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Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.037
 wR factor = 0.103
Data-to-parameter ratio = 16.6

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis(2-pyrimidinyl) disulfide dihydrate: a redetermination

The crystal structure of bis(2-pyrimidinyl) disulfide dihydrate, $\text{C}_8\text{H}_6\text{N}_4\text{S}_2 \cdot 2\text{H}_2\text{O}$, has been redetermined using CCD diffractometer data. This has allowed for a more precise location of the water H atoms and shows the water molecules forming unusual spiral hydrogen-bonded aqua columns, as well as giving inter-column crosslinks through the pyrimidine N-atom acceptors of the disulfide molecules. The structural chemistry of aromatic disulfides has also been reviewed.

Comment

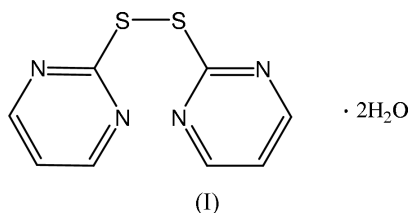
Aromatic disulfides of the type $\text{Ar}-\text{S}-\text{S}-\text{Ar}$ have been known for some considerable time, the bis(2-chlorophenyl) analogue having been reported as being easily obtained from the oxidation of 2-chlorothiophenol (Friedlander & Mauthner, 1904). This facile conversion of thiols to disulfides, which may be achieved with mild oxidizing agents such as iodine, is accelerated by the presence of bases and probably proceeds *via* thioxy free radicals (Roberts & Caserio, 1965).

Organic disulfides are of commercial importance for their anti-wear properties as additives in lubricating oils (Allum & Ford, 1965; Allum & Forbes, 1967; Meyer, 1977), and are also important in biological function, being present in molecules such as cystine, ribonuclease and insulin. The structures of L-cystine (Oughton & Harrison, 1959), L-cystine hydrochloride (Steinrauf *et al.*, 1958) and L-cystine hydrobromide (Peterson *et al.*, 1960) have been determined, as has that of insulin, where the two peptide chains are held together by disulfide bridges (Adams *et al.*, 1969). The crystal structures of many disulfides have also been reported, with $\text{Ar} = \text{phenyl}$ (Lee & Bryant, 1969*a*; Sacerdoti *et al.*, 1975), 2-aminophenyl (Gomes de Mesquita, 1967; Lee & Bryant, 1970), 2-nitrophenyl (Ricci & Bernal, 1970), 2-chlorophenyl (Mak *et al.*, 1989), 3-carboxy-4-nitrophenyl (from Ellman reagent; Shefter & Kalman, 1969), 4-tolyl (Vorontsova *et al.*, 1967), 4-chlorophenyl (Spirlet *et al.*, 1979), 4-bromophenyl (Toussaint, 1945), benzyl (Lee & Bryant, 1969*b*), cinnamyl (Lee & Bryant, 1971) and 2-chlorophenylaminomethyl (Pierrot *et al.*, 1984).

There are fewer structures of the analogous aromatic diselenides and ditellurides. For $\text{Ar}-\text{Se}-\text{Se}-\text{Ar}$, structures have been published with $\text{Ar} = \text{phenyl}$ (Marsh, 1952) and 4-chlorophenyl (Llabres *et al.*, 1972), and for $\text{Ar}-\text{Te}-\text{Te}-\text{Ar}$, structures have been published with $\text{Ar} = \text{phenyl}$ (Kruse *et al.*, 1957) and 4-chlorophenyl (Llabres *et al.*, 1972). Structures of the heteroaromatic disulfides are also less common, with those of bis(4-uridinyl) disulfide (Shefter & Kalman, 1968), bis(2-methyl-4-uridinyl) disulfide (Shefter, 1970), the disulfide from 5-[1-(2'-deoxy- α -D-ribofuranosidyl)uracil (Shefter *et al.*, 1968) and the title compound, bis(2-pyrimidinyl) disulfide

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dihydrate, (I) (Furberg & Solbakk, 1973), having been previously reported. In (I), although the water molecules appear to be quite strongly associated, they exhibit significant lability, resulting in almost total crystal deterioration (92%) in the X-ray beam, commencing rapidly after *ca* 18 h of room-temperature exposure in air using a conventional four-circle diffractometer. This seemingly time-related X-ray-enhanced property prompted recollection of data using a diffractometer with a CCD area-detector, and the results are presented here.



The present structure of (I) (Fig. 1, Table 1) is unusual among the aromatic disulfides because of the presence of solvent water molecules in the crystal structure. This is largely the result of the presence of the four N heteroatom acceptors in the two pyrimidinyl residues of the disulfide, which require additional H-donor molecules to balance the donor-acceptor ratio for hydrogen-bonding interactions. The absorption-corrected CCD diffraction data used for the structure redetermination reported here, together with the use of the more orthogonal cell setting compared with the original analysis, allow a more precise picture of the hydrogen bonding in (I) and the role of water in the crystal structure.

The two water molecules and their *n*-glide-related neighbours participate in unusual hydrogen-bonded column structures which spiral down the *b* axial direction [O1W—H1B···O2Wⁱ 2.770 (3) and O2W—H2A···O1W 2.687 (3) Å; symmetry code: (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$] (Fig. 2). The second H atom of each of these water molecules acts as a donor to one N-acceptor atom of each of the pyrimidinyl residues (atoms N1 and N11) of separate disulfide molecules, linking the columns [O1W—H1A···N11 2.921 (3) and O2W—H2B···N1ⁱⁱ 2.949 (2) Å; symmetry code: (ii) $x - 1, y, z$]. The other N heteroatoms (N3 and N31) are unassociated. The result is a hydrogen-bonded network polymer structure.

