

## (3*R*\*,3'*R*\*)-1,1'-Dimethyl-3,3'-biindoline-2,2'-dithione

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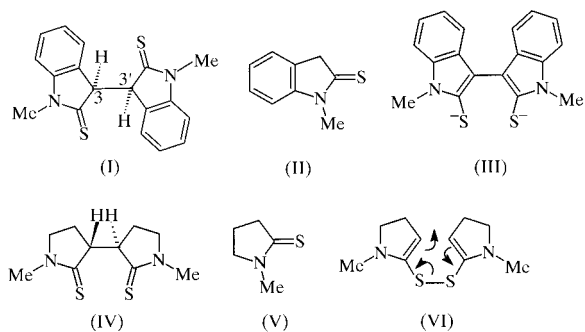
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The (3*R*\*,3'*R*\*) configuration of the title compound, C<sub>18</sub>H<sub>16</sub>N<sub>2</sub>S<sub>2</sub>, (I), has been unambiguously elucidated by X-ray analysis. Molecules of (I) have C<sub>2</sub> symmetry to a good approximation and a strongly folded shape. The interplanar angle between the two halves of a molecule is 67.11 (6)°.

### Comment

1,1'-Dimethyl-3,3'-biindoline-2,2'-dithione, (I), a central intermediate in our synthetic work (Schroth *et al.*, 1994, 2000), was obtained by oxidative dimerization of an indolinethione, (II), using iodine in methanolic solution (Hino *et al.*, 1969). The product is, in principle, able to exist in two diastereomeric forms differing in the chirality at the 3- and 3'-positions. Apart from the (3*R*\*,3'*R*\*) configuration, as formulated for (I), the (3*R*\*,3'*S*\*) counterpart must also be



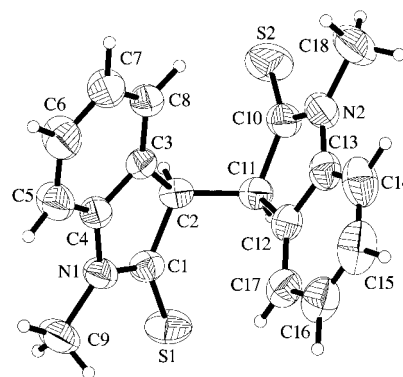
considered [the prefix (3*R*\*,3'*R*\*) corresponds to DL, and (3*R*\*,3'*S*\*) [(3*R*,3'*S*) ≡ (3*S*,3'*R*)] to meso in the older IUPAC recommendations]. According to NMR spectroscopic characterization and thin-layer chromatography findings, the product is homogeneous. Furthermore, its regeneration from the dithiolate, (III), by acidification provides evidence that the (3*R*\*,3'*R*\*) configuration is thermodynamically favoured with respect to the steric alternative (3*R*\*,3'*S*\*) (Schroth *et al.*, 2000). An exact assignment, however, was lacking until now.

A comparison with 1,1'-dimethyl-3,3'-bipyrrolidine-2,2'-dithione, (IV), is useful. This compound arose from the corresponding thiopyrrolidone, (V), *via* deprotonation and treatment with iodine (Tamaru *et al.*, 1978). Here, the assignment of the (3*R*\*,3'*R*\*) configuration was based on chemical transformations and the assumption that a Cope-type rearrangement of the disulfide formed as the major product, (VI), should proceed through a chair-like arrangement.

In order to classify unequivocally the configuration of compound (I), an X-ray analysis has been performed. Its result confirms the presence of the (racemic) (3*R*\*,3'*R*\*) diastereomer.

The molecular structure of (I) and the atomic numbering used are shown in Fig. 1. The molecule has a strongly folded shape and exhibits C<sub>2</sub> symmetry to a good approximation; the (non-crystallographic) twofold axis is a perpendicular bisector of the C2–C11 bond. With respect to the bond lengths, the only significant deviation from the C<sub>2</sub> symmetry is shown by C4–C5 and C13–C14, which differ by 0.023 (4) Å. The two indoline ring systems are planar to a good approximation, the r.m.s. deviations of the fitted endocyclic atoms being 0.013 (N1/C1–C8) and 0.021 Å (N2/C10–C17), respectively. The maximum deviations of the S and methyl-C atoms from the corresponding least squares planes are not greater than 0.1 Å. The dihedral angle subtended by the two planes is 67.11 (6)° and the antiperiplanar conformation is illustrated by the torsion angle C1–C2–C11–C10 = 174.8 (2)°.

