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11-Methyl-12a-phenyl-9a,12a-dihydrophenanthro[9′,10:5,6][1,4]-dioxino[2,3-*d*]thiazole

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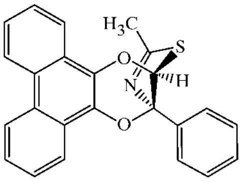
In the title compound, $C_{24}H_{17}NO_2S$, the dioxine and thiazoline rings are distorted from planarity towards a half-chair and an envelope conformation, respectively. The configurations of the dioxine ring, the thiazoline ring and the attached phenyl ring are conditioned by the sp^3 state of the two bridgehead C atoms. The phenanthrene system is nearly coplanar with the dioxine ring, while the attached phenyl ring is orthogonal to the thiazoline ring.

Comment

Photoinduced cycloaddition reactions of excited-state carbonyl compounds with oxazole and thiazole derivatives have not been widely investigated (Secretar *et al.*, 1983; Griesbeck *et al.*, 2000). We have investigated the photoreactions of phenanthroquinone with 2-methyl-4-phenylthiazole, and isolated the title compound, (I), as a product. An X-ray crystal structure analysis has been undertaken to elucidate the relative stereochemistry of (I), and the results are presented here.



(I)

The bond lengths and angles in (I) (Fig. 1) are within normal ranges (Allen *et al.*, 1987). Those of the phenanthrene system (C1–C14) and the dioxine ring (C1/C14/O2/C15/C16/O1) agree with the corresponding values in a related structure (Usman *et al.*, 2002), while those of the thiazoline ring (C15–C17/S1/N1) are comparable with those in a reported thiazole derivative (Ekstrand & van der Helm, 1977).

The thiazoline ring adopts an envelope conformation, with atom C15 displaced by 0.527 (3) Å from the N1/C16/S1/C17 plane. Methyl atom C24, attached to atom C17, deviates by 0.206 (4) Å from the thiazoline mean plane, while the phenyl ring (C18–C23) attached at C16 is nearly orthogonal with respect to the thiazoline plane, corresponding to a dihedral angle of 86.9 (2)° between the two planes. The C15—C16—

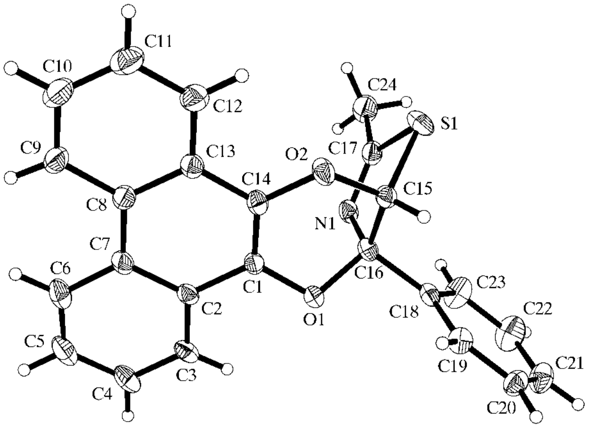


Figure 1
The structure of the *R*,*R* enantiomorph of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

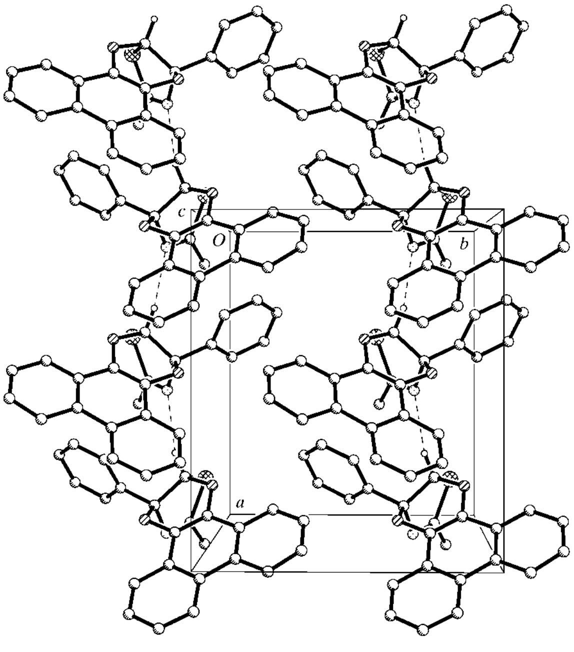


Figure 2
Packing diagram of (I), viewed down the *c* axis. The dashed lines denote the C—H···N intermolecular interactions.

