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Polysulfonylamines. LXXXV. N-Chloro-dimesylamine†

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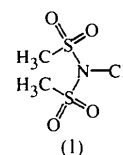
Abstract

In the molecule of the title compound, $C_2H_6ClNO_4S_2$, the N atom has a slightly pyramidal geometry characterized by the angles Cl—N—S 115.71 (7), 114.34 (6) and S—N—S 120.24 (6)°, and the distances S—N 1.7260 (11), 1.6992 (12) and Cl—N 1.7138 (11) Å. The crystal is stabilized by five intermolecular C—H···O

† Part LXXXIV: Linoh *et al.* (1997).

hydrogen bonds and an intermolecular Cl···O interaction of 2.797 (1) Å, the latter linking the molecules to form infinite chains.

Comment

Although a number of N-fluorodisulfonylamines, *i.e.* $(RSO_2)_2N$—F, have emerged in recent years as electrophilic fluorinating agents (Lal, Pez & Syvret, 1996, and references therein), a search of the Cambridge Structural Database (Allen & Kennard, 1993) located no structural information for such a compound or any other N-halogenodisulfonylamine, $(RSO_2)_2N$—X (X = Cl, Br, I). As part of a wider study of N-substituted dimesylamines, we report here the first structure of a representative N-chlorodisulfonylamine, (1).

(1)

The molecule of the title compound shows no crystallographic symmetry (Fig. 1). The N atom lies 0.312 (1) Å out of the plane defined by S1, S2 and Cl, whereas the related molecule $(MeSO_2)_2N$—Me, (2), is essentially planar at the N atom (Blaschette, Näveke & Jones, 1991). In both structures, the S—N—S angle is *ca* 120°, and the slight pyramidality of (1) arises from the relatively small Cl—N—S angles, 115.71 (7) and 114.34 (6)°, as compared with the C—N—S angles of 119.9 (1) and 119.4 (1)° in (2). An interesting trend of increasing pyramidality is seen in the series (1), $MeSO_2$-NCl_2 (Minkwitz, Garzarek, Neikes, Kornath & Preut, 1997) and NCl_3 (Hartl, Schöner, Jander & Schulz, 1975), the angles at the N atom amounting to 108.61 (13)–110.87 (9)° for the dichloro compound (X-ray diffraction at 173 K) and to 105.1 (9)–108.5 (9)° for nitrogen trichloride (X-ray diffraction at 148 K).
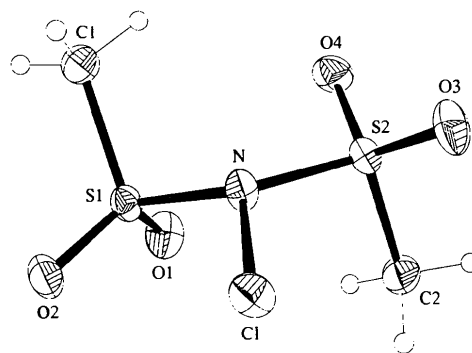

Fig. 1. The molecule of the title compound, (1), in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

The N—Cl bond length in (1), 1.7138 (11) Å, is slightly shorter than the standard value, 1.728 Å, predicted by the modified Schomaker–Stevenson rule (Blom & Haaland, 1985), and significantly shorter than the N—Cl bonds in the N-chloro compounds mentioned above [$MeSO_2$-NCl_2: 1.746 (2) Å; NCl_3: mean 1.75 (1) Å]. As the N—Cl bond lengthening in the two pseudo-tetrahedral molecules may arise from steric hindrance, it seems more appropriate to compare (1) with the structures of N-chlorodiacylamines, $(RCO)_2N$—Cl, expected to have a planar C_2NCl geometry. Surprisingly, only two crystal structures from this class of compounds are known, viz. N-chlorosuccinimide (Brown, 1961) and N-chlorophthalimide (Ghassemzadeh, Harms, Dehnicke & Magull, 1994), both displaying an approximately planar C_2NCl group and comparatively short N—Cl distances of 1.69 (2) and 1.676 (2) Å, respectively.

