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The polysulfonylamines bis(methylsulfonamido) sulfone and bis(trifluoromethylsulfonamido) sulfone

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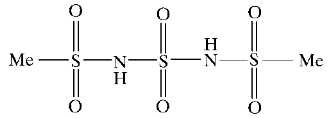
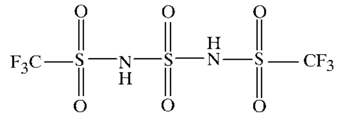
Bis(methylsulfonamido) sulfone, $C_2H_8N_2O_6S_3$ or $SO_2(NHSO_2CH_3)_2$, was synthesized from imidobis(sulfonyl chloride), $HN(SO_2Cl)_2$, and bis(trimethylsilyl)methane, $CH_2[Si(CH_3)_3]_2$, in chlorotrimethylsilane solution. In the solid state, there are two independent molecules linked by two N—H···O hydrogen bridges into infinite chains parallel to the *b* axis. The central S atoms of the independent molecules each lie on a twofold axis. Bis(trifluoromethylsulfonamido) sulfone, $C_2H_2F_6N_2O_6S_3$ or $SO_2(NHSO_2CF_3)_2$, was formed by the reaction of trichlorophosphazosulfuryl trifluoromethane, $Cl_3PNSO_2CF_3$, with fluorosulfonic acid, FSO_3H. The molecules are connected by bifurcated N—H···O bridges into infinite layers parallel to the [001] plane. The central S atom lies on a twofold axis.

Comment

Crystals of the previously unknown compounds bis(methylsulfonamido) sulfone, (I) and bis(trifluoromethylsulfonamido) sulfone, (II), have been formed adventitiously *via* unspecified protolysis and condensation processes. Compound (I) was formed by the reaction of $HN(SO_2Cl)_2$ with $CH_2[Si(CH_3)_3]_2$; similar unspecified protolysis and condensation processes are described by Hiemisch *et al.* (1997) for the reaction of Ph_3GeCl and $AgN(SO_2F)_2$ leading to $SO_2(NHSO_2Ph)_2$. Compound (II) was isolated as a major product from a reaction mixture of $Cl_3PNSO_2CF_3$ and FSO_3H. However, Roesky & Giere (1971) report $HN(SO_2CF_3)_2$ as the only product of this reaction. Although several related substances, derivatives of diimidotris(sulfuric) acid, $SO_2[N(Y)–SO_2–X]_2$ (where *X* is NH_2, Ph or F, and *Y* is H or CH_3), have been described in the literature (Meuwsen & Papenfuss, 1962; Nannelli *et al.*, 1965; Roesky & Hoff, 1968), no analogous structure other than $SO_2(NHSO_2Ph)_2$ could be located in the Cambridge Structural Database (Version 5.24; Allen, 2002). Related structures are those of the parent compound sulfamide, $SO_2(NH_2)_2$ (Belaj *et al.*, 1987), and $SO_2(NHSO_2Ph)_2$ (Hiemisch *et al.*, 1997).


$$\mathrm{Me{-}S(=O)_2{-}NH{-}S(=O)_2{-}NH{-}S(=O)_2{-}Me}$$
(I)


$$\mathrm{F_3C{-}S(=O)_2{-}NH{-}S(=O)_2{-}NH{-}S(=O)_2{-}CF_3}$$
(II)

The bond lengths and angles of (I) and (II) (Tables 1 and 3) are in good agreement with the corresponding parameters of $SO_2(NH_2)_2$ and $SO_2(NHSO_2Ph)_2$. For both symmetry-independent molecules of (I), the S—N, S—O and S—C distances

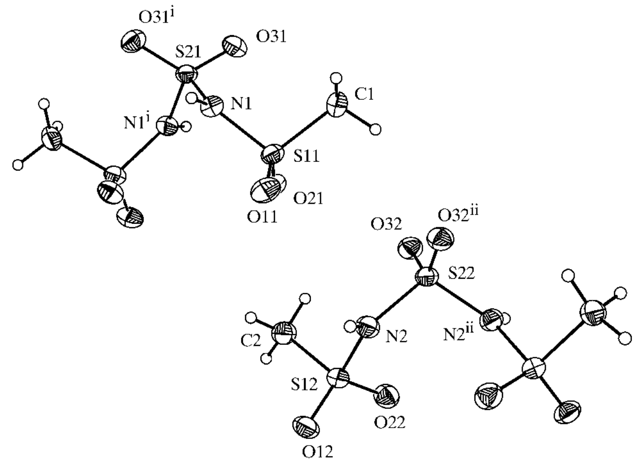


Figure 1
One of the two independent molecules of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry codes are as in Table 1.

