

**Data collection**

Nonius CAD-4 diffractometer	$\theta_{\max} = 71.74^\circ$
$\theta/2\theta$ scans	$h = -6 \rightarrow 8$
Absorption correction: none	$k = 0 \rightarrow 14$
4211 measured reflections	$l = 0 \rightarrow 30$
4211 independent reflections	2 standard reflections
4010 reflections with $I > 2\sigma(I)$	frequency: 60 min
	intensity decay: none

**Refinement**

Refinement on $F^2$	$\Delta\rho_{\max} = 0.323 \text{ e } \text{\AA}^{-3}$
$R[F^2 > 2\sigma(F^2)] = 0.060$	$\Delta\rho_{\min} = -0.250 \text{ e } \text{\AA}^{-3}$
$wR(F^2) = 0.179$	Extinction correction:
$S = 1.062$	<i>SHELXL93</i>
4211 reflections	Extinction coefficient:
665 parameters	0.0014 (4)
H atoms riding	Scattering factors from
$w = 1/[\sigma^2(F_o^2) + (0.1137P)^2 + 1.7798P]$	<i>International Tables for Crystallography</i> (Vol. C)
where $P = (F_o^2 + 2F_c^2)/3$	Absolute configuration:
$(\Delta/\sigma)_{\max} = -0.013$	Flack (1983)
	Flack parameter = $-0.2$ (3)

The disordered atoms in (1) were refined using the *SAME*, *SADI* and *SIMU* restraints in *SHELXL93* (Sheldrick, 1993); the disordered atoms in (2') were refined using *SAME* and *SADI* restraints. The C15', C15B, C16', C16B and methyl ester disordered atoms at C13 were kept isotropic to avoid unrealistic displacement parameters.

For both compounds, data collection: *NRCCAD DATCOL* (Le Page, White & Gabe, 1986); cell refinement: *NRCCAD TRUANG*; data reduction: *NRCVAX DATRD2* (Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to solve structures: *NRCVAX SOLVER*; program(s) used to refine structures: *SHELXL93* (Sheldrick, 1993); molecular graphics: *ORTEP* in *Xtal\_GX* (Johnson, 1995); software used to prepare material for publication: *SHELXL93 ACTA*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1287). Services for accessing these data are described at the back of the journal.

**References**

- Couturier, M. (1997). PhD thesis, Université de Sherbrooke, Québec, Canada.
- Couturier, M., Dory, Y., Rouillard, F., Fortin, J. B. & Deslongchamps, P. (1997). *J. Am. Chem. Soc.* Submitted.
- Desiraju, G. R., Kashino, S., Coombs, M. M. & Glusker, J. P. (1993). *Acta Cryst.* **B49**, 880–892.
- Deslongchamps, P. (1992). *Pure Appl. Chem.* **64**, 1831–1847.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- Johnson, C. K. (1995). *ORTEP* in *Xtal\_GX*, edited by S. R. Hall & D. du Boulay, University of Western Australia, Australia.
- Lamothe, S., Ndiwbami, A. & Deslongchamps, P. (1988a). *Tetrahedron Lett.* **29**, 1639–1640.
- Lamothe, S., Ndiwbami, A. & Deslongchamps, P. (1988b). *Tetrahedron Lett.* **29**, 1641–1644.
- Le Page, Y., White, P. S. & Gabe, E. J. (1986). *NRCCAD. An Enhanced CAD-4 Control Program. Proc. Am. Crystallogr. Hamilton Meet. Abstr.* PA23.