The crystal structure of (1) is stabilized by intermolecular Cl$\cdots$O1 interactions and a three-dimensional network of C—H$\cdots$O hydrogen bonds (Desiraju, 1996) built up by five out of six methyl protons and the three O atoms not involved in the Cl$\cdots$O interaction (see Table 2). The Cl$\cdots$O1 distance (operator for O1: $\frac{1}{2} + x$, $\frac{3}{2} - y$, $-\frac{1}{2} + z$) is 2.797 (1) Å, much shorter than the Cl$\cdots$O van der Waals sum of 3.27 Å (Bondi, 1964). These interactions link the molecules to form chains parallel to the diagonal $(a-c)$ (Fig. 2). The intermolecular angles are N—Cl$\cdots$O1 175.61 (5) and Cl$\cdots$O1—S1 125.55 (6)°, close to the ideal geometry of 180 and 120° for an electrostatic interaction N—Cl(δ+)$\cdots$(δ−)O=S. Similar chain-forming halogen-oxygen bonds have been reported for the structures of N-chlorosuccinimide and N-chlorophthalimide, both with significantly longer Cl$\cdots$O distances of 2.88 and 2.946 Å, respectively, and for the structures of the homologues N-bromosuccinimide (Jabay, Pritzkow & Jander, 1977) and N-iodosuccinimide (Padmanabhan, Paul & Curtin, 1990). It may be surmised that the shorter N—Cl bonds in the N-chlorodiacylamines correlate with the weaker Cl$\cdots$O interactions.
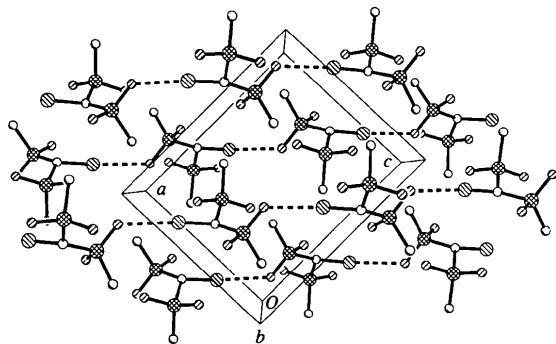
There are several conspicuous dissimilarities between chemically equivalent geometric parameters of molecule (1). They are most probably associated with a conformational adaptation of the molecule to the requirements of the intermolecular Cl$\cdots$O attraction. Thus, as quantified by the O—S—N—S torsion angles [28.64 (10), 43.14 (9), 157.69 (8) and 169.79 (8)° for, in order, the O atoms O1, O4, O2 and O3], the $N(SO_2Me)_2$ group is far from C_2 symmetry. The close cisoid approach of O1 to the plane defined by the NS_2 subunit leads to a short intramolecular Cl$\cdots$O2 distance [2.868 (1) Å; torsion angle Cl—N—S1—O2 13.59 (9)°] causing distortions such as Cl—N—S1 > Cl—N—S2, N—S1—Cl < N—S2—C2 and S1—N > S2—N (see Table 1). Similar discrepancies are not observed in the N-methyl analogue (2), where the $N(SO_2Me)_2$ moiety approximates to ideal C_2 symmetry [O—S—N—S torsion angles 35.9 (1), 35.7 (1), 164.0 (1) and 164.3 (1), N—S—C 105.7 (1) and 105.0 (1)°, and S—N 1.663 (2) and 1.670 (2) Å].

Experimental

Crystal data

$C_2H_6ClNO_4S_2$	Mo $K\alpha$ radiation
$M_r = 207.65$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 61
$P2_1/n$	reflections
$a = 7.8306 (8)$ Å	$\theta = 5.0$–$12.5°$
$b = 10.0242 (8)$ Å	$\mu = 1.025$ mm^{-1}
$c = 9.5404 (12)$ Å	$T = 173 (2)$ K
$\beta = 92.282 (10)°$	Irregular tablet
$V = 748.28 (14)$ Å^3	$0.55 \times 0.40 \times 0.35$ mm
$Z = 4$	Colourless
$D_x = 1.843$ Mg m^{-3}	
D_m not measured	

