N1	0.4944 (2)	0.18132 (6)	0.6035 (2)	0.0499 (4)
N2	0.3223 (2)	−0.02538 (6)	1.1032 (2)	0.0385 (4)
C1	0.3158 (2)	0.07010 (7)	0.8805 (2)	0.0464 (5)
C2	0.2458 (3)	0.11444 (8)	0.8448 (3)	0.0672 (7)
C3	0.4467 (2)	0.16351 (7)	0.7116 (2)	0.0443 (5)
C4†	0.4336 (6)	0.1863 (3)	0.4670 (6)	0.040 (2)
C5†	0.396 (1)	0.1430 (3)	0.394 (1)	0.041 (2)
C6†	0.352 (1)	0.1561 (3)	0.2498 (9)	0.055 (2)
C7†	0.2176 (9)	0.1857 (3)	0.2458 (8)	0.062 (2)
C8†	0.257 (1)	0.2285 (4)	0.3232 (9)	0.050 (2)
C9†	0.2993 (6)	0.2162 (2)	0.4684 (5)	0.042 (1)
C4′†	0.3820 (7)	0.1833 (3)	0.4831 (6)	0.045 (2)
C5′†	0.420 (1)	0.1498 (4)	0.380 (1)	0.059 (4)
C6′†	0.305 (1)	0.1457 (3)	0.264 (1)	0.080 (3)
C7′†	0.261 (1)	0.1901 (3)	0.2049 (8)	0.069 (2)
C8′†	0.222 (1)	0.2236 (4)	0.307 (1)	0.066 (4)
C9′†	0.337 (1)	0.2277 (2)	0.4228 (8)	0.082 (2)
C10†	0.6554 (6)	0.1945 (2)	0.6253 (7)	0.042 (2)
C11†	0.7446 (9)	0.1799 (3)	0.5105 (7)	0.061 (2)
C12†	0.904 (1)	0.1942 (4)	0.555 (2)	0.089 (5)
C13†	0.9047 (9)	0.2450 (4)	0.5420 (7)	0.071 (3)
C14†	0.817 (1)	0.2607 (4)	0.654 (1)	0.070 (3)
C15†	0.657 (1)	0.2455 (3)	0.623 (2)	0.060 (4)
C10′†	0.6293 (7)	0.2037 (2)	0.5866 (9)	0.059 (2)
C11′†	0.7447 (8)	0.1702 (3)	0.5723 (9)	0.075 (3)
C12′†	0.885 (1)	0.1910 (4)	0.532 (2)	0.080 (4)
C13′†	0.926 (1)	0.2338 (4)	0.599 (1)	0.106 (4)
C14′†	0.807 (2)	0.2674 (4)	0.611 (1)	0.088 (5)
C15′†	0.663 (1)	0.2484 (3)	0.645 (2)	0.064 (4)
C16	0.2513 (2)	−0.01666 (6)	1.2271 (2)	0.0407 (5)
C17	0.3392 (3)	0.01768 (8)	1.3071 (2)	0.0585 (6)
C18	0.2706 (3)	0.02832 (9)	1.4344 (2)	0.0720 (7)
C19	0.2476 (3)	−0.01305 (9)	1.5130 (2)	0.0739 (8)
C20	0.1617 (3)	−0.04737 (9)	1.4305 (2)	0.0680 (7)
C21	0.2335 (3)	−0.05847 (7)	1.3066 (2)	0.0532 (6)
C22	0.2592 (2)	−0.06181 (6)	1.0154 (2)	0.0386 (4)
C23	0.3407 (2)	−0.06333 (8)	0.8933 (2)	0.0496 (5)
C24	0.2819 (3)	−0.10060 (9)	0.8023 (2)	0.0609 (6)
C25	0.1196 (3)	−0.09669 (9)	0.7688 (2)	0.0664 (7)
C26	0.0394 (2)	−0.09350 (9)	0.8915 (2)	0.0626 (7)
C27	0.0976 (2)	−0.05567 (8)	0.9792 (2)	0.0486 (5)

† Site occupancy = 0.50.

