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Bis(perfluoroalkanesulfonyl)methylene dimethyloxosulfonium ylids $(R_FSO_2)_2\overset{-}{C}-\overset{+}{S}(O)Me_2$: formation and X-ray structure of $Me_2(O)\overset{+}{S}-\overset{-}{C}\overline{SO_2(CF_2)_3SO_2}$

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Abstract

Air oxidation of bis(perfluoroalkanesulfonyl)methylene dimethylsulfonium ylids obtained from the photoreactions of phenyliodonium bis(perfluoroalkanesulfonyl)methides with dimethyl sulfide afforded the title compounds. The X-ray structure of $Me_2(O)\overset{+}{S}-\overset{-}{C}\overline{SO_2(CF_2)_3SO_2}$ is presented.

Introduction

Sulfoxonium ylids are generally prepared by capture of the corresponding carbene intermediates with DMSO, for example see ref. 1, bis(phenylsulfonyl)methylene dimethyloxosulfonium ylid was obtained by heating or photolysis of $(PhSO_2)_2C-Y^+$ in DMSO [2, 3]:

$$Y-C(PhSO_2)_2+Me_2SO \xrightarrow[-Y]{h\nu \text{ or } \Delta} Me_2(O)S-C(SO_2Ph)_2$$

$(Y=PhI \text{ or } N_2)$

However, attempts to prepare the fluorine-containing analogues using the same reaction failed. Photolysis or thermolysis of phenyliodonium bis(perfluoroalkanesulfonyl)methides in DMSO gave only the 1:1 adducts [4]:

$$\underset{(1)}{Ph\overset{+}{I}-\overset{-}{C}(SO_2R_F)_2}+DMSO \xrightarrow{h\nu \text{ or } \Delta} \underset{(2)}{DMSO\cdot[PhI-C(SO_2R_F)_2]}$$

When compounds **1** were decomposed in dimethyl sulfide, the sulfonium ylids $Me_2\overset{+}{S}-C(SO_2R_F)_2$ formed in high yield [5]:

$$1+Me_2S \xrightarrow{h\nu} \underset{(3)}{Me_2\overset{+}{S}-\overset{-}{C}(SO_2R_F)_2}+PhI$$

Results and discussion

It was interesting to find that, after storage for two months in a flask at room temperature, the ylids **3** were completely oxidized to the sulfoxonium ylids, thus:

$$3 \xrightarrow{\text{air, r.t.}} \underset{(4)}{Me_2(O)\overset{+}{S}-\overset{-}{C}Y^1Y^2}$$

[$Y^1=Y^2=CF_3SO_2$ (**4a**); $Y^1=Y^2=C_4F_9SO_2$ (**4b**); $Y^1,Y^2=-SO_2(CF_2)_3SO_2-$ (**4c**)]

Their structures have been characterized by NMR, IR and mass spectrometry, and by microanalysis. An X-ray diffraction analysis of **4c** has shown that the crystal contains two independent molecules in one asymmetric unit (see Fig. 1). The bond distances between the C(11) atom and the S(10), S(12), S(16) are 1.75 Å, 1.67 Å and 1.69 Å, respectively. All are shorter than the normal C–S single bond (1.86 Å), [6] but the C(11)–S(12) and C(11)–S(16) bonds have the most multiple bond character. This shows that, even if the S atom of the DMSO is positively charged, electron delocalization of the carbanion C(11) is shifted significantly towards the perfluoroalkanesulfonyl group because of its stronger electron-withdrawing ability [7] (see Scheme 1).

The chemistry of compounds **4** is under investigation.

Experimental

Melting points were measured on a Thiele apparatus and are uncorrected. ^1H and ^{19}F NMR spectra were