Data collection

Siemens $P4$ diffractometer	$R_{int} = 0.013$
ω scans	$\theta_{max} = 27.48°$
Absorption correction:	$h = -10 \rightarrow 10$
ψ scans (XEMP; Siemens,	$k = -13 \rightarrow 10$
1994a)	$l = -12 \rightarrow 12$
$T_{min} = 0.612$, $T_{max} = 0.699$	3 standard reflections
4280 measured reflections	every 297 reflections
1709 independent reflections	intensity decay: none
1615 reflections with	
$I > 2\sigma(I)$	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} = -0.001$
$R[F^2 > 2\sigma(F^2)] = 0.021$	$\Delta\rho_{max} = 0.446$ e Å^{-3}
$wR(F^2) = 0.056$	$\Delta\rho_{min} = -0.287$ e Å^{-3}

Fig. 2. Packing diagram viewed parallel to the y axis. H atoms have been omitted. Dashed contacts are Cl$\cdots$O (see text). Radii are arbitrary.

$S = 1.070$
1709 reflections
94 parameters
H-atom parameters
    constrained
$w = 1/[\sigma^2(F_o^2) + (0.0303P)^2 + 0.3539P]$
    where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction:
SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.033 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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Table 1. *Selected geometric parameters (Å, °)*

S1—O2	1.4249 (11)	S2—O4	1.4272 (10)
S1—O1	1.4272 (11)	S2—N	1.6992 (12)
S1—N	1.7260 (11)	S2—C2	1.7505 (15)
S1—C1	1.7531 (15)	C1—N	1.7138 (11)
S2—O3	1.4251 (11)		
O2—S1—O1	119.52 (7)	O4—S2—N	103.43 (6)
O2—S1—N	105.16 (6)	O3—S2—C2	110.27 (7)
O1—S1—N	108.61 (6)	O4—S2—C2	110.42 (7)
O2—S1—C1	110.71 (7)	N—S2—C2	106.04 (7)
O1—S1—C1	109.76 (7)	S2—N—C1	114.34 (6)
N—S1—C1	101.40 (7)	S2—N—S1	120.24 (6)
O3—S2—O4	119.72 (7)	C1—N—S1	115.71 (7)
O3—S2—N	105.77 (6)		
O3—S2—N—C1	−45.65 (9)	O2—S1—N—S2	157.69 (8)
O4—S2—N—C1	−17230 (7)	O1—S1—N—S2	28.64 (10)
C2—S2—N—C1	71.47 (9)	C1—S1—N—S2	−86.94 (9)
O3—S2—N—S1	169.79 (8)	O2—S1—N—C1	13.59 (9)
O4—S2—N—S1	43.14 (9)	O1—S1—N—C1	−11546 (8)
C2—S2—N—S1	−73.09 (9)	C1—S1—N—C1	128.96 (8)

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

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O4[i]	0.98	2.45	3.208 (2)	134
C1—H1B···O2[ii]	0.98	2.69	3.628 (2)	161
C1—H1C···O3[iii]	0.98	2.39	3.316 (2)	157
C2—H2A···O2[iv]	0.98	2.69	3.374 (2)	127
C2—H2B···O4[v]	0.98	2.58	3.417 (2)	144

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

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93*. Molecular graphics: *XP* (Siemens, 1994b). Software used to prepare material for publication: *SHELXL93*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1321). Services for accessing these data are described at the back of the journal.

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2,13-Dithia[3]metacyclo[3](2,3)naphthaleno-phane and 2,13-Dithia[3]metacyclo[3](1,7)-naphthalenophane†

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Abstract

The title compounds are isomeric, $C_{20}H_{18}S_2$. The (2,3) isomer has an *anti* conformation, parallel ring systems and approximate mirror symmetry. The (1,7) isomer has

† Alternative names: 3,16-dithiatetracyclo[16.3.1.0⁵,¹⁴.0⁷,¹²]docos-ane-1(22),5,7(12),8,10,13,18,20-octaene and 3,11-dithiatetracyclo[11.-6.2.1⁵,⁹.0¹⁷,²¹]docosane-1(20),5(22),6,8,13,15,17(21),18-octaene.