Table 2. *Selected geometric parameters (Å, °)*

S1—C2	1.789 (2)	N1—C10	1.538 (6)
S1—C3	1.770 (2)	N1—C4′	1.539 (6)
S2—C3	1.667 (2)	N1—C10′	1.442 (6)
O1—C1	1.252 (3)	N2—C16	1.501 (2)
O2—C1	1.240 (3)	N2—C22	1.501 (3)
N1—C3	1.338 (3)	N2—O1	2.706 (2)
N1—C4	1.464 (6)	N2—O2$^{\rm i}$	2.757 (2)
C2—S1—C3	104.7 (1)	S2—C3—S1	120.1 (1)
C3—N1—C4	134.5 (3)	N1—C4—C5	115.5 (6)
C3—N1—C10	111.8 (3)	N1—C4—C9	107.0 (4)
C3—N1—C4′	115.2 (3)	C9′—C4′—N1	120.0 (6)
C3—N1—C10′	129.8 (4)	C5′—C4′—N1	110.1 (6)
C16—N2—C22	117.1 (2)	C15—C10—N1	105.6 (6)
C4—N1—C10	113.2 (4)	C11—C10—N1	113.0 (6)
C4′—N1—C10′	114.4 (4)	C11′—C10′—N1	109.4 (6)
O1—C1—O2	126.5 (2)	C15′—C10′—N1	121.7 (7)
O2—C1—C2	120.6 (2)	C17—C16—N2	108.8 (2)
O1—C1—C2	112.9 (2)	C21—C16—N2	112.6 (2)
C1—C2—S1	117.5 (2)	C23—C22—N2	108.6 (2)
N1—C3—S2	124.8 (2)	C27—C22—N2	112.2 (2)
N1—C3—S1	115.1 (2)		

Symmetry code: (i) $1 - x, -y, 2 - z$.

The two cyclohexyl rings bonded to the thiocarbamoyl N atom are both disordered over two positions and were refined with site occupancies of 0.5, subject to constraints in bond distances (1,2-related C atoms 1.54±0.01, 1,3-related C atoms 2.52±0.02 and N—C 1.45±0.01 Å).

Data collection: *CAD*-4 *VAX*/*PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX*/*PC*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*/*PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXL*93.

The author thanks the University of Malaya (F102/96 and F677/96) for supporting this work.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: KH1126). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 781–783

Polysulfonylamines. LXXXII. Oxalyl Chloride Dimesylamide†

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(*Received 5 December 1996; accepted 3 February 1997*)

Abstract

The molecule of the previously unknown title compound, *N*,*N*-dimesyloxamoyl chloride, $C_4H_6ClNO_6S_2$, is characterized by a long C_{sp^2}—N_{sp^2} bond [1.408 (2) Å]

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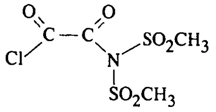
† Part LXXXI: Wirth, Henschel, Blaschette & Jones (1997).

Acta Crystallographica Section C
ISSN 0108-2701 © 1997

and a skew conformation of the oxalyl subunit [torsion angle O—C—C—O 130.7 (2)°]. The molecules are linked *via* C—H···O hydrogen bonds.

Comment

We are interested in the molecular structures and the reactivities of covalent compounds containing an $(RSO_2)_2N—E$ moiety, where *E* is, for example, C, Si, P, As, S (Jones, Hamann, Schaper, Lange & Blaschette, 1995, and references cited therein). As a part of this work, the previously unknown title compound, (I), was prepared by treatment of silver dimesylamide with oxalyl chloride (Dalluhn, 1995) and subjected to X-ray crystal structure determination.



