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(±)-(*rel*-3*R*,3′*R*)-1,1′-Dimethyl-3,3′-bipyrrolidine-2,2′-dithione

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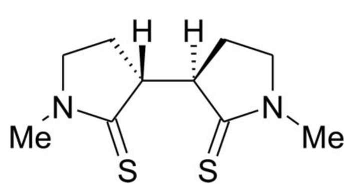
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.003 Å; R factor = 0.030; wR factor = 0.077; data-to-parameter ratio = 15.7.

The asymmetric unit of the racemic title compound, $C_{10}H_{16}N_2S_2$, a C_2-symmetric bis(thiolactam), contains one half-molecule, the complete molecule being generated by a twofold axis symmetry operation. The five-membered ring is nearly planar, with a maximum deviation of 0.025 (1) Å. In the crystal, the molecules are linked *via* weak C—H⋯S interactions, forming infinite chains along the *b*-axis direction.

Related literature

For related synthesis, see: Tamaru *et al.* (1978); Schroth *et al.* (2000).



Experimental

Crystal data

$C_{10}H_{16}N_2S_2$
M_r = 228.37
Monoclinic, $C2/c$
a = 20.520 (3) Å
b = 5.7237 (7) Å
c = 11.220 (2) Å
β = 122.009 (5)°
V = 1117.4 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.44 mm^{-1}
T = 173 K
0.45 × 0.42 × 0.16 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996) T_{min} = 0.827, T_{max} = 0.933
1759 measured reflections
1022 independent reflections
957 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.030
$wR(F^2)$ = 0.077
S = 1.09
1022 reflections
65 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C5—H5B⋯S1^{i}	0.98	2.98	3.8373 (18)	146

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

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT-Plus* (Bruker, 2004); data reduction: *SAINT-Plus* and *XPREP* (Bruker 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *DIAMOND* (Brandenburg, 1999); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2009).

This work was supported by the University of the Witwatersrand and the Molecular Sciences Institute, which are thanked for providing the infrastructure required to do this work. Dr R. B. Katz is thanked for performing the preliminary syntheses.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT6851).

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supporting information

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(±)-(*rel*-3*R*,3′*R*)-1,1′-Dimethyl-3,3′-bipyrrolidine-2,2′-dithione

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S1. Comment

The title compound, (±)-(*rel*-3*R*,3′*R*)-1,1′-dimethyl-3,3′- bipyrrolidine-2,2′-dithione, was obtained as a minor product from the attempted $S_{RN}1$ arylation of deprotonated 1-methylpyrrolidine-2-thione with 4-bromoanisole under photolytic conditions. Previous workers had reported the same dimer from the reaction of deprotonated 1-methylpyrrolidine-2-thione with molecular iodine – apparently incorrectly as the *meso* diastereomer (Tamaru *et al.*, 1978), later corrected to the C_2-symmetric isomer (Schroth *et al.*, 2000).

The asymmetric unit of the title compound consists of half a molecule around a twofold axis, and Fig. 1 shows the atomic numbering scheme. The complete molecule is generated by the twofold axis. Both stereogenic centres have the same relative configuration, which is depicted in Fig. 1 as *rel*-(*R,R*′). The opposite enantiomer in the crystal is generated by the c-glide in *C*2/c. The hydrogen bonding of the title compound consists of weak C—H···S hydrogen bonds from the methyl group to generate hydrogen bonded chains along the *b*-axis by unit cell translations only (Fig. 2).

S2. Experimental

A solution of 1-methylpyrrolidine-2-thione (580 mg, 5.5 mmol) in dry tetrahydrofuran (20 ml) was treated at 0 °C with a solution of *n*-butyllithium in hexane (5.5 mol). After 20 min 4-bromoanisole (690 μl, 5.5 mmol) was added, and the solution was irradiated for 30 min with a mercury lamp (125 W). The reaction mixture was poured into aq. NH_4Cl solution, and the organic components were extracted with dichloromethane. Chromatography of the residue on silica gel after evaporation of the solvent returned unreacted 4-bromoanisole (50%), thiolactam (38%) and (±)-(*rel*-3*R*,3′*R*)-1,1′- dimethyl-3,3′-bipyrrolidine-2,2′-dithione (104 mg, 18%). The product was recrystallized from acetone to give colourless cubes, m.p. 476–477 K.

S3. Refinement

The C-bound H atoms were geometrically placed (C—H bond lengths of 0.99 for methylene CH_2 and 0.98 for methyl CH_3) and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.5U_{eq}(C)$.

