Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

(4*R*,9*S*)-4-Hydroxymethyl-3,8-dioxa-1,6-diazaspiro[4.4]nonane-2,7-dithione monohydrate

Gianluca Cioci,[a] Nicolas Leconte,[b] Arnaud Tatibouët,[b] Patrick Rollin,[b] Serge Pérez[a] and Anne Imberty[a]*

[a]CERMAV–CNRS (affiliated to Université Joseph Fourier), BP 53, 38041 Grenoble CEDEX 9, France, and [b]ICOA–UMR 6005, Université d'Orléans, BP 6759, F-45067 Orléans, France

Correspondence e-mail: imberty@cermav.cnrs.fr

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.051
wR factor = 0.130
Data-to-parameter ratio = 8.6

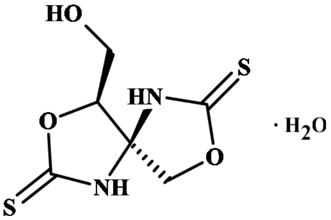
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_6H_8N_2O_3S_2\cdot H_2O$, was synthesized from L-erythrulose and the structure of the enantiopure (4*R*,9*S*) diastereoisomer has been determined. The structure is a hydrate and the water molecules establish a hydrogen-bond network that involves the hydroxymethyl group as well as one N and one S atom.

Received 21 October 2004
Accepted 16 November 2004
Online 27 November 2004

Comment

Chiral 1,3-oxazolidine-2-thiones (OZT) attract much interest because of their use as auxiliaries in asymmetric synthesis (Crimmins *et al.*, 2001), as precursors in the elaboration of nucleoside analogues (Girniene *et al.*, 2004) or as potential inhibitors of the fructose transporter GLUT-5 (Girniene *et al.*, 2003). Bis-OZT compounds, particularly those involving a spiro junction, constitute an exciting new class of multipurpose chiral OZT. The crystal structure of the parent spiro-bis-OZT in racemic form has been reported previously (Saul *et al.*, 2000). The title compound, (I), was synthesized from L-erythrulose. Two diastereoisomers are formed and the major compound, (I), readily crystallizes in the space group $P2_12_12_1$ with one OZT molecule and one water molecule in the asymmetric unit.



(I)

The two five-membered rings of (I) are significantly twisted (Fig. 1), with values of 19.8 (3) and 17.3 (3)° for torsion angles O3—C4—C9—N1 and N5—C9—C8—O7, respectively. The hydroxymethyl group has a *gauche* conformation relative to the ring O atom. It interacts directly with the water molecule, which also accepts a hydrogen bond from one NH group. Interestingly, this water molecule also donates one hydrogen bond to an S atom. Hydroxyl···S hydrogen bonds are rarer and weaker than their OH···O/N counterparts. Nevertheless, as reported previously (Allen *et al.*, 1997), the conjugation of C═S with the neighbouring N atom increases the electronegativity of the S atom and results in a resonance-induced hydrogen bond, with S···O 3.234 (3) Å and S···H 2.45 (3) Å. All hydrogen bonds are bridged by the water molecules, resulting in a three-dimensional framework (Fig. 2).

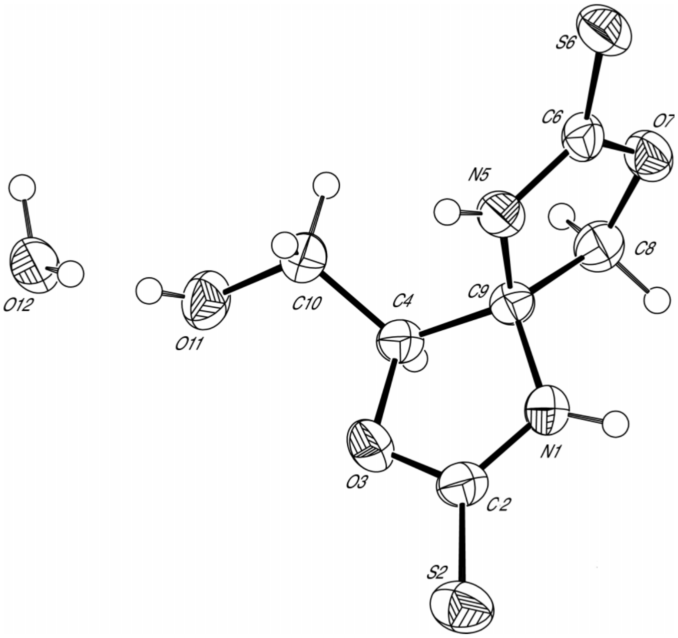


Figure 1
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

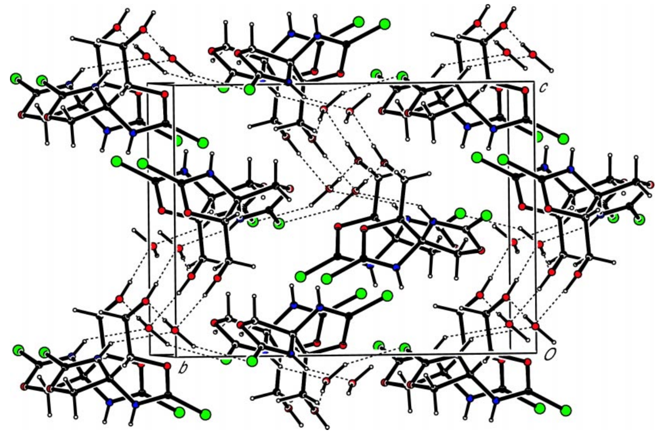


Figure 2
A packing diagram for (I), with hydrogen bonds indicated as dashed lines.