(I)

The most striking feature of the molecule (Fig. 1) is the long amide bond C3—N1, 1.408 (2) Å, compared with the average $C_{sp^2}—N_{sp^2}$ distances of 1.325, 1.334 and 1.346 Å for acyclic amides $RC(O)—NH_2$, $RC(O)—NHR$ and $RC(O)—NR_2$, respectively (Allen *et al.*, 1987), or especially with the C(O)—N bonds, *ca* 1.34 Å, in *N*-organyl-substituted oxamides (see, for example, Yamaguchi, Matsumura, Haga & Shudo, 1992). Dimesylaminocarbonyl groups displaying C—N bonds lengthened to 1.40–1.45 Å have also been observed in a series of molecules related to (I), *viz.* $X—C(O)—N(SO_2CH_3)_2$, where *X* = Cl or OCN (Dalluhn, Pröhl, Blaschette, Lange & Jones, 1994), $CCl_3—C(O)—N(SO_2CH_3)_2$ (Blaschette, Dalluhn, Fischer & Jones, 1994) and $RO—C(O)—N(SO_2CH_3)_2$, where *R* = CH_3 or CCl_3 (Dalluhn, Pröhl, Henschel, Blaschette & Jones, 1996).

The coordination at the N atom of (I) is slightly non-planar; it lies 0.130 (1) Å out of the plane of its substituents. Within the $N(SO_2CH_3)_2$ subunit, the bond lengths and angles do not differ appreciably from the corresponding geometric parameters in similar molecules (see above). The distances C3—C4 1.535 (2), C4—Cl 1.734 (2) Å and the angle C3—C4—Cl 111.66 (12)° are in close agreement with the values found in a gas-phase electron-diffraction study of oxalyl chloride at 273 K [1.534 (5), 1.744 (2) Å and 111.7 (2)°; Hagen & Hedberg, 1973]. In (I), the C—O distances and O—C—C angles differ by 0.015 Å and 3.7°, respectively, the longer bond and smaller angle pertaining to the dimesylaminocarbonyl group. The deviations of the carbonyl C atoms from the least-squares planes of their substituents are 0.048 (2) Å for C3 and 0.050 (2) Å for C4. The planes defined by N1, S1, S2 and C3, O5, C4 subtend an angle of 34.3 (1)°.

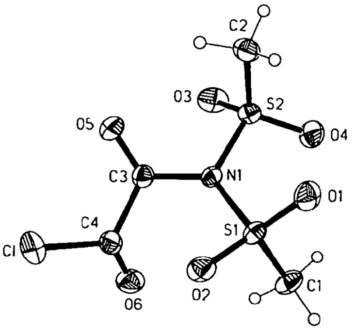


Fig. 1. The molecule of the title compound in the crystal. Displacement ellipsoids are drawn at the 50% probability level. H-atom radii are arbitrary.

The oxalyl group adopts an unusual skew conformation quantified by the torsion angle O5—C3—C4—O6 130.7 (2)° and possibly induced by non-bonded intramolecular interactions [O3···O5 2.832 (2) and O2···O6 2.947 (2) Å]. For comparison, the electron-diffraction pattern obtained from gaseous oxalyl chloride at 273 K revealed it to consist of a mixture of *trans* and *gauche* conformers (68% *trans*; *gauche* torsion angle O—C—C—O *ca* 55°; Hagen & Hedberg, 1973), whereas in crystalline oxalyl chloride at low (unspecified) temperature the molecule has a crystallographically centrosymmetric *trans* conformation (Groth & Hassel, 1962).

The crystal packing displays four intermolecular C—H···O sequences that appear to match the accepted geometric criteria for hydrogen bonds (Desiraju, 1996). They originate from one H atom bound to C1 and the three H atoms of the C2 methyl group and involve the O atoms O1, O4 (twice) and O5. The H···O distances lie in the range 2.56–2.65 Å and the angles at hydrogen in the range 123–150° (see Table 2).