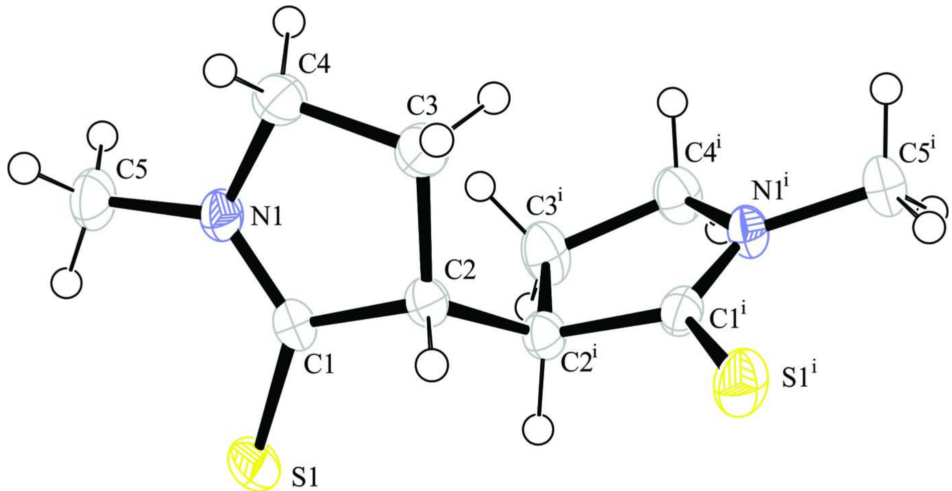

Figure 1

The asymmetric unit of (I) showing the atomic numbering scheme. Displacement ellipsoids are shown at the 50% probability level. Atoms with superscript (i) are at the symmetry position (-*x*, *y*, -*z* + 1/2).

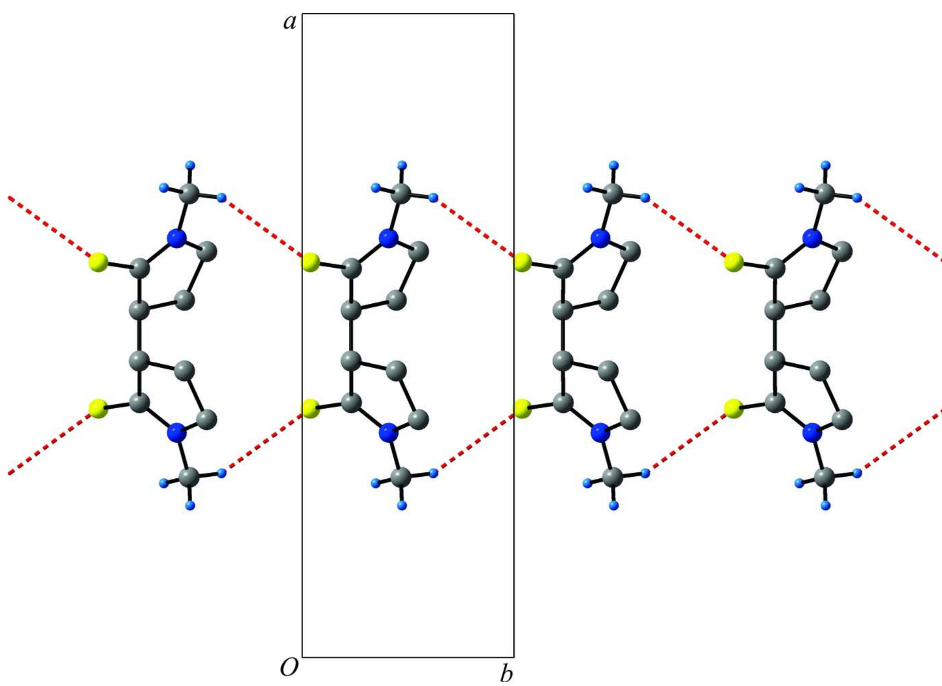

Figure 2

View of the hydrogen bonded chains of (I). C—H···S are shown as dashed red lines.

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b = 5.7237 (7) Å
c = 11.220 (2) Å
β = 122.009 (5)°
V = 1117.4 (3) Å^3
Z = 4

