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

O1—C1	1.238 (2)	C3—C4	1.534 (2)
N2—C1	1.335 (2)	C4—C5	1.526 (2)
N2—C3	1.460 (2)	N1···O2^{i}	2.922 (2)
C1—C5	1.518 (2)		
C1—N2—C3	114.11 (13)	C5—C4—C3	104.30 (13)
O1—C1—N2	125.90 (14)	C1—C5—C4	104.35 (13)
O1—C1—C5	125.64 (14)	C1—N2···O1^{i}	116.0 (1)
N2—C1—C5	108.46 (13)	C1—O1···N2^{i}	117.5 (1)
N2—C3—C4	103.05 (13)		

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

All quantum-mechanical calculations were performed with the *GAUSSIAN*94 package (Frisch *et al.*, 1996). The B3LYP total energies for the monomer and dimer were −286.630098 and −573.288245 a.u., respectively. Non-H atoms were refined anisotropically and H atoms isotropically. The maximum residual electron density of 0.46 e Å^{-3} was situated midway between C1 and N2.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1995). Cell refinement: *CAD*-4 *EXPRESS*. Data reduction: *DATAP* (Coppens *et al.*, 1965). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1205). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 504–507

Polysulfonylamines. C. Bis(4-nitrobenzenesulfonyl)amine Monohydrate†

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Abstract

In the title hydrate, $C_{12}H_9N_3O_8S_2.H_2O$, the disulfonylamine molecule adopts an elongated (open) conformation approximating to point group symmetry C_2. A short N—H···O*W* hydrogen bond [N···O*W* 2.716 (4) Å and N—H···O*W* 163 (3)°] connects the amine with the water molecule. In the molecular packing, formula units related *via* a translation of **b** are linked into stacks through an O*W*—H···O(S) hydrogen bond; the stacks

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† Part XCIX: Wirth *et al.* (1998).

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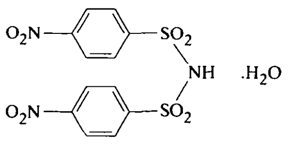
are further connected through an *O*W—H′[···O(S)]$_2$ three-centre hydrogen bond to form layers parallel to the *xy* plane.

Comment

Di(organosulfonyl)amines, (RSO$_2$)$_2$NH, are strong proton donors and form hydrogen-bonded adducts, (RSO$_2$)$_2$N—H···*A*, with appropriate acceptors *A* such as Ph$_3$PO, Me$_2$SO, 18-crown-6 or MeCN (Jones *et al.*, 1997, and references therein). A search of the Cambridge Structural Database (April 1997 version; Allen & Kennard, 1993) revealed three structures of binary hydrates, (RSO$_2$)$_2$NH.nH$_2$O. In two of these, *viz.* bis(2,4-dichloro-5-carboxybenzenesulfonyl)amine tetrahydrate (Goldberg, 1984) and di(5-acetylamino-1,3,4-thiadiazole-2-sulfonyl)amine dihydrate (Vinković *et al.*, 1994), the NH function of the (SO$_2$)$_2$NH moiety appears not to be involved in hydrogen bonding. In bis(methanesulfonyl)amine monohydrate, (1), on the other hand, a short N—H···*O*W bond [N···*O*W 2.737 (2) Å] connects the amine with the water molecule; both are further linked into an endless double chain by two weak *O*W—H···O hydrogen bonds from the water molecule to two amine molecules (Attig & Mootz, 1975). We report here the structure of the analogous title monohydrate, (2), in which a different hydrogen-bond pattern leads to layered packing.



(2)

The asymmetric unit of (2) is shown in Fig. 1 (selected intramolecular dimensions in Table 1 and hydrogen-bonding geometry in Table 2). The amine molecule adopts an elongated (open) conformation, in which the N(SO$_2$C)$_2$ moiety approximates to point symmetry C_2 [*cf.* torsion angles in Table 1; for a database study of disulfonylamine conformations see the report of Bombicz *et al.* (1996)]. The interplanar angles between the phenyl rings and the S1—N1—S2 plane amount to 76.66 (10)° for ring C1–C6 and 79.67 (7)° for ring C7–C12. The nitro groups O3—N2—O4 and O7—N3—O8 are twisted by 10.5 (5) and 20.1 (4)°, respectively, out of the corresponding phenyl plane. For convenience, the sulfonyl O atoms will be differentiated as *cisoid* (O1 and O5) or *transoid* (O2 and O6), according to their position with respect to the N—H bond.