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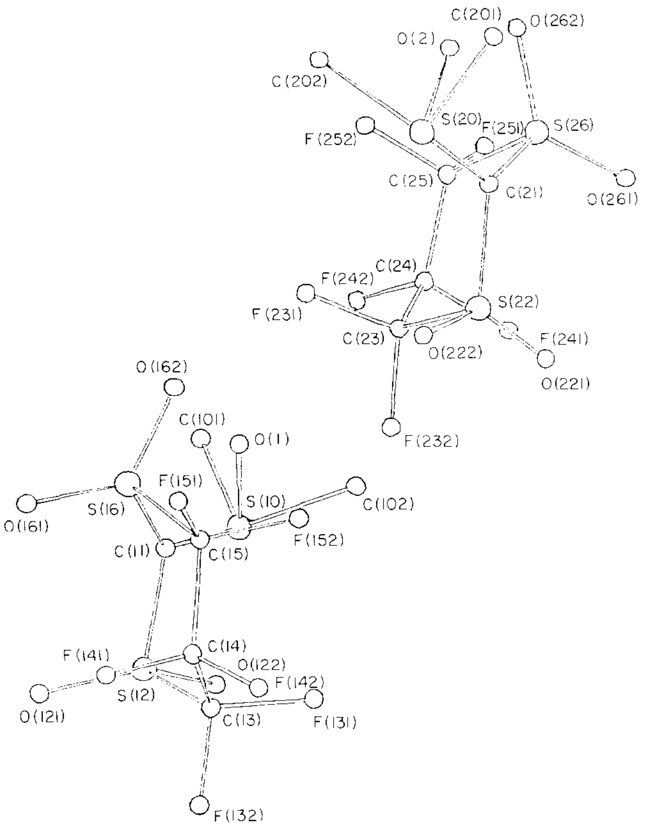
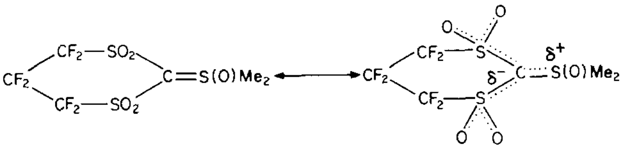


Fig. 1. The structure of compound **4c** with the appropriate atom-numbering system.



Scheme 1.

recorded on a Varian 360L instrument with Me_4Si and TFA as internal and external standards, respectively ($\delta_{TFA} = \delta_{F11} + 76.8$ ppm positive upfield). IR spectra were obtained on an IR-440 Shimadzu spectrophotometer. Low resolution mass spectra were taken on a Finnigan GC–MS 4021 instrument. Elemental analyses were performed by the Analysis Department of this Institute. The preparation of compounds **3** has been reported previously [5].

Oxidation of compounds 3

Compound **3a** (1.8 g, 5.3 mmol) was stored in a 5 ml bottle for 2 months under air, when it was found that **3a** had been oxidized completely to **4a**.

Compounds **3b** and **3c** were similarly transformed to **4b** and **4c**.

Compound **4a**: M.p. 146 °C. IR (KBr) (ν_{max}) (cm^{-1}): 3010 (m); 2900 (m); 2810 (w); 1401 (m); 1360 (s); 1350

TABLE 1. Bond lengths (Å) for compound **4c**

C(101)−S(10)	1.82(3)	C(102)−S(10)	1.79(3)
C(11)−S(10)	1.75(2)	O(1)−S(10)	1.46(2)
S(12)−C(11)	1.67(2)	S(16)−C(11)	1.69(2)
O(121)−S(12)	1.40(2)	O(122)−S(12)	1.48(2)
C(13)−S(12)	1.86(2)	F(131)−C(13)	1.28(3)
F(132)−C(13)	1.34(3)	C(14)−C(13)	1.49(3)
F(141)−C(14)	1.37(3)	F(142)−C(14)	1.32(2)
C(15)−C(14)	1.47(3)	F(151)−C(15)	1.35(3)
F(152)−C(15)	1.36(3)	S(16)−C(15)	1.82(2)
O(161)−S(16)	1.41(2)	O(162)−S(16)	1.48(5)
C(201)−S(20)	1.79(3)	C(202)−S(20)	1.61(4)
C(21)−S(20)	1.79(2)	O(2)−S(20)	1.35(1)
S(22)−C(21)	1.66(2)	S(26)−C(21)	1.67(2)
O(221)−S(22)	1.44(2)	O(222)−S(22)	1.49(2)
C(23)−S(22)	1.79(3)	F(231)−C(23)	1.29(2)
F(232)−C(23)	1.38(3)	C(24)−C(23)	1.55(5)
F(241)−C(24)	1.26(3)	F(242)−C(24)	1.34(3)
C(25)−C(24)	1.45(4)	F(251)−C(25)	1.42(4)
F(252)−C(25)	1.35(3)	S(26)−C(25)	1.84(2)
O(261)−S(26)	1.48(2)	O(262)−S(26)	1.59(3)