Experimental

The title compound was prepared in quantitative yield according to the procedure described by Saul *et al.* (2000). The reaction gave a mixture of two diastereoisomers in the ratio 85:15, from which the major compound crystallized in pure form. Suitable crystals of (I) were obtained by recrystallization from water (m.p. 442–447 K). Spectroscopic analysis: $[\alpha]_D$ = +22 (c = 1.0; MeOH); ^{1}H NMR (DMSO-d_6, δ, p.p.m.): 3.71 (*m*, 2H, CH_2OH), 4.62 (*d*, 1H, ^2J = 11.3 Hz, H8*A*), 4.66 (*d*, 1H, ^2J = 11.0 Hz, H8*B*), 4.80 (*t*, 1H, ^3J = 5.8 Hz, H4), 5.30 (*s*, 1H, OH), 10.91 (*s*, 1H, NH), 10.97 (*s*, 1H, NH); ^{13}C NMR (DMSO-d_6, δ, p.p.m.): 57.9 (CH_2OH), 76.0 (C8), 81.3 (C9), 85.1 (C4), 186.9 (C2 or C6), 188.0 (C2 or C6); MS: m/z 221 $[M+H]^+$; high-resolution MS, calculated for $C_6H_8N_2O_3S_2$: 219.9976; found: 219.9989.

Crystal data

$C_6H_8N_2O_3S_2 \cdot H_2O$
M_r = 238.28
Orthorhombic, $P2_12_12_1$
a = 7.036 (2) Å
b = 10.336 (3) Å
c = 13.814 (3) Å
V = 1004.6 (5) Å^3
Z = 4
D_x = 1.575 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 24 reflections
θ = 20.2–23.5°
μ = 4.80 mm^{-1}
T = 293 (2) K
Prism, colourless
0.7 × 0.2 × 0.2 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: none
1164 measured reflections
1164 independent reflections
1150 reflections with $I > 2\sigma(I)$
θ_{max} = 75.0°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = 0 \rightarrow 17$
2 standard reflections every 120 reflections intensity decay: 3.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.051$
$wR(F^2) = 0.130$
S = 1.08
1164 reflections
136 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0629P)^2 + 0.1989P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.37 e Å^{-3}
Absolute structure: Flack (1983); no Friedel pairs
Flack parameter = 0.04 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
O11—H11···O12	0.82	1.94	2.746 (4)	169
N5—H5···O12^{i}	0.86	1.99	2.791 (4)	155
O12—H121···S6^{ii}	0.84 (2)	2.45 (3)	3.234 (3)	156 (5)
O12—H122···O11^{i}	0.83 (4)	1.86 (2)	2.685 (4)	178 (5)

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

All H atoms were initially located in a difference Fourier map. Atoms H121 and H122 were refined freely. All other H atoms were treated as riding on their parent atoms, with C—H = 0.97–0.98 Å, O—H = 0.82 Å and N—H = 0.86 Å, and with $U_{iso}(H) = 1.5U_{eq}(O)$ or $1.2U_{eq}$(C,N). Although there were no Friedel pairs, the absolute configuration could be determined unambiguously.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

GC was suppported by an EEC postdoctoral grant (HPRN-CT2000-00001). The excellent assistance of Christian Philouze is acknowledged.

References

Allen, F. A., Bird, C. M., Rowland, R. S. & Raithby, P. R. (1997). *Acta Cryst.* B**53**, 680–695.

o2400 Gianluca Cioci *et al.* • $C_6H_8N_2O_3S_2 \cdot H_2O$ *Acta Cryst.* (2004). E**60**, o2399–o2401

Crimmins, M. T., King, B. W., Tabet, E. A. & Chaudhary, K. (2001). *J. Org. Chem.* **66**, 894–902.

Enraf–Nonius (1989). *CAD*-4 *Software*. Enraf–Nonius, Delft, The Netherlands.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Girniene, J., Apremont, G., Tatibouët, A., Sackus, A. & Rollin, P. (2004). *Tetrahedron*, **60**, 2609–2619.

Girniene, J., Tatibouët, A., Sackus, A., Yang, J., Holman, G. D. & Rollin, P. (2003). *Carbohydr. Res.* **338**, 711–719.

Saul, R., Kern, T., Kopf, J., Pinter, I. & Köll, P. (2000). *Eur. J. Org. Chem.* pp. 205–209.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst* **36**, 7–13.

Acta Cryst. (2004). E**60**, o2399–o2401 Gianluca Cioci *et al.* • $C_6H_8N_2O_3S_2{\cdot}H_2O$ **o2401**