The disulfide molecules, which adopt an eclipsed conformation with the pyrimidinyl residues *cis*-related [torsion angles C2—S1—S11—C21 -82.50 (7), S1—S11—C21—N11 -178.3 (1) and S11—S1—C2—N1 -174.1 (1)°], are essentially unchanged compared with the original determination. This conformation is more common among the disulfides, but examples with the extended *trans*-related ring systems are known, *e.g.* dibenzyl disulfide (Lee & Bryant, 1969*b*).

Experimental

Compound (I) was formed as the sole product from the attempted synthesis of a bismuth complex of 2-pyrimidinethiol (2-mercapto-pyrimidine), by adding 2-pyrimidinethiol (3.0 g) to a stirred solution

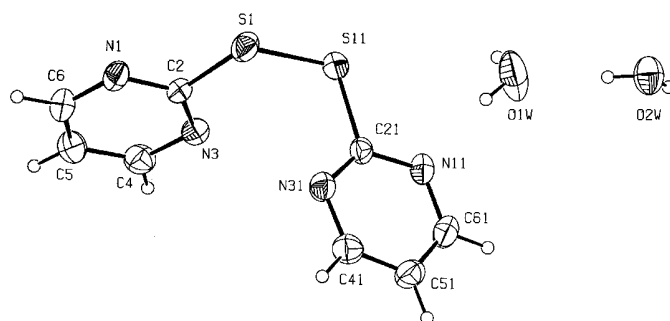


Figure 1

The structure of (I), showing the atom-numbering scheme for the disulfide and water molecules. This follows the scheme employed by Furberg & Solbakk (1973). Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

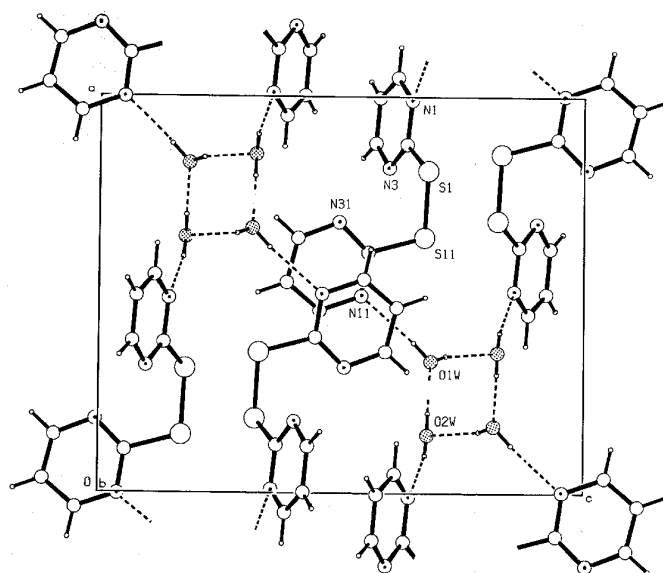


Figure 2

The chain structure of (I) viewed down *b*, showing the *n*-glide-related water molecules in the core structural columns, linking together the disulfide molecules through peripheral hydrogen-bonding associations (dashed lines).

of freshly prepared bismuth(III) hydroxide (1.2 g) in 28% *w/v* ammonia solution (100 ml). Partial room temperature evaporation of the filtered solution gave colourless prisms of (I) (m.p. 407–409 K). IR spectroscopic data (KBr pressed disc, ν , cm^{-1}): 3400 (*m, br*), 1553 (*s*), 1427 (*m*), 1376 (*s*), 1196 (*m*), 1165 (*s*), 800 (*m*), 767 (*m*), 741 (*m*), 626 (*m*), 448 (*m*); CHN elemental analysis indicated a bis-pyrimidine-substituted disulfide dihydrate. The previously reported synthesis of (I) (Furberg & Solbakk, 1973) involved heating 2-pyrimidinethiol in aqueous ammonia solution.

Crystal data

$\text{C}_8\text{H}_6\text{N}_4\text{S}_2 \cdot 2\text{H}_2\text{O}$
 $M_r = 258.32$
 Monoclinic, $P2_1/n$
 $a = 11.824$ (1) Å
 $b = 6.9357$ (6) Å
 $c = 14.4896$ (12) Å
 $\beta = 90.423$ (2)°
 $V = 1188.27$ (17) Å³
 $Z = 4$

$D_x = 1.444$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3253 reflections
 $\theta = 2.2$ – 27.2 °
 $\mu = 0.44$ mm⁻¹
 $T = 295$ (2) K
 Block, colourless
 $0.50 \times 0.40 \times 0.25$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 1999)
 $T_{\min} = 0.805$, $T_{\max} = 0.900$
 7142 measured reflections

2693 independent reflections
 2273 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.019$
 $\theta_{\text{max}} = 27.5^\circ$
 $h = -11 \rightarrow 15$
 $k = -9 \rightarrow 7$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.103$
 $S = 1.03$
 2693 reflections
 162 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1574P)^2 + 0.2085P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.24 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXTL (Bruker, 1997)
 Extinction coefficient: 0.0103 (19)

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O1W-H1A\cdots N11$	0.77 (3)	2.16 (3)	2.921 (3)	171 (3)
$O1W-H1B\cdots O2W^i$	0.76 (3)	2.02 (3)	2.770 (3)	174 (3)
$O2W-H2A\cdots O1W$	0.83 (4)	1.86 (4)	2.687 (3)	175 (3)
$O2W-H2B\cdots N1^ii$	0.80 (3)	2.17 (3)	2.949 (2)	166 (3)

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

The H atoms of the water molecules were located by difference methods and their positional and isotropic displacement parameters were refined. Other H atoms were included in the refinement at calculated positions, with $C-H = 0.93 \text{ \AA}$, and were treated as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 1999); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 1997); program(s) used to refine structure: SHELXTL; molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

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