

***R,R*-(+)-Bis[(3-benzyloxazolan-4-yl)methyl] disulfide**

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Key indicators

Single-crystal X-ray study

$T = 293$ K

Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å

R factor = 0.034

wR factor = 0.087

Data-to-parameter ratio = 9.4

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

R,R-Bis[(3-benzyloxazolan-4-yl)-methyl] disulfide, $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$, is a chiral disulfide which is a highly effective catalyst for the enantioselective addition of diethylzinc to aldehydes, including aliphatic ones. The molecule has crystallographic twofold rotation symmetry.

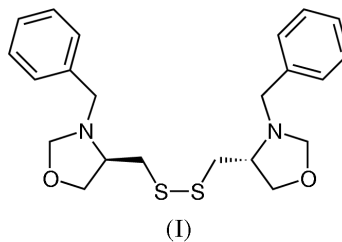
Received 26 October 2000

Accepted 27 November 2000

Online 8 December 2000

Comment

The title compound [alternatively called 3,3'-dibenzyl-4,4'-dithiodi(oxazoline)], (I), a chiral disulfide, was prepared from *L*-cysteine in a short synthetic sequence and applied successfully as a highly efficient catalyst (Braga *et al.*, 1999).



The asymmetric unit contains a half molecule of the disulfide. The complete molecule is generated by a twofold axis parallel to *b*, bisecting the S—S bond.

All bond distances and angles are normal. The torsion angle $\text{C1}-\text{S1}-\text{S1}^i-\text{C1}^i$ [symmetry code: (i) $1-x, y, 1-z$] of $90.4(2)^\circ$ is close to the average found for similar compounds in the Cambridge Structural Database (Allen & Kennard, 1983) (86.29°). No close intermolecular contacts are seen, though the S—S bonds are almost aligned along the *z* axis and the intermolecular $\text{S} \cdots \text{S}$ distance is $4.0177(17)$ Å.

The Cremer & Pople (1975) puckering parameters for the five-membered ring $\text{C2}-\text{N3}-\text{C4}-\text{O5}-\text{C6}$ were calculated by *PLATON* (Spek, 1995) to be $Q_2 = 0.373$ Å and $\varphi_2 = 14.92^\circ$, corresponding to a twist conformation with the axis through C2.

Experimental

In a 50 ml round-bottomed flask fitted with a Dean–Stark apparatus, benzene (30 ml), *N,N'*-dibenzyl-(*R*)-cystinol (392 mg, 1 mmol), paraformaldehyde (90 mg, 3 mmol) and *p*-toluenesulfonic acid (10 mg) were added. The mixture was heated at reflux for 5 h and cooled to room temperature. The benzene was removed under vacuum and the residue dissolved in CH_2Cl_2 (30 ml), washed with 0.5 *N* NaOH aqueous solution, dried with MgSO_4 , filtered, and the solvent removed under vacuum to afford 353 mg (yield 87%) of the title compound. A crystal suitable for X-ray analysis was grown by slow evaporation of a dichloromethane solution (m.p. $320\text{--}321$ K). Elemental analysis for $\text{C}_{22}\text{H}_{28}\text{N}_2\text{O}_2\text{S}_2$, calculated: C 63.43, H 6.77, N

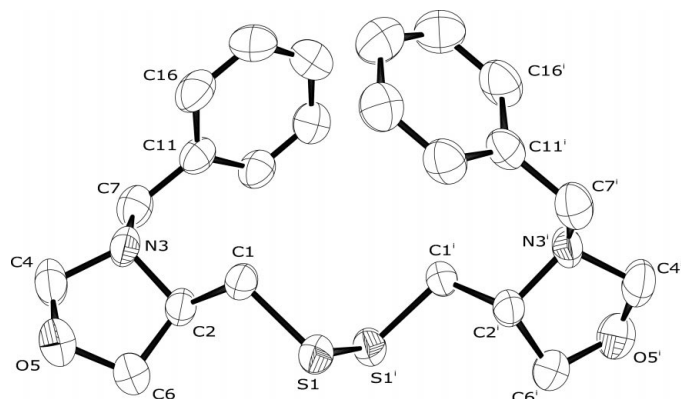


Figure 1
The molecular structure of (I) with 50% probability ellipsoids. H atoms have been omitted for clarity. The C atoms of the phenyl ring are numbered consecutively.

