Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1279). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3-Dihydro-1,4-dithiaphenanthrene 1,4-Dioxide

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Abstract

The crystal and molecular structure of the title compound, $C_{12}H_{10}O_2S_2$, has been determined. The most relevant features are the *trans* disposition of the sulfinyl groups and the distorted 1,3-diplanar form of the 1,4-dithiane 1,4-dioxide ring.

Comment

As part of an investigation of the synthesis of organic compounds having possible pharmacological activity (Plumet, 1995), 2,3-dihydro-1,4-dithiaphenanthrene 1,4-

dioxide, (I), was obtained and its structure analyzed by standard analytical techniques (microanalysis, MS, NMR and IR). In order to obtain information about the stereochemistry of the sulfinyl groups in the 1,4-dithiane 1,4-dioxide ring and to confirm the assigned structure, the X-ray analysis of (I) was undertaken.

(I)
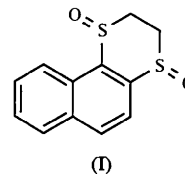
The structure of (I) consists of an essentially planar naphthalene ring condensed with a 1,4-dithiane 1,4-dioxide ring. The S atoms lie only 0.166 (2) and 0.202 (2) Å from the plane of the aromatic ring. Bond lengths and angles are in good agreement with those found in analogous compounds, in spite of the possible disorder of the C2 atom; the crystallographic data used were retrieved from the Cambridge Structural Database (Allen *et al.*, 1979). According to the data so far accumulated (Allen *et al.*, 1987), a normal S—C single-bond length is about 1.79 (1) Å. The C—S distances found in the present compound [1.772 (7), 1.802 (4), 1.782 (4) and 1.795 (5) Å] imply a mostly single-bond character and consequently there is no evidence of conjugation between the naphthalene ring and the sulfinyl groups. The S=O bond lengths of 1.467 (4) and 1.506 (4) Å are very close to the corresponding double-bond length of 1.497 (13) Å found by Allen *et al.* (1987). The C—S—C angles of 100.8 (3) and 96.7 (3)° are also typical.
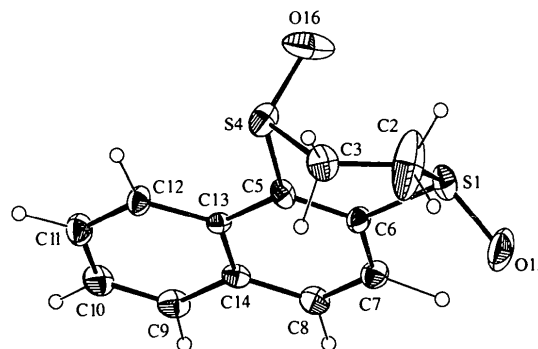

Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids.

The 1,4-dithiane 1,4-dioxide ring has a distorted 1,3-diplanar form (Toromanoff, 1980) as may be deduced from the torsion angles C2—S1—C6—C5 36.3 (5), C6—S1—C2—C3 −14.8 (10), S1—C2—C3—S4 −35.9 (11), C2—C3—S4—C5 64.8 (7), C3—S4—C5—C6 −46.8 (4) and S4—C5—C6—S1 −2.0 (6)°. The sulfinyl groups were found to be mutually *trans* in this ring.

Experimental

The synthesis of the title compound was carried out by reaction of 2,3-dihydro-1,4-dithiaphenanthrene and m-chloroperoxy-benzoic acid (molar ratio 1:2) in CCl_4 solution for 4 h at 298 K. Recrystallization was from ethanol solution.

Crystal data

$C_{12}H_{10}O_2S_2$	Cu $K\alpha$ radiation
$M_r = 250.32$	$\lambda = 1.54180$ Å
Orthorhombic	Cell parameters from 47
$Pbca$	reflections
$a = 9.391\,(2)$ Å	$\theta = 6–33°$
$b = 11.140\,(2)$ Å	$\mu = 4.367$ mm^{-1}
$c = 20.373\,(4)$ Å	$T = 293\,(2)$ K
$V = 2131.3\,(7)$ Å^3	Prism
$Z = 8$	$0.33 \times 0.13 \times 0.10$ mm
$D_x = 1.560$ Mg m^{-3}	Colourless
D_m not measured	