TABLE 2. Bond angles (°) for compound **4c**

C(102)−S(10)−C(101)	99(1)	C(11)−S(10)−C(101)	108.3(9)
C(11)−S(10)−C(102)	110(1)	O(1)−S(10)−C(101)	63(1)
O(1)−S(10)−C(102)	61(1)	O(1)−S(10)−C(11)	76(1)
S(12)−C(11)−S(10)	131(1)	S(16)−C(11)−S(10)	109.3(9)
S(16)−C(11)−S(12)	118.3(9)	O(121)−S(12)−C(11)	112(1)
O(122)−S(12)−C(11)	103(1)	O(122)−S(12)−O(121)	129(1)
C(13)−S(12)−C(11)	99.9(9)	C(13)−S(12)−O(121)	104.4(9)
C(13)−S(12)−O(122)	105(1)	F(131)−C(13)−S(12)	109(1)
F(132)−C(13)−S(12)	106(1)	F(132)−C(13)−F(131)	106(2)
C(14)−C(13)−S(12)	117(2)	C(14)−C(13)−F(131)	110(2)
C(14)−C(13)−F(132)	109(2)	F(141)−C(14)−C(13)	108(2)
F(142)−C(14)−C(13)	110(2)	F(142)−C(14)−F(141)	104(1)
C(15)−C(14)−C(13)	116(2)	C(15)−C(14)−F(141)	106(2)
C(15)−C(14)−F(142)	113(2)	F(151)−C(15)−C(14)	104(2)
F(152)−C(15)−C(14)	109(2)	F(152)−C(15)−F(151)	108(2)
S(16)−C(15)−C(14)	120(2)	S(16)−C(15)−F(151)	109(2)
S(16)−C(15)−F(152)	107(2)	C(15)−S(16)−C(11)	100(1)
O(161)−S(16)−C(11)	109(1)	O(161)−S(16)−C(15)	107(1)
O(162)−S(16)−C(11)	121(2)	O(162)−S(16)−C(15)	100(2)
O(162)−S(16)−O(161)	118(2)	C(202)−S(20)−C(201)	106(2)
C(21)−S(20)−C(201)	104(1)	C(21)−S(20)−C(202)	115(2)
O(2)−S(20)−C(201)	63(1)	O(2)−S(20)−C(202)	73(1)
O(2)−S(20)−C(21)	71.5(8)	S(22)−C(21)−S(20)	137(1)
S(26)−C(21)−S(20)	103.6(9)	S(26)−C(21)−S(22)	119(1)
O(221)−S(22)−C(21)	113.6(9)	O(222)−S(22)−C(21)	99(1)
O(222)−S(22)−O(221)	128(1)	C(23)−S(22)−C(21)	102(1)
C(23)−S(22)−O(221)	103(1)	C(23)−S(22)−O(222)	108(1)
F(231)−C(23)−S(22)	111(2)	F(232)−C(23)−S(22)	109(2)
F(232)−C(23)−F(231)	106(2)	C(24)−C(23)−S(22)	115(2)
C(24)−C(23)−F(231)	110(2)	C(24)−C(23)−F(232)	106(2)
F(241)−C(24)−C(23)	108(2)	F(242)−C(24)−C(23)	110(2)
F(242)−C(24)−F(241)	109(2)	C(25)−C(24)−C(23)	116(2)
C(25)−C(24)−F(241)	108(2)	C(25)−C(24)−F(242)	107(2)
F(251)−C(25)−C(24)	110(2)	F(252)−C(25)−C(24)	113(3)
F(252)−C(25)−F(251)	102(2)	S(26)−C(25)−C(24)	119(2)
S(26)−C(25)−F(251)	105(2)	S(26)−C(25)−F(252)	107(1)
C(25)−S(26)−C(21)	99.3(9)	O(261)−S(26)−C(21)	112(1)
O(261)−S(26)−C(25)	102(1)	O(262)−S(26)−C(21)	92(1)
O(262)−S(26)−C(25)	108(2)	O(262)−S(26)−O(261)	138(1)

TABLE 3. Positional and thermal parameters for compound **4c** with estimated standard deviations[a]