A short but markedly bent N—H···O hydrogen bond connects the amine with the water molecule. In contrast to (1), where the N—H···*O*W sequence lies on a crystallographic twofold axis, the water molecule in the present structure is appreciably displaced from the S1—N1—S2 bisector [O1*W* lies 1.743 (10) Å out of the S1—N1—S2 plane; O1*W*···S1 3.745 (3), O1*W*···S2 3.559 (3) Å, O1*W*···N1—S1 114.96 (14) and O1*W*···N1—S2 106.90 (13)°]. This distortion is presumably caused by the overall geometric demands of the hydrogen-bond network.

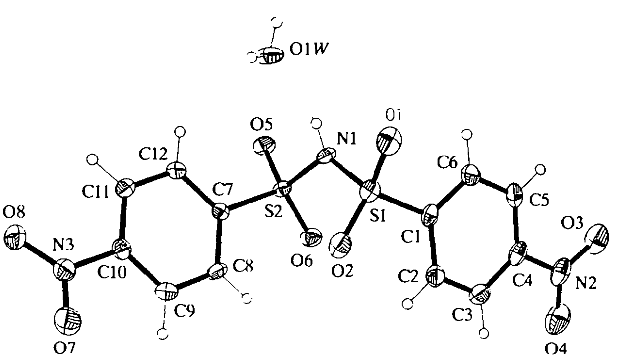


Fig. 1. The structure of the title compound in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

In the molecular packing (Fig. 2), formula units related by translation are piled up into stacks that propagate parallel to **b**. Within a stack, adjacent amine molecules are held together by the N—H···*O*W bond and an *O*W—H···O bond to the *cisoid* O5 atom of the second molecule. These stacks are further connected into layers parallel to the *xy* plane *via* an asymmetric *O*W—H(···O)$_2$ three-centre hydrogen bond formed between the remaining water H and *transoid* O6 and O2 atoms belonging to consecutive amine molecules in the neighbouring stack. It should be noted that the *cisoid* O1 atom and the four nitro O atoms are not involved in hydrogen bonding. The fairly strong *O*W—H···O5 two-centre hydrogen bond induces a significant lengthening of S2—O5 [1.440 (2) *versus* an average of 1.429 (2) Å for the other S—O bonds] and, in accordance with the bond-order conservation principle and the VSEPR (valence-shell electron-pair repulsion) rules, concomitant inequalities such as N1—S2 < N1—S1, S2—C7 < S1—C1 and O5—S2—O6 < O1—S1—O2 (*cf.* Bombicz *et al.*, 1996, and references therein).

The sandwich-type layers in the structure of (2) display an inner polar sublayer composed of N(SO$_2$)$_2$ groups and water molecules, and two outer regions of nitrophenyl groups. In the interlayer area, there exist two relatively short O···N contacts between NO$_2$ groups belonging to different layers [O4···N3 2.990 (4) and O7···N2 2.939 (4) Å; symmetry code for N3: $-x+2$, $-y$, $z-\frac{1}{2}$; for N2: $-x+2$, $-y+1$, $z+\frac{1}{2}$]; these contacts seem to be attractive, since the intramolecular N—O bonds at the O atoms involved are slightly longer than the other two N—O distances (see Table 1).