Data collection

Seifert XRD 3000S diffrac-tometer	929 observed reflections $[I > 2\sigma(I)]$
$\omega/2\theta$ scans	$\theta_{max} = 60°$
Absorption correction:	$h = 0 \rightarrow 10$
refined from ΔF	$k = 0 \rightarrow 11$
($DIFABS$; Walker &	$l = 0 \rightarrow 22$
Stuart, 1983)	2 standard reflections
$T_{min} = 0.463$, $T_{max} = 0.838$	frequency: 90 min intensity decay: none
1524 measured reflections	
1524 independent reflections	

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R(F) = 0.0435$	$\Delta\rho_{max} = 0.42$ e Å^{-3}
$wR(F^2) = 0.1058$	$\Delta\rho_{min} = -0.22$ e Å^{-3}
$S = 0.883$	Extinction correction: none
1524 reflections	Atomic scattering factors
185 parameters	from $International\ Tables$
H atoms refined isotropically	$for\ Crystallography$ (1992,
$w = 1/[\sigma^2(F_o^2) + (0.057P)^2]$	Vol. C, Tables 4.2.6.8 and
where $P = \frac{1}{3}[\max(F_o^2,0) + 2F_c^2]$	6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
S1	0.97424 (14)	0.18203 (12)	0.05255 (5)	0.0425 (4)
C2	0.8118 (10)	0.1284 (10)	0.0194 (4)	0.096 (4)
C3	0.7017 (6)	0.0698 (6)	0.0584 (3)	0.048 (2)
S4	0.77086 (15)	−0.02313 (11)	0.12301 (5)	0.0405 (4)
C5	0.8512 (5)	0.0946 (4)	0.1692 (2)	0.0244 (10)
C6	0.9337 (5)	0.1803 (4)	0.1390 (2)	0.0273 (11)
C7	1.0074 (5)	0.2680 (4)	0.1761 (2)	0.0338 (12)
C8	0.9961 (5)	0.2670 (4)	0.2423 (2)	0.0354 (12)
C9	0.8992 (6)	0.1830 (5)	0.3456 (2)	0.0378 (13)
C10	0.8165 (6)	0.1007 (5)	0.3764 (2)	0.0404 (13)
C11	0.7389 (6)	0.0164 (5)	0.3404 (2)	0.0377 (12)
C12	0.7474 (6)	0.0146 (4)	0.2739 (2)	0.0313 (11)
C13	0.8345 (5)	0.0954 (4)	0.2389 (2)	0.0229 (10)
C14	0.9118 (4)	0.1831 (4)	0.2760 (2)	0.0282 (10)
O15	0.9876 (5)	0.3088 (3)	0.0340 (2)	0.0701 (12)
O16	0.8927 (5)	−0.0924 (3)	0.0934 (2)	0.0770 (14)

Table 2. *Selected geometric parameters (Å, °)*

S1—O15	1.467 (4)	C3—S4	1.795 (5)
S1—C2	1.772 (7)	S4—O16	1.506 (4)
S1—C6	1.802 (4)	S4—C5	1.782 (4)
C2—C3	1.459 (9)	C5—C6	1.376 (5)
O15—S1—C2	107.5 (4)	O16—S4—C3	106.1 (3)
O15—S1—C6	106.2 (2)	C5—S4—C3	96.7 (3)
C2—S1—C6	100.8 (3)	C6—C5—S4	120.8 (3)
C3—C2—S1	123.5 (5)	C13—C5—S4	118.9 (3)
C2—C3—S4	113.7 (5)	C5—C6—S1	124.3 (3)
O16—S4—C5	105.5 (2)	C7—C6—S1	114.3 (3)
C6—S1—C2—C3	−14.8 (10)	C3—S4—C5—C6	−46.8 (4)
S1—C2—C3—S4	−35.9 (11)	S4—C5—C6—S1	−2.0 (6)
C2—C3—S4—C5	64.8 (7)	C2—S1—C6—C5	36.3 (5)

The thermal motion parameters of the C2 atom suggest that there could be some disorder affecting this atom. This is also indicated by the S2—C2 and C2—C3 distances and the S2—C2—C3 angle, but no disorder model could be found. The molecular parameters of C2, however, may be less reliable than others. The H atoms attached to C2 could not therefore be localized in the ΔF maps and so were placed geometrically.

Data collection: Seifert XRD 3000S software. Cell refinement: *LSUCRE* (Appleman, 1971). Data reduction: *XRAY*80 (Stewart, Kundell & Baldwin, 1980). Program(s) used to solve structure: *MULTAN*80 (Main *et al.*, 1980). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *Xtal*3.0 (Hall & Stewart, 1990). Software used to prepare material for publication: *SHELXL*93.