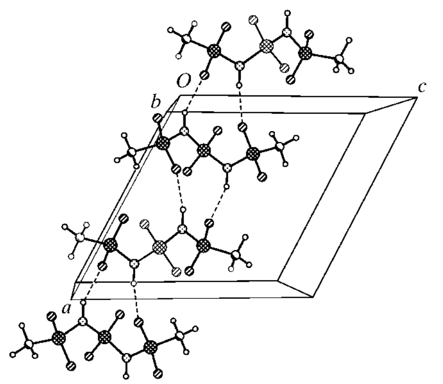


Figure 2
Perspective view of the hydrogen-bonded chain of (I). Hydrogen bonds are indicated by dashed lines.

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are in the ranges 1.638 (3)–1.669 (3), 1.421 (3)–1.437 (3) and 1.742 (4)–1.743 (4) Å, respectively, while the S—N—S angles range from 123.2 (2) to 125.7 (2)°. The S atoms exist in the tetrahedral configuration (Table 1). For both independent molecules of (II), the S—N, S—O and S—C distances are 1.630 (2)–1.639 (2), 1.4080 (19)–1.4092 (18) and 1.823 (3) Å, respectively, while the S—N—S angle is 126.1 (1)°.

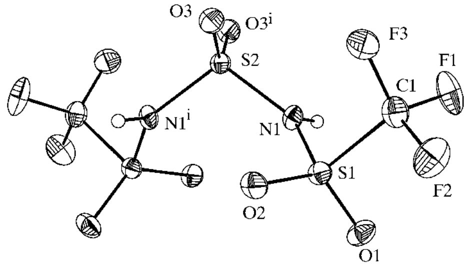

Figure 3
View of the molecule of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Symmetry codes as in Table 3.

The asymmetric unit of (I) consists of two independent $SO_2(NHSO_2CH_3)_2$ molecules, denoted *A* and *B*, with point symmetry C_2. Molecule *A* is depicted in Fig. 1. In the crystal packing (Fig. 2), molecules *A* and *B* are joined alternately by double N—H···O hydrogen bonds into $[ABAB]_\infty$ strands extending in the *b* direction (Fig. 2). Details of the two independent N—H···O bonds are shown in Table 2.

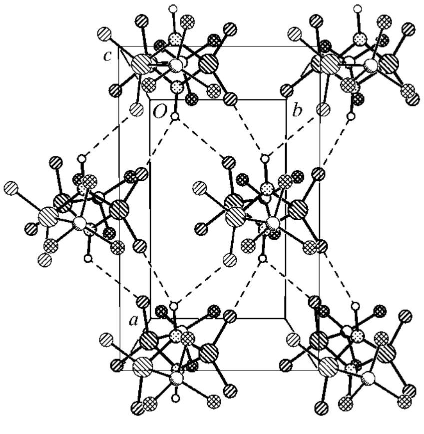

Figure 4
Perspective view of the hydrogen-bonded chain of (II). Hydrogen bonds are indicated by dashed lines.

The point-group symmetry of compound (II) is C_2. The S atom of the central SO_2 group (Fig. 3) is located on the C_2 axis. The molecules are bonded by two bifurcated N—H···O bridges into infinite layers parallel to the [001] plane (Fig. 4). Details of the two independent N—H···O bonds are given in Table 4. All O atoms are involved in hydrogen bonds to N—H groups of neighbouring molecules.

Experimental

The synthesis of (I) was performed by the reaction of $HN(SO_2Cl)_2$ with an equimolar amount of $CH_2[Si(CH_3)_3]_2$. Thus, $HN(SO_2Cl)_2$ (0.8 g, 3.7 mmol) was dissolved in $(CH_3)_3SiCl$ (1 ml) and added to $CH_2[Si(CH_3)_3]_2$ (0.6 g, 3.7 mmol). The vessel was closed, heated to 353 K in an oil bath for 3–4 h and then left to cool to room temperature. White transparent needle-shaped crystals of (I) were formed on cooling (yield: 0.44 g, 1.72 mmol, 69.7%). The best-looking crystal was selected from the mother liquor and immediately subjected to data collection at 150 K. The synthesis of (II) was performed by the reaction of $Cl_3PNSO_2CF_3$ with an equimolar amount of FSO_3H. Thus, $Cl_3PNSO_2CF_3$ (2.8 g, 9.85 mmol) was dissolved in CCl_4 (5 ml) and added to FSO_3H (0.98 g, 0.98 mmol). The vessel was closed, heated to 473 K in an oil bath for 2 h and then left to cool to room temperature. White transparent needle-shaped crystals of (II) were formed on cooling (yield: 0.79 g, 2.20 mmol, 44.4%). The best-looking crystal was selected from the mother liquor and immediately subjected to data collection at 120 K.

