Bis(2-pyrimidinyl) disulfide dihydrate: a redetermination

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The crystal structure of bis(2-pyrimidinyl) disulfide dihydrate, C₉H₈N₂S₂·2H₂O, 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 Ar—S—S—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 Ar = phenyl (Lee & Bryant, 1969a; 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; Shetter & Kalman, 1969), 4-tolyl (Vorontsova et al., 1967), 4-chlorophenyl (Spirlet et al., 1979), 4-bromophenyl (Toussaint, 1945), benzyl (Lee & Bryant, 1969b), cinnamyl (Lee & Bryant, 1971) and 2-chlorophenylaminomethyl (Pierrot et al., 1984).

There are fewer structures of the analogous aromatic diselenides and ditellurides. For Ar—Se—Se—Ar, structures have been published with Ar = phenyl (Marsh, 1952) and 4-chlorophenyl (Llabres et al., 1972), and for Ar—Te—Te—Ar, structures have been published with Ar = 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 (Shetter & Kalman, 1968), bis(2-methyl-4-uridinyl) disulfide (Shetter, 1970), the disulfide from 5-[1-(2’-deoxy-α-D-ribofuranosanoyl)uracil (Shetter et al., 1968) and the title compound, bis(2-pyrimidinyl) disulfide...
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-glade-related neighbours participate in unusual hydrogen-bonded column structures which spiral down the b axial direction [O1W−H1B⋅⋅⋅O2W′ 2.770 (3) Å and O2W−H2A⋅⋅⋅O1W 2.687 (3) Å; symmetry code: (i) ½ − x, y, ½ − 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) Å and O2W−H2B⋅⋅⋅N11 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 pyrimidyl residues cis-related [torsion angles C2−S1−C11−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, 1969b).

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 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, v, 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

\begin{align*}
C_{8}H_{6}N_{4}S_{2} & \cdot 2H_{2}O \\
M_{r} & = 258.32 \\
Monoclinic, P_{2}/n \\
a & = 11.824 (1) \text{ Å} \\
b & = 6.9357 (6) \text{ Å} \\
c & = 14.4896 (12) \text{ Å} \\
\beta & = 118.32 (1)° \\
V & = 1188.27 (17) \text{ Å}^3 \\
Z & = 4 \\
D_{c} & = 1.444 \text{ Mg m}^{-3} \\
Mo \text{ K}_{\alpha} \text{ radiation} \\
Cell parameters from 3253 reflections \\
\theta & = 2.2–27.2° \\
\mu & = 0.44 \text{ mm}^{-1} \\
T & = 295 (2) \text{ K} \\
\text{Block, colourless} \\
0.50 \times 0.40 \times 0.25 \text{ mm}
\end{align*}
Data collection
Bruker SMART CCD area-detector diffractometer
\( \varphi \) and \( \omega \) scans
Absorption correction: multi-scan
\( \alpha \) = 0.019
\( T_{\text{min}} = 0.805, T_{\text{max}} = 0.900 \)
7142 measured reflections
2693 independent reflections
2273 reflections with \( I > 2 \sigma (I) \)

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
Extinction correction: SHELXTL
\( \mu = 0.2085 \mathrm{mm}^{-1} \)
Extinction coefficient: 0.0103 (19)

Table 1
Hydrogen-bonding geometry (Å, °).

<table>
<thead>
<tr>
<th>D—H .. A</th>
<th>D—H</th>
<th>H .. A</th>
<th>D .. A</th>
<th>D—H .. A</th>
</tr>
</thead>
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<tr>
<td>O1W—IHA—N11</td>
<td>0.77 (3)</td>
<td>2.16 (3)</td>
<td>2.921 (3)</td>
<td>171 (3)</td>
</tr>
<tr>
<td>O1W—IHB—O2W+1</td>
<td>0.76 (3)</td>
<td>2.02 (3)</td>
<td>2.770 (3)</td>
<td>174 (3)</td>
</tr>
<tr>
<td>O2W—IHA—O1W</td>
<td>0.83 (4)</td>
<td>1.86 (4)</td>
<td>2.687 (3)</td>
<td>175 (3)</td>
</tr>
<tr>
<td>O2W—IHB—N11+1</td>
<td>0.80 (3)</td>
<td>2.17 (3)</td>
<td>2.949 (2)</td>
<td>166 (3)</td>
</tr>
</tbody>
</table>

Symmetry codes: (i) \( \frac{1}{2} - x, y - \frac{1}{2} - z \); (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 Å, and were treated as riding atoms, with \( U_{eq}(H) = 1.2U_{eq}(C) \).

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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References

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Schrödinger, New York.