- Ndiwbami, A., Lamothe, S., Soucy, P., Goldstein, S. & Deslongchamps, P. (1993). *Can. J. Chem.* **71**, 714–725.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

*Acta Cryst.* (1997). **C53**, 1701–1703

**Dimethyl *N,N'*-Bis(*endo*-himmoyl)-(R,R)-cystine†**

DAVID E. HIBBS,<sup>a</sup> MICHAEL B. HURSTHOUSE,<sup>a</sup> K. M. ABDUL MALIK<sup>a</sup> AND MICHAEL NORTH<sup>b</sup>

<sup>a</sup>*Department of Chemistry, University of Wales Cardiff, PO Box 912, Park Place, Cardiff CF1 3TB, Wales, and*

<sup>b</sup>*Department of Chemistry, University of Wales Bangor, Gwynedd LL57 2UW, Wales. E-mail: sackam@cardiff.ac.uk*

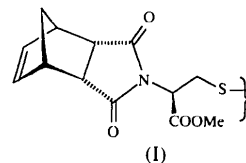
(Received 2 October 1996; accepted 13 May 1997)

**Abstract**

The title compound, C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>, contains two norbornene rings, both with *endo* substituents, and an (*M*)-helical disulfide. Both ester groups adopt the *s-cis* conformation, and the bond lengths and angles are within the expected values.

**Comment**

As part of an ongoing study concerned with the synthesis of biomimetic polymers derived from amino acids (Coles *et al.*, 1994; Biagini *et al.*, 1995), the synthesis of the title compound, (I), was undertaken (Biagini *et al.*, 1995). It was envisaged that polymerization or copolymerization of (I) by a ring-opening metathesis procedure would lead to synthetic polymers in which the cystine units mimic the crosslinking role of cystine residues in proteins. An X-ray structure determination of (I) was undertaken to allow its conformation to be compared with those of other cystine derivatives.



This study confirmed the structure (Fig. 1) and relative stereochemistry of (I). The imide substituents on both norbornene rings adopt the *endo* configuration, and the two chiral centres (C10 and C10') have the same

† Alternative systematic name: dimethyl 2,7-bis(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-4,7-methano-2-isoindolyl)-4,5-dithiaoctanedioate.

absolute configuration, known to be *R* since (*R*)-cystine was used as the starting material in the synthesis of (I). The correct determination of the absolute structure was also indicated by the Flack (1983) parameter, which refined to 0.1 (2). The methyl esters of (I) adopt the *s-cis* conformation, as is found in other esters. The Me—O—C—O torsion angles are close to 0°, *i.e.* 1.7 (8) and -4.0 (8)°, which suggests planarity of the ester groups. The dimensions of the two chemically equivalent halves of the molecule are mutually comparable, showing only minor differences. The bond lengths and angles are as expected for this type of molecule. The O atoms attached to the five-membered imide rings are only slightly displaced out of the respective ring planes [O1 0.005 (14), O2 0.105 (9), O1' 0.079 (8) and O2' 0.048 (9) Å], probably as a result of steric/hydrogen-bonded interactions. Several weak intermolecular hydrogen bonds involving these O atoms can be identified (see Table 2).

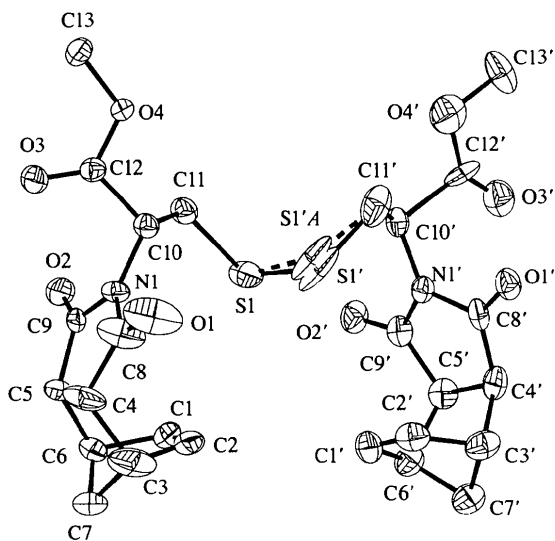


Fig. 1. Molecular structure of (I) showing the atom-numbering scheme. S1' and S1'A denote the two positions (67 and 33%, respectively) of the disordered S atom. Displacement ellipsoids are drawn at 35% probability.