Compound (I)

Crystal data

$C_2H_8N_2O_6S_3$
$M_r = 252.28$
Monoclinic, $P2/n$
$a = 10.107$ (2) Å
$b = 9.715$ (2) Å
$c = 10.620$ (2) Å
$\beta = 118.01$ (3)°
$V = 920.6$ (3) Å^3
$Z = 4$
$D_x = 1.820$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1867 reflections
$\theta = 3.3$–15.2°
$\mu = 0.81$ mm^{-1}
$T = 153$ (2) K
Prism, white
0.30 × 0.15 × 0.15 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
ω scans
5552 measured reflections
1599 independent reflections
1337 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.047$
$\theta_{\rm max} = 25°$
$h = -12 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.148$
$S = 1.15$
1599 reflections
121 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0784P)^2 + 1.2973P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.56$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.61$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

S11—O21	1.434 (3)	S12—O12	1.436 (2)
S11—N1	1.652 (3)	S12—N2	1.666 (3)
S11—C1	1.742 (4)	S22—N2	1.640 (3)
S21—N1	1.644 (3)	S22—N2^{ii}	1.640 (3)
S21—N1^{i}	1.644 (3)		
N1—S11—C1	104.09 (16)	N2—S12—C2	103.86 (15)
N1—S21—N1^{i}	109.0 (2)	N2—S22—N2^{ii}	107.9 (2)
S21—N1—S11	125.64 (18)	S22—N2—S12	123.21 (18)

Symmetry codes: (i) $\frac{3}{2} - x, y, -\frac{1}{2} - z$; (ii) $\frac{3}{2} - x, y, \frac{1}{2} - z$.

Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O12^{i}	0.88	2.00	2.790 (4)	149
N2—H2$\cdots$O21^{ii}	0.88	2.02	2.834 (4)	154

Symmetry codes: (i) $2 - x, -y, -z$; (ii) $\frac{1}{2} + x, -y, \frac{1}{2} + z$.

Compound (II)

Crystal data

$C_2H_2F_6N_2O_6S_3$
$M_r = 360.24$
Monoclinic, $C2/c$
$a = 9.007$ (2) Å
$b = 5.5370$ (10) Å
$c = 20.776$ (4) Å
$\beta = 94.97$ (3)°
$V = 1032.2$ (4) Å^3
$Z = 4$

$D_x = 2.318$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1166 reflections
$\theta = 2.8$–22.8°
$\mu = 0.84$ mm^{-1}
$T = 120$ (2) K
Prism, white
0.25 × 0.13 × 0.02 mm

Data collection

Kuma KM-4 CCD area-detector diffractometer
ω scans
Absorption correction: ψ scans (*SHELXTL*; Bruker, 1997)
$T_{\min} = 0.672$, $T_{\max} = 1.000$
3536 measured reflections

1183 independent reflections
1046 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.062$
$\theta_{\max} = 28.4$°
$h = -11 \rightarrow 7$
$k = -6 \rightarrow 7$
$l = -27 \rightarrow 27$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.096$
$S = 1.09$
1183 reflections
87 parameters
H atoms: see below

$w = 1/[\sigma^2(F_o^2) + (0.0410P)^2 + 2.8145P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.43$ e Å^{-3}
$\Delta\rho_{\min} = -0.48$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (II).

S1—O2	1.4085 (18)	N1—S2	1.639 (2)
S1—O1	1.4091 (19)	S2—O3^{i}	1.4093 (18)
S1—N1	1.630 (2)	S2—O3	1.4093 (17)
S1—C1	1.831 (3)	S2—N1^{i}	1.639 (2)
N1—S1—C1	102.77 (12)	O3^{i}—S2—O3	123.24 (17)
S1—N1—S2	126.13 (12)	N1—S2—N1^{i}	106.00 (15)

Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N1—H1$\cdots$O3^{i}	0.92	2.11	2.963 (3)	154
N1—H1$\cdots$O2^{ii}	0.92	2.39	2.989 (3)	123

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} + y, z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$.

H atoms of the CH_3 groups in (I) were positioned by geometry and treated as riding. H atoms of the NH groups of both (I) and (II) were located in a difference Fourier map and refined freely (N—H = 0.88–0.92 Å).

For both compounds, data collection: *CrysAlis* (Oxford Diffraction, 2002); cell refinement: *KM*-4 *Software* (Kuma, 1995); data reduction: *KM*-4 *Software*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1137). Services for accessing these data are described at the back of the journal.

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