Experimental

The hydrolytically labile title compound was obtained in 76% yield by treating a stirred suspension of $[AgN(SO_2CH_3)_2]$ (11.2 g, 40.0 mmol) in dry dichloromethane (150 ml) with oxalyl chloride (2.54 g, 20.0 mmol) for 6 h at reflux temperature, then 16 h at ambient temperature. The second substitution step, resulting in the formation of oxalyl bis(dimesylamide) (Blaschette, Linoh, Koch & Ernst, 1989), was not observed under these conditions. Physical data for (I): m.p. 409 K; ^1H NMR ($CDCl_3$, 200 MHz): 3.60 (*s*); ^{13}C NMR ($CDCl_3$, 50 MHz): 44.5 (CH_3), 157.0 and 162.8 (CO). Elemental analysis: found C 18.17, H 2.35, N 5.32, S 24.27%; $C_4H_6ClNO_6S_2$ requires C 18.22, H 2.29, N 5.31, S 24.32%. Single crystals of (I) were grown by the diffusion method from benzene/petrol ether.

Crystal data

$C_4H_6ClNO_6S_2$	Mo $K\alpha$ radiation
$M_r = 263.67$	$\lambda = 0.71073$ Å
Orthorhombic	Cell parameters from 56 reflections
$P2_12_12_1$	

$a = 8.939\,(2)$ Å
$b = 9.360\,(2)$ Å
$c = 11.438\,(2)$ Å
$V = 957.0\,(3)$ Å^3
$Z = 4$
$D_x = 1.830$ Mg m^{-3}
D_m not measured

$\theta = 10.0$–$11.5°$
$\mu = 0.839$ mm^{-1}
$T = 143\,(2)$ K
Prism
$0.5 \times 0.4 \times 0.4$ mm
Colourless

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: none
2418 measured reflections
2195 independent reflections
2162 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.0188$

$\theta_{\max} = 27.51°$
$h = -11 \rightarrow 11$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 14$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0201$
$wR(F^2) = 0.0575$
$S = 1.073$
2188 reflections
130 parameters
H atoms: methyls refined as rigid groups
$w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 0.2238P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.247$ e Å^{-3}
$\Delta\rho_{\min} = -0.220$ e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0221 (14)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.02 (5)

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

N1—C3	1.408 (2)	S2—O4	1.4237 (13)
N1—S1	1.7168 (12)	S2—C2	1.747 (2)
N1—S2	1.7198 (14)	C3—O5	1.192 (2)
S1—O1	1.4191 (13)	C3—C4	1.535 (2)
S1—O2	1.4305 (12)	C4—O6	1.177 (2)
S1—C1	1.745 (2)	C4—C1	1.734 (2)
S2—O3	1.4140 (13)		
C3—N1—S1	119.51 (11)	N1—C3—C4	115.40 (13)
C3—N1—S2	117.78 (10)	O6—C4—C3	124.1 (2)
S1—N1—S2	120.77 (7)	O6—C4—C1	123.85 (14)
O5—C3—N1	123.8 (2)	C3—C4—C1	111.66 (12)
O5—C3—C4	120.40 (15)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1*B*···O4$^{\text{i}}$	0.98	2.58	3.338 (2)	134.3
C2—H2*A*···O4$^{\text{ii}}$	0.98	2.65	3.289 (2)	122.9
C2—H2*B*···O1$^{\text{iii}}$	0.98	2.56	3.440 (2)	150.0
C2—H2*C*···O5$^{\text{iv}}$	0.98	2.60	3.377 (2)	136.8

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

Data collection: *DIF*4 (Stoe & Cie, 1991*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

The authors thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: FG1267). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 783–786

2,4,6-Tris(diazo)cyclohexane-1,3,5-trione

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(*Received 17 December 1996; accepted 3 February 1997*)

Abstract

The title compound, $C_6N_6O_3$, displays crystallographic $\bar{6}$ symmetry. All atoms lie in mirror planes. The actual symmetry is close to the ideal $\bar{6}m2$. Ring angles alternate