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(I)
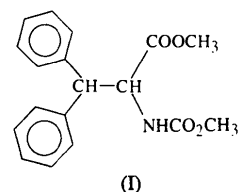
Methyl 2-Methoxycarbonylamino-3,3-diphenylpropionate, an Interesting Diphenylalanine (DIP) Derivative

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Abstract

Molecules of the interesting racemic 3,3-diphenylalanine derivative, $C_{18}H_{19}NO_4$, contain a DIP amino acid residue which adopts a semi-extended conformation. The values of φ and ψ are −91.0 (5) and 130.4 (4)°, respectively, for the L enantiomer. The crystal structure consists of cyclic (urethane)N—H···O=C(methyl ester) hydrogen-bonded dimers piled up in columns running parallel to the crystallographic a axis.

Comment

Models for bioactive conformations of peptides have been deduced from structure–activity relationships involving local or large-size constraints of the backbone orientation *via* the incorporation of *N*-methylamino acids or proline, or through cyclization. However, in order to probe the relative arrangement of the side chain of each amino acid and then generate a more precise three-dimensional envelope representing the space-filling requirements of the bioactive conformation, topographic probes which will stabilize one or two rotamers of the side chain have to be designed (Kazmierski, Yamamura & Hruby, 1991). Diphenylalanine (DIP) (Chen, Beylin, Marlatt, Leja & Guel, 1992; Josien, Martin & Chassaing, 1991) was first selected because the aromatic rings of phenylalanine often play a crucial role in peptide–receptor recognition. Recently, D-3,3-diphenylalanine (D-DIP) has proved to be a key substructural substituent in a potent peptidyl antagonist of the ET_A and ET_B endothelin receptors (Cody *et al.*, 1992). We now report the stereochemical details of the title compound, (I), an interesting DIP derivative.

The urethane linkage is found in the usual *trans* conformation [torsion angle ω_0 (C3—N—C4—O4) is 178.6 (4)°]. This, together with the *trans* arrangement of the C5—O4 bond relative to C4—N [torsion angle θ_1 (C5—O4—C4—N) is 178.0 (4)°], allows us to classify the urethane moiety as type *b* (*trans,trans*) (Benedetti *et al.*, 1980) (Fig. 1).
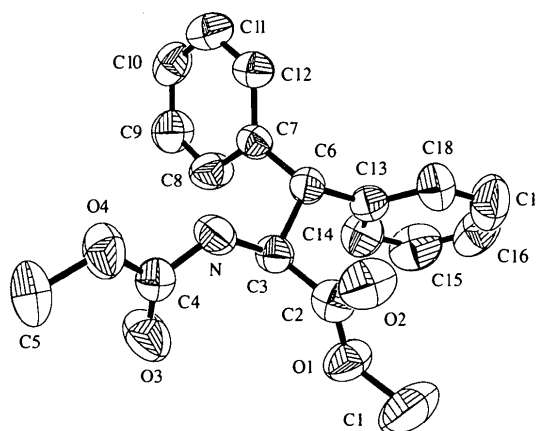

Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids. H atoms have been omitted for clarity.

The methyl ester group has the C1—O1—C2—C3 sequence in a *trans* disposition [176.1 (4)°] and the angle between the average planes of the urethane and methyl ester groups is 73.4 (2)°.

The DIP residue adopts a semi-extended conformation (IUPAC–IUB Commission on Biochemical Nomenclature, 1970); for the L enantiomer, the backbone torsion angles [C4—N—C3—C2 (φ) −91.0 (5) and N—C3—C2—O1 (ψ) 130.4 (4)°] fall in the *F* region of the conformational map (Zimmerman, Pottle, Nemethy & Scheraga, 1977). The two phenyl groups are *gauche* and *trans* with respect to the peptide chain, since the torsion angles around the C_α—C_β bond of the side chain [N—C3—C6—C7 (χ^{11}) and N—C3—C6—C13 (χ^{12})] are −60.3 (5) and 171.1 (4)°. The dihedral angle between the phenyl rings is 68.8 (2)°.

The crystal structure of (I) consists of cyclic hydrogen-bonded centrosymmetric dimers piled up along the crystallographic a axis. The urethane H atom is hydrogen bonded to the methyl ester O2 atom of the nearest symmetry-related molecule [H···O2^i 2.28, N···O2^i 3.109 (6) Å and N—H···O2^i 162°; symmetry code: (i) $2 - x$, $-1 - y$, $-1 - z$].