6.72%; found C 63.20, H 7.26, N 7.10%. $[\alpha]_D^{20} = +14.8$ (c 1.96, CHCl_3). ^1H NMR (200 MHz, CDCl_3 , Bruker): δ 2.47 (*dd*, 2H, $J = 8.4$ Hz, $J = 13.2$ Hz), 2.76 (*dd*, 2H, $J = 5.8$ Hz, $J = 13.2$ Hz), 3.21–3.36 (*m*, 2H), 3.48 (*dd*, 2H, $J = 5.0$ Hz, $J = 8.4$ Hz), 3.70–3.76 (*m*, 4H), 4.04 (*dd*, 2H, $J = 7.0$ Hz, $J = 8.4$ Hz), 4.29 (*s*, 4H), 7.19–7.34 (*m*, 10H). ^{13}C NMR (50 MHz, CDCl_3): δ 41.08, 58.92, 62.06, 69.06, 85.98, 127.97, 128.24, 128.60.

Crystal data

$\text{C}_{11}\text{H}_{14}\text{NOS}$
 $M_r = 208.29$
Monoclinic, C_2
 $a = 20.281$ (3) Å
 $b = 8.925$ (2) Å
 $c = 6.053$ (1) Å
 $\beta = 93.112$ (12)°
 $V = 1094.1$ (3) Å³
 $Z = 4$

$D_x = 1.265$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 10.5$ – 14.3°
 $\mu = 0.26$ mm⁻¹
 $T = 293$ (2) K
Plate, yellow
 $0.2 \times 0.2 \times 0.1$ mm

Data collection

CAD-4 diffractometer
 $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.949$, $T_{\max} = 0.974$
1307 measured reflections
1272 independent reflections
996 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

$\theta_{\max} = 27.0^\circ$
 $h = 0 \rightarrow 25$
 $k = -11 \rightarrow 0$
 $l = -7 \rightarrow 7$
3 standard reflections every 200 reflections
frequency: 60 min
intensity decay: 4.3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.034$
 $wR(F^2) = 0.087$
 $S = 1.10$
1272 reflections
136 parameters
H-atom parameters not refined

$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.1198P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.18$ e Å⁻³
 $\Delta\rho_{\min} = -0.20$ e Å⁻³
Absolute structure: Flack (1983), no Friedel pairs
Flack parameter = 0.1 (3)

Table 1

Selected geometric parameters (Å, °).

S1–C1	1.814 (3)	N3–C4	1.452 (4)
S1–S1 ⁱ	2.0363 (16)	N3–C7	1.462 (4)
C1–C2	1.520 (4)	C4–O5	1.399 (5)
C2–N3	1.482 (4)	O5–C6	1.427 (4)
C2–C6	1.520 (5)	C7–C11	1.502 (5)
C1–S1–S1 ⁱ	102.98 (11)	C4–N3–C2	105.4 (3)
C2–C1–S1	112.6 (2)	C7–N3–C2	115.5 (2)
N3–C2–C6	103.0 (2)	O5–C4–N3	105.2 (3)
N3–C2–C1	109.7 (2)	C4–O5–C6	104.0 (3)
C6–C2–C1	113.8 (3)	O5–C6–C2	105.7 (3)
C4–N3–C7	112.3 (2)	N3–C7–C11	112.8 (3)

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

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1992); cell refinement: *CAD-4 EXPRESS*; data reduction: *HELENA* (Spek, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

We are grateful for the financial assistance provided by FAPERGS and CNPq (Brazil).

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