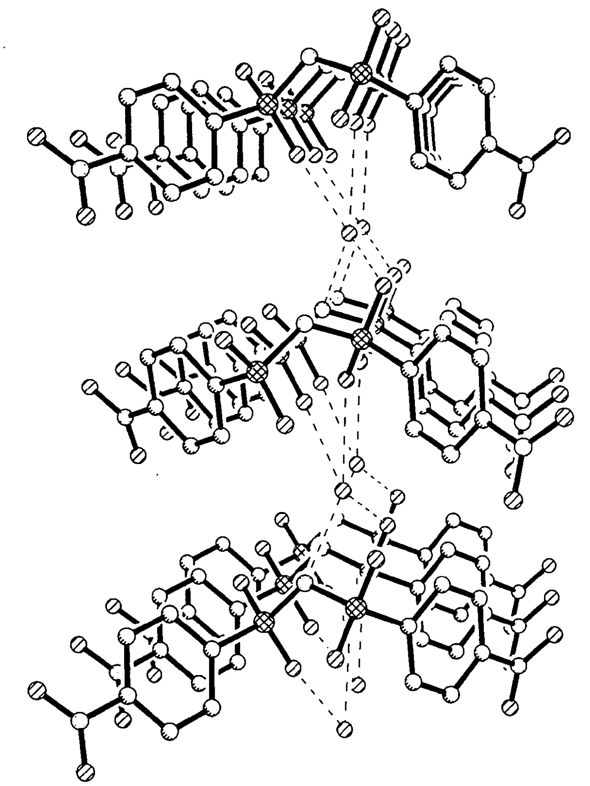


Fig. 2. Packing diagram of the title compound. H atoms have been omitted for clarity. Hydrogen bonds (N···O and O···O) are indicated by dashed lines. The view direction is approximately parallel to the *y* axis, with *x* down and *y* right to left. There are two such motifs per cell, occupying the regions 0 to 0.5 and 0.5 to 1.

Experimental

A hot solution containing 2.50 g (5.40 mmol) of $NaN(SO_2C_6H_4\text{-}4\text{-}NO_2)_2.3H_2O$ (preparation and crystal structure to be published) in 80 ml of deionized water was acidified with 5 ml of concentrated HCl. On cooling to ambient temperature, compound (2) separated as light-yellow needles; yield 1.85 g (84%). The crystals lose water at *ca* 363 K, the residue melting at 508 K [reported m.p. of pure $HN(SO_2C_6H_4\text{-}4\text{-}NO_2)_2$: 513–514 K (Dykhanov & Roshchenko, 1965)].

Crystal data

$C_{12}H_9N_3O_8S_2.H_2O$
$M_r = 405.36$
Orthorhombic
$Pna2_1$
$a = 12.558 (4)$ Å
$b = 5.4771 (15)$ Å
$c = 23.207 (5)$ Å
$V = 1596.2 (7)$ Å^3
$Z = 4$
$D_x = 1.687$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 62 reflections
$\theta = 10.0\text{–}12.5°$
$\mu = 0.391$ mm^{-1}
$T = 173 (2)$ K
Tablet
0.6 × 0.4 × 0.1 mm
Pale yellow

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3069 measured reflections
2821 independent reflections
2495 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.021$

$\theta_{\text{max}} = 25.00°$
$h = -14 \rightarrow 1$
$k = -6 \rightarrow 0$
$l = -27 \rightarrow 27$
3 standard reflections every 247 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.074$
$S = 1.063$
2821 reflections
248 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.005$

$\Delta\rho_{\text{max}} = 0.305$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.191$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.36 (7)

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

N1—S2	1.643 (3)	S2—O5	1.440 (2)
N1—S1	1.675 (3)	S2—C7	1.760 (3)
S1—O1	1.427 (2)	N2—O3	1.218 (4)
S1—O2	1.430 (2)	N2—O4	1.235 (4)
S1—C1	1.769 (3)	N3—O8	1.229 (3)
S2—O6	1.431 (2)	N3—O7	1.236 (3)
S2—N1—S1	124.34 (17)	O5—S2—N1	104.44 (13)
O1—S1—O2	121.61 (16)	O6—S2—C7	109.87 (14)
O1—S1—N1	102.45 (14)	O5—S2—C7	107.66 (14)
O2—S1—N1	109.95 (14)	N1—S2—C7	106.96 (13)
O1—S1—C1	109.09 (15)	O3—N2—O4	124.2 (3)
O2—S1—C1	107.23 (15)	O8—N3—O7	123.9 (3)
N1—S1—C1	105.43 (14)	H01—N1—S1	111 (2)
O6—S2—O5	120.18 (13)	H01—N1—S2	116 (2)
O6—S2—N1	106.92 (14)		
S2—N1—S1—O1	−163.65 (19)	S1—N1—S2—O6	−43.5 (2)
S2—N1—S1—O2	−33.0 (2)	S1—N1—S2—O5	−171.84 (18)
S2—N1—S1—C1	82.2 (2)	S1—N1—S2—C7	74.2 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H01···O1*W*	0.80 (3)	1.94 (3)	2.716 (4)	163 (3)
O1*W*—H02···O5^{i}	0.81 (4)	2.07 (4)	2.869 (4)	166 (4)
O1*W*—H03···O6^{ii}	0.77 (6)	2.18 (6)	2.840 (3)	144 (6)
O1*W*—H03···O2^{iii}	0.77 (6)	2.56 (6)	3.122 (3)	131 (5)