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
S(10)	0.8671(6)	0.5319(4)	0.8044(7)	0.089(4)
C(101)	0.738(2)	0.574(1)	0.824(3)	0.08(2)
C(102)	0.970(2)	0.645(2)	0.859(3)	0.08(2)
C(11)	0.843(1)	0.495(1)	0.580(2)	0.045(7)
S(12)	0.8005(4)	0.5519(3)	0.3924(8)	0.064(3)
O(121)	0.855(1)	0.529(1)	0.266(2)	0.08(1)
*O(122)	0.792(1)	0.649(1)	0.458(2)	0.08(1)
*O(122′)	0.778(5)	0.643(4)	0.317(9)	0.02(4)
C(13)	0.647(2)	0.485(2)	0.303(3)	0.07(1)
F(131)	0.586(1)	0.5114(9)	0.397(2)	0.10(1)
F(132)	0.605(1)	0.517(1)	0.140(2)	0.13(1)
C(14)	0.628(2)	0.376(1)	0.290(3)	0.06(1)
F(141)	0.673(1)	0.350(1)	0.158(2)	0.12(1)
F(142)	0.515(1)	0.3386(9)	0.227(2)	0.094(9)
C(15)	0.6866(2)	0.329(1)	0.450(3)	0.08(2)
F(151)	0.623(1)	0.340(1)	0.565(2)	0.12(1)
F(152)	0.671(1)	0.2323(9)	0.410(2)	0.14(1)
S(16)	0.8410(5)	0.3737(4)	0.5633(9)	0.071(4)
O(161)	0.864(2)	0.338(1)	0.736(2)	0.15(2)
*O(162)	0.882(3)	0.342(3)	0.461(6)	0.10(3)
*O(162′)	0.912(4)	0.360(3)	0.417(7)	0.03(2)
O(1)	0.838(2)	0.617(1)	0.708(3)	0.17(2)
S(20)	0.1336(7)	0.0758(5)	−0.2940(9)	0.121(6)
C(201)	0.271(3)	0.146(2)	−0.300(4)	0.08(2)
C(202)	0.041(3)	0.148(2)	−0.352(4)	0.08(2)
C(21)	0.161(1)	0.042(1)	−0.066(2)	0.05(1)
S(22)	0.2090(4)	0.0988(3)	0.1363(8)	0.069(3)
O(221)	0.148(1)	0.056(1)	0.259(2)	0.09(1)
*O(222)	0.226(2)	0.202(1)	0.085(3)	0.07(2)
*O(222′)	0.233(3)	0.200(3)	0.211(4)	0.06(2)
C(23)	0.351(2)	0.068(2)	0.221(3)	0.09(2)
F(221)	0.402(1)	0.103(1)	0.384(2)	0.12(1)
F(232)	0.4210(9)	0.1126(8)	0.122(2)	0.092(9)
C(24)	0.352(2)	−0.043(2)	0.208(3)	0.09(2)
F(241)	0.304(1)	−0.084(1)	0.318(2)	0.14(1)
F(242)	0.463(1)	−0.056(1)	0.252(2)	0.12(1)
C(25)	0.293(2)	−0.093(2)	0.033(4)	0.10(2)
F(251)	0.359(1)	−0.061(1)	−0.088(2)	0.103(9)
F(252)	0.294(1)	−0.190(1)	0.032(3)	0.17(2)
S(26)	0.1427(5)	−0.0794(4)	−0.0840(3)	0.079(4)
O(262)	0.078(1)	−0.127(1)	0.036(2)	0.10(2)
*O(262)	0.129(3)	−0.050(2)	−0.293(3)	0.11(2)
*O(262′)	0.109(4)	−0.144(2)	−0.248(3)	0.05(2)
O(2)	0.1770(9)	0.1377(7)	−0.135(1)	0.042(3)

Occupancy of disordered atoms
O(122): 0.36 O(122′): 0.14 O(162): 0.66 O(162′): 0.34
O(222): 0.66 O(222′): 0.34 O(262): 0.64 O(262′): 0.36

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a2B(1,1)+b2B(2,2)+c2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$.

(s); 1230–1170 (vs); 1120 (s); 1020 (s); 992 (s); 955 (s); 690 (m); 650 (s); 610 (s); 570 (m); 507 (m). ^{1}H NMR (acetone-d_6) δ 3.33 (s, 2×CH_3) ppm. ^{19}F NMR δ: 3.5 (s, 2×CF_3) ppm. MS (*m*/*e*): 356 (M^+, 0.51); 355 (M^+-1, 4.91); 341 (M^+-CH_3, 47.61); 308 (M^+-SO, 6.64); 287 (M^+-CF_3, 0.38); 272 ($M^+-CF_3-CH_3$, 100); 255 (M^+-CF_3S, 13.61); 239 (M^+-CF_3SO, 1.82); 75 ($^+C{=}S(O)CH_3$ and $M^+-2CF_3SO_2-CH_3$, 1.99); 69 (CF_3^+, 5.15); 62 (Me_2S^+, 29.69); 47 (CH_3S^+, 1.59). Analysis: Calc. for $C_5H_6F_6O_5S_3$: C, 16.85; H, 1.68; F, 32.02%. Found: C, 17.28; H, 1.51; F, 32.78%.