The dihedral angle around the disulfide unit of (I) is -88.1 (6)° (for S1—S1'), which is comparable with the approximately 90° dihedral angle commonly found in disulfides, and corresponding to an (*M*)-helical disulfide. Both (*M*)- and (*P*)-helical disulfides have been found in cystine and penicillamine derivatives (Peterson, Steinrauf & Jensen, 1960; Ananthakrishnan & Srinivasan, 1964; Cumberbatch, North & Zagotto, 1993).

## Experimental

Single crystals of the title compound were grown from *d*<sub>8</sub>-toluene by slow evaporation of the solvent in a narrow-necked tube.

## Crystal data

C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>8</sub>S<sub>2</sub>  
*M<sub>r</sub>* = 560.62  
 Orthorhombic  
*P*2<sub>1</sub>2<sub>1</sub>  
*a* = 8.3900 (9) Å  
*b* = 13.270 (2) Å  
*c* = 23.2580 (15) Å  
*V* = 2589.4 (5) Å<sup>3</sup>  
*Z* = 4  
*D<sub>x</sub>* = 1.438 Mg m<sup>-3</sup>  
*D<sub>m</sub>* not measured

## Data collection

Delft Instruments FAST area detector  
 Intensity data collected according to Darr, Drake, Hursthouse & Malik (1993)  
 Absorption correction: none  
 8735 measured reflections

## Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.073  
*wR*(*F*<sup>2</sup>) = 0.194  
*S* = 1.088  
 3896 reflections  
 348 parameters  
 H atoms riding  
*w* = 1/[σ<sup>2</sup>(*F*<sub>o</sub><sup>2</sup>) + (0.1187*P*)<sup>2</sup>]  
 where *P* = (*F*<sub>o</sub><sup>2</sup> + 2*F*<sub>c</sub><sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = -0.001

## Mo Kα radiation

λ = 0.71069 Å  
 Cell parameters from 250 reflections  
 θ = 1.77–24.97°  
 μ = 0.259 mm<sup>-1</sup>  
*T* = 293 (2) K  
 Prism  
 0.24 × 0.16 × 0.12 mm  
 Colourless

3896 independent reflections  
 2982 reflections with *I* > 2σ(*I*)  
*R*<sub>int</sub> = 0.054  
 θ<sub>max</sub> = 24.97°  
*h* = -9 → 5  
*k* = -15 → 14  
*l* = -27 → 27

Δρ<sub>max</sub> = 1.140 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.447 e Å<sup>-3</sup>  
 Extinction correction: none  
 Scattering factors from *International Tables for Crystallography* (Vol. C)  
 Absolute configuration: Flack (1983)  
 Flack parameter = 0.1 (2)

Table 1. Selected geometric parameters (Å, °)

S1—C11	1.817 (4)	S1'—C11'	1.809 (5)
S1—S1'A	2.041 (5)	S1'A—C11'	1.809 (5)
S1—S1'	2.042 (4)	N1'—C8'	1.390 (7)
N1—C8	1.396 (8)	N1'—C9'	1.396 (8)
N1—C9	1.400 (8)	N1'—C10'	1.453 (8)
N1—C10	1.441 (7)	O1'—C8'	1.203 (7)
O1—C8	1.201 (9)	O2'—C9'	1.184 (7)
O2—C9	1.197 (7)	O3'—C12'	1.191 (7)
O3—C12	1.183 (7)	O4'—C12'	1.279 (8)
O4—C12	1.324 (7)	O4'—C13'	1.496 (9)
O4—C13	1.464 (7)	C1'—C2'	1.342 (10)
C1—C2	1.297 (11)	C1'—C6'	1.502 (9)
C1—C6	1.476 (9)	C2'—C3'	1.506 (10)
C2—C3	1.475 (12)	C3'—C7'	1.543 (10)
C3—C7	1.529 (12)	C3'—C4'	1.570 (9)
C3—C4	1.570 (13)	C4'—C8'	1.515 (9)
C4—C8	1.487 (10)	C4'—C5'	1.534 (9)
C4—C5	1.529 (10)	C5'—C9'	1.530 (9)
C5—C9	1.497 (8)	C5'—C6'	1.549 (9)
C5—C6	1.581 (9)	C6'—C7'	1.526 (9)
C6—C7	1.507 (10)	C10'—C11'	1.527 (9)
C10—C11	1.527 (7)	C10'—C12'	1.528 (2)
C10—C12	1.543 (7)		
C11—S1—S1'A	99.4 (9)	O4—C12—C10	109.0 (5)
C11—S1—S1'	106.9 (4)	C11'—S1'—S1	103.8 (3)
C8—N1—C9	111.9 (5)	C11'—S1'A—S1	103.8 (4)
C8—N1—C10	123.1 (5)	C8'—N1'—C9'	114.2 (5)
C9—N1—C10	124.9 (4)	C8'—N1'—C10'	123.3 (5)
C12—O4—C13	115.6 (5)	C9'—N1'—C10'	121.3 (5)
C2—C1—C6	107.1 (7)	C12'—O4'—C13'	109.4 (6)