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

Amine and hydroxy H atoms were refined freely, others riding. The origin was fixed by the method of Flack & Schwarzenbach (1988). The structure was refined as a racemic twin with components 0.36 (7) and 0.64 (7).

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. 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.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1400). Services for accessing these data are described at the back of the journal.

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(*R*)- and (*S*)-2-(4-Bromophenyl)-2-oxoethyl 2-Methoxymethylpyrrolidine-1-dithiocarboxylate

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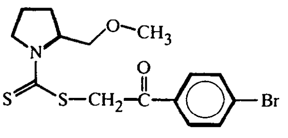
(*Received 28 August 1997; accepted 12 November 1997*)

Abstract

The absolute configurations of both the enantiomers of the title compound, $C_{15}H_{18}BrNO_2S_2$, have been determined. As expected, the molecular dimensions of both forms are insignificantly different. The phenacyl and dithiocarbamate fragments are planar and approximately perpendicular to one another. The short N—C(=S) bond length [1.330 (7) Å] indicates involvement of the N-atom lone pair in the thiocarbonyl π system.

Comment

(*R*)- and (*S*)-2-methoxymethylpyrrolidine have long been known as very valuable chiral auxiliaries (Enders & Klatt, 1996, and references therein). Recently, we tried to use these compounds for the synthesis of enantiomerically pure thiols *via* diastereoselective alkylation and subsequent cleavage of chiral dithiocarbamates (Dölling *et al.*, 1997). In the course of those investigations, both enantiomeric title compounds [(*R*)-(1) and (*S*)-(1)] were synthesized and their assumed absolute configurations confirmed by X-ray analyses. The two structure analyses were performed in exactly the same way. Therefore, comparison of the results enables a realistic judgement of geometric parameters (bond lengths, *etc.*) obtained by the present standard routine of X-ray analysis. Considering the *R* values and s.u.'s, the results obtained for (*R*)-(1) seem to be a little more precise than those obtained for (*S*)-(1), possibly due to a small difference in quality of the crystals. But an inspection of the geometric parameters reveals only insignificant differences. The differences in corresponding bond lengths (angles) amount to less than 0.5σ (0.8σ) in most cases and maximally 1.5σ (1.8σ). In the following, only numerical values for (*R*)-(1) are considered; the deposited data include those of (*S*)-(1) [data for (*S*)-(1) have been deposited† in the Cambridge Structural Database (Allen *et al.*, 1983)].



(1)

The essential structural features of (1) can be seen in Fig. 1 and Table 1. The molecule has a chiral centre at atom C1 of the pyrrolidine ring, which adopts an envelope conformation with the C2 atom deviating by 0.502 (9) Å from the plane through the other four atoms. There are two other planar moieties in the molecule, the phenacyl fragment [atoms C8–C15; maximum deviation from planarity 0.039 (8) Å for C11] and the dithiocarbamate moiety (atoms N1, C7, S1 and S2; exactly planar within 3σ), which are nearly perpendicularly oriented [86.2 (2)°] to one another.

Most of the observed bond lengths and angles in (1) are in good agreement with standard values. However, the C7—N1 distance of 1.330 (7) Å is markedly shorter than the normal C_{sp^2}—N_{sp^3} single bond (1.43 Å; Rademacher, 1987) and indicates an obvious participation of the N-atom lone pair in the π system of

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† CCDC deposit No. 100834.

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