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C18 and S1—C15—C16 bond angles and the O2—C15—C16—O1 torsion angle are 103.1 (2), 110.4 (3) and −37.7 (4)°, respectively, indicating a staggered configuration of the sp^3 states of atoms C15 and C16 joining the thiazoline, dioxine and phenyl rings. These two atoms also govern the angle between the thiazoline and dioxine rings, which is 76.9 (2)°.

The dioxine ring is distorted from planarity towards a half-chair conformation, with atoms O1 and C16 displaced by −0.268 (2) and 0.381 (3) Å, respectively, from the C1/C14/O2/C15 plane. A local pseudo-twofold axis (for the dioxine ring) passes through the midpoints of the O1—C16 and O2—C14 bonds.

The planar phenanthrene moiety has a maximum deviation of 0.044 (5) Å at atom C10. The dihedral angles between the benzene rings in the phenanthrene moiety are within 1.3 (2)°, while that between the phenanthrene and dioxine rings is 11.0 (1)°.

Fig. 1 shows the *R*,*R* enantiomorph, but the crystal contains equal numbers of the *R*,*R* and *S*,*S* enantiomorphs. The photoinduced cycloaddition reaction of both achiral phenanthroquinone and 2-methyl-4-phenylthiazole gives chiral C atoms at the additional ring of the title compound.

The molecules are packed into chains along the *a* direction (Fig. 2) by a weak C15—H15···N1$^{\rm i}$ interaction (see Table 2 for symmetry code and details). The packing is stabilized by this interaction, together with dipole–dipole and van der Waals interactions.

Experimental

A solution of phenanthroquinone (0.05 *M*) in the presence of an excess of 2-methyl-4-phenylthiazole in benzene solution was irradiated with light of wavelength longer than 400 nm. After completion of the reaction, the solvent was removed *in vacuo* and the residue was separated by column chromatography on silica gel to afford the title compound. Single crystals suitable for X-ray diffraction analysis were obtained from slow evaporation of an acetone–petroleum ether solution.

Crystal data

$C_{24}H_{17}NO_2S$
$M_r = 383.45$
Orthorhombic, $Pna2_1$
$a = 10.7999$ (1) Å
$b = 9.2851$ (1) Å
$c = 18.7949$ (3) Å
$V = 1884.72$ (4) Å^3
$Z = 4$
$D_x = 1.351$ Mg m^{-3}

Mo *K*α radiation
Cell parameters from 7025 reflections
$\theta = 2.5$–28.3°
$\mu = 0.19$ mm^{-1}
$T = 213$ (2) K
Block, yellow
0.50 × 0.32 × 0.22 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\rm min} = 0.910$, $T_{\rm max} = 0.959$
10 677 measured reflections

2375 independent reflections
1924 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.098$
$\theta_{\rm max} = 28.3°$
$h = -14 \rightarrow 13$
$k = -10 \rightarrow 12$
$l = -22 \rightarrow 24$

Table 1
Selected interatomic distances (Å).

S1—C17	1.776 (3)	O2—C14	1.373 (4)
S1—C15	1.806 (4)	O2—C15	1.438 (4)
O1—C1	1.382 (4)	N1—C17	1.268 (5)
O1—C16	1.430 (4)	N1—C16	1.443 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···N1$^{\rm i}$	0.98	2.51	3.385 (4)	149

Symmetry code: (i) $x - \frac{1}{2}, \frac{3}{2} - y, z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.130$
$S = 1.00$
2375 reflections
255 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.074P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.41$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.011 (2)

H atoms were fixed geometrically and treated as riding on their parent C atoms, with C—H distances in the range 0.93–0.97 Å and $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$. In the absence of significant anomalous dispersion effects, the 2268 Friedel equivalents were merged and the absolute structure was chosen arbitrarily.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL, PARST* (Nardelli, 1995) and *PLATON* (Spek, 1990).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1114). Services for accessing these data are described at the back of the journal.

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