C1—C2—C3	108.9 (7)	C2'—C1'—C6'	107.6 (6)
C2—C3—C7	100.2 (7)	C1'—C2'—C3'	107.4 (6)
C2—C3—C4	106.4 (5)	C2'—C3'—C7'	100.5 (6)
C7—C3—C4	98.9 (7)	C2—C3—C4'	106.2 (5)
C8—C4—C5	104.3 (5)	C7'—C3'—C4'	98.7 (5)
C8—C4—C3	115.3 (8)	C8'—C4'—C5'	105.4 (5)
C5—C4—C3	103.1 (5)	C8'—C4'—C3'	116.6 (5)
C9—C5—C4	106.3 (5)	C5'—C4'—C3'	102.8 (5)
C9—C5—C6	116.8 (5)	C9'—C5'—C4'	105.2 (5)
C4—C5—C6	101.8 (5)	C1'—C6'—C7'	100.5 (6)
C1—C6—C7	101.7 (6)	C1'—C6'—C5'	106.4 (5)
C1—C6—C5	107.4 (5)	C7'—C6'—C5'	99.8 (6)
C7—C6—C5	99.0 (6)	C6'—C7'—C3'	94.1 (6)
C6—C7—C3	93.4 (5)	O1'—C8'—N1'	123.7 (6)
O1—C8—N1	120.9 (6)	O1'—C8'—C4'	128.3 (5)
O1—C8—C4	129.5 (6)	N1'—C8'—C4'	107.9 (5)
N1—C8—C4	109.6 (6)	O2'—C9'—N1'	123.7 (6)
O2—C9—N1	124.1 (5)	O2'—C9'—C5'	129.0 (6)
O2—C9—C5	128.3 (6)	N1'—C9'—C5'	107.2 (5)
N1—C9—C5	107.6 (5)	N1'—C10'—C11'	111.2 (5)
N1—C10—C11	114.5 (4)	N1'—C10'—C12'	104.9 (4)
N1—C10—C12	110.4 (4)	C11'—C10'—C12'	118.2 (5)
C11—C10—C12	109.2 (4)	C10'—C11'—S1'A	120.1 (8)
C10—C11—S1	113.5 (4)	C10'—C11'—S1'	113.8 (5)
O3—C12—O4	125.2 (5)	O3'—C12'—C10'	124.6 (6)
O3—C12—C10	125.8 (5)	O4'—C12'—C10'	110.8 (6)

Table 2. Hydrogen-bonding geometry (Å, °)

D—H...A	H...A	D...A	D—H...A
C11—H11A...O1 <sup>i</sup>	2.402 (8)	3.102 (8)	128.7 (6)
C3—H3...O2 <sup>ii</sup>	2.454 (9)	3.323 (9)	147.5 (7)
C4'—H4'...O2 <sup>iii</sup>	2.511 (8)	3.484 (8)	172.0 (6)
C13F'—H13F...O2 <sup>iv</sup>	2.38 (2)	3.289 (9)	158 (1)
C6—H6...O4 <sup>v</sup>	2.482 (8)	3.286 (8)	139.1 (6)