$F(000) = 488$
$D_x = 1.357$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 419 reflections
$\theta = 3.8–30°$
$\mu = 0.44$ mm^{-1}
$T = 173$ K
Cube, colourless
0.45 × 0.42 × 0.16 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.827$, $T_{max} = 0.933$
1759 measured reflections
1022 independent reflections
957 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 25.5°$, $\theta_{min} = 2.3°$
$h = -19 \rightarrow 23$
$k = -6 \rightarrow 6$
$l = -13 \rightarrow 5$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.077$
$S = 1.09$
1022 reflections
65 parameters
0 restraints
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0336P)^2 + 0.8972P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.22$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	$U_{iso}*/U_{eq}$
C1	0.60416 (8)	0.7676 (3)	0.29080 (15)	0.0237 (3)
C2	0.53949 (8)	0.7690 (3)	0.31920 (15)	0.0238 (3)
H2	0.544	0.9137	0.373	0.029*
C3	0.55488 (10)	0.5558 (3)	0.41423 (18)	0.0342 (4)
H3A	0.5591	0.6041	0.5028	0.041*
H3B	0.5127	0.4406	0.366	0.041*
C4	0.63050 (9)	0.4508 (3)	0.44413 (17)	0.0318 (4)
H4A	0.6706	0.4624	0.5453	0.038*
H4B	0.6238	0.2846	0.4155	0.038*
C5	0.72017 (9)	0.5339 (3)	0.36087 (19)	0.0343 (4)
H5A	0.7294	0.6527	0.3086	0.051*
H5B	0.7139	0.3809	0.3168	0.051*
H5C	0.764	0.5289	0.4582	0.051*
N1	0.65091 (7)	0.5918 (2)	0.35941 (13)	0.0254 (3)
S1	0.61374 (2)	0.96194 (8)	0.18993 (4)	0.03401 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0208 (7)	0.0274 (8)	0.0243 (7)	−0.0042 (6)	0.0130 (6)	−0.0032 (6)
C2	0.0227 (8)	0.0261 (8)	0.0265 (7)	0.0000 (6)	0.0157 (6)	0.0012 (6)
C3	0.0330 (9)	0.0395 (10)	0.0391 (9)	0.0072 (7)	0.0252 (8)	0.0136 (7)
C4	0.0318 (9)	0.0333 (9)	0.0366 (9)	0.0046 (7)	0.0225 (7)	0.0090 (7)
C5	0.0244 (9)	0.0406 (10)	0.0429 (10)	0.0030 (7)	0.0213 (7)	−0.0010 (7)
N1	0.0211 (6)	0.0296 (7)	0.0294 (6)	0.0014 (5)	0.0160 (5)	0.0015 (5)
S1	0.0327 (3)	0.0375 (3)	0.0394 (3)	−0.00300 (17)	0.0242 (2)	0.00804 (17)

Geometric parameters (Å, º)

C1—N1	1.320 (2)	C3—H3B	0.99
C1—C2	1.520 (2)	C4—N1	1.4672 (19)
C1—S1	1.6711 (15)	C4—H4A	0.99
C2—C3	1.539 (2)	C4—H4B	0.99
C2—C2^{i}	1.539 (3)	C5—N1	1.451 (2)
C2—H2	1	C5—H5A	0.98
C3—C4	1.526 (2)	C5—H5B	0.98
C3—H3A	0.99	C5—H5C	0.98
N1—C1—C2	109.09 (12)	N1—C4—C3	104.31 (12)
N1—C1—S1	126.33 (12)	N1—C4—H4A	110.9
C2—C1—S1	124.58 (11)	C3—C4—H4A	110.9
C1—C2—C3	105.06 (12)	N1—C4—H4B	110.9
C1—C2—C2^{i}	110.96 (14)	C3—C4—H4B	110.9
C3—C2—C2^{i}	114.74 (10)	H4A—C4—H4B	108.9
C1—C2—H2	108.6	N1—C5—H5A	109.5
C3—C2—H2	108.6	N1—C5—H5B	109.5
C2^{i}—C2—H2	108.6	H5A—C5—H5B	109.5
C4—C3—C2	106.00 (13)	N1—C5—H5C	109.5
C4—C3—H3A	110.5	H5A—C5—H5C	109.5
C2—C3—H3A	110.5	H5B—C5—H5C	109.5
C4—C3—H3B	110.5	C1—N1—C5	125.84 (13)
C2—C3—H3B	110.5	C1—N1—C4	115.37 (12)
H3A—C3—H3B	108.7	C5—N1—C4	118.76 (13)
N1—C1—C2—C3	−1.74 (17)	C2—C1—N1—C5	−179.01 (14)
S1—C1—C2—C3	178.97 (11)	S1—C1—N1—C5	0.3 (2)
N1—C1—C2—C2^{i}	−126.30 (10)	C2—C1—N1—C4	−1.04 (18)
S1—C1—C2—C2^{i}	54.41 (12)	S1—C1—N1—C4	178.24 (11)
C1—C2—C3—C4	3.64 (17)	C3—C4—N1—C1	3.37 (18)
C2^{i}—C2—C3—C4	125.78 (16)	C3—C4—N1—C5	−178.51 (14)
C2—C3—C4—N1	−4.13 (17)		

Symmetry code: (i) $-x+1, y, -z+1/2$.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C5—H5*B*···S1^{ii}	0.98	2.98	3.8373 (18)	146

Symmetry code: (ii) *x*, *y*−1, *z*.