Compound **4b**: M.p. 162 °C. IR (KBr) (ν_{max}) (cm^{-1}): 3008 (m); 2910 (m); 2814 (m); 1408 (m); 1365 (s); 1350 (s); 1330 (m); 1205–1110 (vs); 1018 (s); 990 (m); 952 (m); 648 (s); 610 (s); 560 (m). ^{1}H NMR δ: 3.33 (s, 2×CH_3) ppm. ^{19}F NMR δ: 6.0 (s, 2×CF_3); 34.0 (m, 2×CF_2S); 45.3 (m, 2×CF_3); 50.6 (m, 2×CF_2) ppm. MS (*m*/*e*): 657 (M^+H, 1.33); 656 (M^+, 1.96); 421 ($M^+-O-C_4F_9$, 100); 341 ($M^+-2O-C_4F_9SO_2$, 1.88); 219 ($C_4F_9^+$, 15.86); 122 (Me_2SCSO^+, 8.221); 69 (CF_3^+, 18.84); 63 ($MeSO^+$, 7.28); 62 (Me_2S^+, 83.20); 47 (MeS^+, 5.66). Analysis: Calc. for $C_{11}H_6F_{18}O_5S_3$: C, 20.12; H, 0.91; F, 52.13%. Found: C, 19.98; H, 0.87; F, 52.49%.

Compound **4c**: M.p. 188 °C. IR (KBr) (ν_{max}) (cm^{-1}): 3008 (m); 2892 (m); 2820 (w); 1420 (m); 1368 (s); 1350 (m); 1330 (m); 1205 (m); 1180 (s); 1150 (s); 1012 (m); 970 (m); 950 (s); 700 (m); 642 (m); 612 (m); 540 (m). ^{1}H NMR δ: 3.30 (s, 2×CH_3) ppm. ^{19}F NMR δ: 43.0 (m, 2×CF_2S); 50.0 (m, CF_2) ppm. MS (*m*/*e*): 369 (M^++1, 1.43); 367 (M^+-1, 2.49); 353 (M^+-CH_3, 36.63); 352 (M^+-O, 28.75); 288 (M^+-O-SO_2, 7.48); 273 ($M^+-O-2SO_2-CH_3$, 22.60); 260 ($M^+-C_2F_4$, 10.97); 209 ($M^+-O-2SO_2-CH_3$, 25.05); 159 ($M^+-O-2SO_2-CH_3-CF_2$, 6.23); 124 ($M^+-O-2SO_2-C_2F_4$, 32.76); 109 ($M^+-O-2SO_2-CH_3-C_2F_4$, 18.76); 79 ($CH_3SO_2^+$, 10.74); 78 (Me_2SO^+, 1.77); 63 (CH_3SO^+, 20.42); 62 (Me_2S^+, 100). Analysis: Calc. for $C_6H_6F_6O_5S_3$: C, 19.57; H, 1.63; F, 30.98%. Found: C, 19.69; H, 1.51; F, 30.63%.

Crystal data

Compound **4c**: $C_6H_6F_6O_5S_3$, M = 368.3, triclinic, space group $P\bar{1}$, $a = 12.162(2)$, $b = 14.952(2)$, $c = 7.803(1)$ Å, $\alpha = 90.24(1)°$, $\beta = 106.67(1)°$, $\gamma = 100.82(1)$, $V = 1243.4(3)$ Å^3, $Z = 4$; $D_c = 1.90$ g cm^{-3}, $F(000) = 736.0$, $\lambda = 1.5418$ Å, μ (CuKα) = 61.60 mm^{-1}; crystal dimension 0.2×0.05×0.05 mm. Intensity data were collected at 20 °C with a Rigaku AFC-5R diffractometer using CuKα radiation and employing the $w/2\theta$ scanning technique. Cell parameters determined from 24 reflections with $14° \leqslant 2\theta \leqslant 36°$ and 1635 unique reflections ($R_{int} = 0.105$) measured with $2\theta_{max} = 114°$, $0 \leqslant h \leqslant 13$, $-15 \leqslant k \leqslant 15$, $-8 \leqslant l \leqslant 8$. Two standard reflections were monitored after every 120 reflections, but no significant variation in their intensities was found. The structure was determined by direct methods indicating that one asymmetric unit contained two molecules. All non-H atoms were positioned and anisotropic thermal parameters refined from 1474 observed reflections with $F > 4\sigma(F)$ by a block-matrix least-squares technique to $R = 0.096$ and $Rw = 0.062$. All calculations were performed on a MICRO II computer with SHELXS 76 and SHELXS 86 programs. Atomic scattering factors were taken from

International Tables for X-ray Crystallography (1974, Vol. IV).

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