile material contained three constituents (by gas chromatography on a SE-30 column, 45/60, of 3 m length at 95°C); the major constituent ($R_t=15$ min) was collected via preparative gas chromatography with the above column, yielding 0.25 g of product as a colorless, mobile, volatile liquid of a peculiar odor. This liquid, upon standing in a Pyrex glass tube at −12°C is partially converted (~2 weeks) to a solid.

^1H NMR spectrum (400 MHz, $CDCl_3$, $Si(CH_3)_4$): ABX: $\delta_A=4.45$ ppm, doublet of multiplet, probably a doublet of a quintet, $J_{AB}=12.9$ Hz, $\delta_B=4.51$ ppm, doublet (each line has shoulders), area A + B = 2.00 (CH^AH^B), $\delta_X=5.98$ ppm, multiplet, area = 0.85 (F_5SCH).

^{19}F NMR spectrum: (375 MHz, $CDCl_3$, internal CCl_3F); AB_4X: $\phi_A=76.5$ ppm, nine lines (area = 1.00), $\phi_B=68.3$ ppm, skewed doublet, area = 3.95; $\phi_X=62.3$ ppm, ill-resolved pentet (some lines have shoulders), area = 1.05, $J_{AB}=146.6$ Hz, $J_{BX}\approx11.7$ Hz.

Infrared spectrum (neat sample, KBr, cm^{-1}): 2972, m; 2909, vw; 1431, vs; 1377, m; 1257, m; 1237, m, sh; 1222, s; 1202, m–s; 1143, s; 1080, m; 1060, m; 1045, m; 988, m; 940, vw; 877, s–vs, sh; 857, vs; 803, s; 743, m–s; 726, m–s; 706, m; 677, m–s; 649, m; 634, m–s; 620, m–s; 600, m; 580, s–vs; 554, s; 534, s; 483, s.

Anal. calc. for $C_2H_3F_6O_{5/2}S_2$: C, 9.80; H, 1.23; F, 46.5; S, 26.15%. Found: C, 9.99; H, 1.24; F, 45.7%.

4. Supplementary material available

Lists of structure factors, anisotropic thermal parameters and hydrogen atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication. Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acknowledgements

We thank Dr. Enno Lork of the Institut für Anorganische und Physikalische Chemie, Bremen, Germany for his kind help.

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