Most of the bond lengths and angles in (I) agree well with expected values but some details are worthy of discussion. The N atoms in (I) are sp<sup>2</sup> hybridized (the bond angles sum to 360.0° at N1 and 359.9° at N2). Due to their different environment, the non-equivalent endocyclic N–C bonds have significantly unequal lengths. The standard values for an Nsp<sup>2</sup>–Csp<sup>2</sup> single or double bond are given as 1.40 and 1.29 Å, respectively, in the literature (Rademacher, 1987). Compared with these values, N1–C4 [1.424 (3) Å] and N2–C13 [1.413 (3) Å] are slightly longer than a normal single bond, and N1–C1 [1.335 (3) Å] and N2–C10 [1.339 (4) Å] are near the mean value of a single and a double bond. On



**Figure 1**  
The molecular structure and atomic numbering of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

checking the 1998 version of the Cambridge Structural Database (Allen & Kennard, 1993), it appeared that no crystal structure containing a bis(thioxindole) moiety is known. Of the corresponding bis(oxindoles), the racemic (Suyama *et al.*, 1994) and *meso* (Kato *et al.*, 1985) forms of 1,1',3,3'-tetramethylleucoisoidigo are the most suitable for structural comparison. In their crystal structures the N—C bond lengths discussed above also differ, but less remarkably, by about 0.04 Å. The C2—C11 bond linking the molecular halves has a normal length of 1.537 (2) Å in (I), whereas in the bis(oxindoles) it is markedly lengthened (1.581 and 1.575 Å, respectively).

## Experimental

Compound (I) was synthesized according to the literature method of Hino *et al.* (1969), recrystallized from benzene and vacuum dried to give colourless prisms [thin-layer chromatography with benzene/*n*-hexane (2:1):  $R_f = 0.15$ ; m.p. 455 K].

### Crystal data

$C_{18}H_{16}N_2S_2$	$D_x = 1.307 \text{ Mg m}^{-3}$
$M_r = 324.45$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 80 reflections
$a = 17.635 (5) \text{ \AA}$	$\theta = 7.6\text{--}13.9^\circ$
$b = 8.418 (2) \text{ \AA}$	$\mu = 0.320 \text{ mm}^{-1}$
$c = 22.591 (5) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 100.50 (3)^\circ$	Prism, yellow
$V = 3297.5 (14) \text{ \AA}^3$	$0.49 \times 0.21 \times 0.15 \text{ mm}$
$Z = 8$	

### Data collection

Stoe Stadi-4 four-circle diffractometer	$\theta_{\max} = 24.97^\circ$
Scan width ( $\omega$ ) = 1.05–1.20, scan ratio $2\theta:\omega = 1.00$	$h = -20 \rightarrow 20$
5790 measured reflections	$k = -10 \rightarrow 10$
2895 independent reflections	$l = -26 \rightarrow 26$
1664 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.036$	frequency: 60 min
	intensity decay: 3.4%

### Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.057P)^2]$
$wR(F^2) = 0.106$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.991$	$(\Delta/\sigma)_{\max} = 0.023$
2895 reflections	$\Delta\rho_{\max} = 0.194 \text{ e \AA}^{-3}$
241 parameters	$\Delta\rho_{\min} = -0.269 \text{ e \AA}^{-3}$

The quadrants  $\pm h, +k, +l$  and  $\pm h, -k, -l$  were measured. H atoms were located by a difference Fourier synthesis and refined with isotropic displacement parameters, with the exception of the methyl-H atom positions, which were idealized by geometrical considerations and allowed to rotate but not tip.

**Table 1**

Selected geometric parameters (Å, °).

S1—C1	1.649 (2)	N2—C13	1.413 (3)
S2—C10	1.650 (3)	C1—C2	1.522 (3)
N1—C1	1.335 (3)	C2—C11	1.537 (3)
N1—C4	1.424 (3)	C10—C11	1.515 (3)
N2—C10	1.339 (4)		
N1—C1—C2	107.7 (2)	N2—C10—C11	107.6 (2)
N1—C1—S1	126.02 (18)	N2—C10—S2	126.3 (2)
C1—C2—C11	112.03 (19)	C10—C11—C2	110.7 (2)
C3—C2—C11—C12	49.3 (3)	C3—C2—C11—C10	−67.0 (3)
C1—C2—C11—C12	−68.9 (3)	C1—C2—C11—C10	174.8 (2)

Data collection: *DIF4* (Stoe & Cie, 1991); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1991); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP/PC* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: *JZ1394*). Services for accessing these data are described at the back of the journal.

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