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

One S atom of the disulfide bridge was disordered between two positions (S1' and S1'A with 0.67 and 0.33 occupancies, respectively). Final refinement (Sheldrick, 1993) included (a) the displacement-coefficient restraints *ISOR* of 0.005 for C12' and 0.008 for O1 to prevent these atoms becoming 'non-positive definite', and *EADP* for S1' and S1'A to force these partially occupied atoms to have identical displacement coefficients, and (b) bond-length restraints *DFIX* of 1.810 (5) Å for C11—S1, C11'—S1' and C11'—S1'A, 2.040 (5) Å for S1—S1', and 1.520 (5) Å for C10'—C12'. The problem of disorder around the sulfur site gave rise to rather elongated ellipsoids for S1' and S1'A. The highest residual electron density peak (1.14 Å) did not indicate any feature of chemical significance.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *REFINE* (incorporated in *MADNES*). Data reduction: *ABSMAD* (Karaulov, 1991). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL93*.

We thank the EPSRC for support of the X-ray Crystallography Service at UWC.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: KA1223). Services for accessing these data are described at the back of the journal.

## References

Ananthkrishnan, N. & Srinivasan, R. (1964). *Indian J. Pure Appl. Phys.* **2**, 62–64.

- Biagini, S. C. G., Bush, S. M., Gibson, V. C., Mazzariol, L., North, M., Teasdale, W. G., Williams, C. M., Zagotto, G. & Zamuner, D. (1995). *Tetrahedron*, **51**, 7247–7262.
- Coles, M. P., Gibson, V. C., Mazzariol, L., North, M., Teasdale, W. G., Williams, C. M. & Zamuner, D. (1994). *J. Chem. Soc. Chem. Commun.* pp. 2505–2506.
- Cumberbatch, S., North, M. & Zagotto, G. (1993). *Tetrahedron*, **49**, 9049–9066.
- Darr, J. A., Drake, S. R., Hursthouse, M. B. & Malik, K. M. A. (1993). *Inorg. Chem.* **32**, 5704–5708.
- Davies, K. (1983). *SNOOPI. Program for Crystal Structure Drawing*. University of Oxford, England.
- Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.
- Karaulov, A. I. (1991). *ABSMAD. Program for FAST Data Processing*. University of Wales, Cardiff, Wales.
- Peterson, J., Steinrauf, L. K. & Jensen, L. H. (1960). *Acta Cryst.* **13**, 104–109.
- Pflugrath, J. W. & Messerschmidt, A. (1989). *MADNES*. Version of 11 September 1989. Distributed by Delft Instruments, Delft, The Netherlands.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

*Acta Cryst.* (1997). **C53**, 1703–1705

## Chiral Hydroxylamines. IV. 1-(*N*-Benzyl-*N*-hydroxyamino)-2:3;4:5-di-*O*-isopropylidene- $\alpha$ -D-mannofuranose

PEDRO MERINO, FRANCISCO L. MERCHAN, TOMAS TEJERO AND SANTIAGO FRANCO

*Departamento de Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, E-50009 Zaragoza, Spain. E-mail: pmerino@posta.unizar.es*

(Received 4 June 1997; accepted 18 June 1997)

## Abstract

The title compound, C<sub>19</sub>H<sub>27</sub>NO<sub>6</sub>, was synthesized from the reaction of the known D-mannose diacetonide with *N*-benzylhydroxylamine in the presence of zinc dichloride. The absolute configuration at the anomeric center has been deduced from that of the mannose used in the synthesis. In the crystal, molecules are joined by O—H...O intermolecular hydrogen bonds.

## Comment

In previous reports we have described the synthesis of nitrones by condensation of the corresponding parent carbonyl compounds with *N*-substituted hydroxylamines (Franco, Merchan, Merino & Tejero, 1995; Dondoni, Franco, Junquera, Merchan, Merino & Tejero, 1994). Application of that methodology to the protected