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11-Methyl-12a-phenyl-9a,12a-dihydrophenanthro[9′,10′:5,6]-[1,4]dioxino[2,3-*d*]oxazole and 9a-(10-hydroxyphenanthren-9-yl)-11,12a-diphenyl-9a,12a-dihydro-phenanthro[9′,10′:5,6][1,4]dioxino-[2,3-*d*]oxazole

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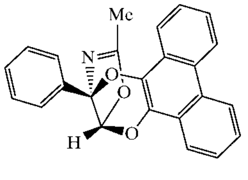
In the title compounds, $C_{24}H_{17}NO_3$, (I), and $C_{43}H_{27}NO_5$, (II), the dioxine ring is not planar and tends toward a boat conformation. The oxazoline ring adopts a twisted conformation in molecule (I) but is essentially planar in molecule (II). The configuration of the dioxine–oxazoline system is determined by the sp^3 state of the two shared atoms. The phenanthrene moiety is nearly coplanar with the dioxine ring, while the phenyl ring is perpendicular to the attached oxazole ring. The triclinic unit cell of (II) contains two crystallographically independent molecules related by a pseudo-inversion centre.

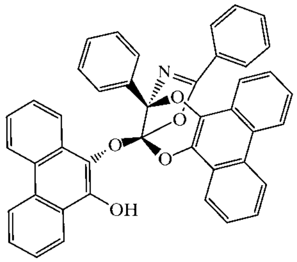
Comment

Photoinduced cycloaddition reactions of excited-state carbonyl compounds with oxazole derivatives have not been widely investigated (Secretar *et al.*, 1983; Griesbeck *et al.*, 2000). In relation to our interest in heterocyclic photochemistry, we have recently investigated the photoinduced reactions of phenathroquinone with several oxazole derivatives (Zhang & Xu, 2002). The title compounds, (I) and (II), were obtained from the photoinduced reactions of phenathroquinone with an excess of 2-methyl-4-phenyloxazole and 2,4-diphenyloxazole, respectively, in benzene. We have undertaken X-ray crystal structure analyses of the title compounds in order to elucidate their steric structures, and the results are presented here.

The bond lengths and angles in (I) (Table 1 and Fig. 1) are within normal ranges (Allen *et al.*, 1987). Those within the oxazoline (C15/C16/C17/O3/N1) and dioxine (C1/C14/O2/C15/C17/O1) rings agree with the corresponding values in the structures of oxazole derivatives (Fustero *et al.*, 1996; Usman *et al.*, 2002) and a dioxine derivative (Cherni *et al.*, 1998) reported earlier.



(I)



(II)

In compound (I), the oxazoline ring is not planar and tends towards a twisted conformation, with atoms C15 and C17 displaced slightly, by 0.102 (4) and −0.045 (4) Å, respectively, from the N1/C16/O3 plane. The local pseudo-twofold axis passes through atom C16 and the midpoint of the C15—C17 bond. This conformation is also confirmed by the puckering parameters (Cremer & Pople, 1975) of Q_2 = 0.087 (4) Å and φ_2 = 48 (3)°. The methyl atom C24 deviates by −0.009 (5) Å from the oxazoline mean plane, while the C18–C23 phenyl ring attached at C17 is nearly perpendicular to the oxazole ring, with the corresponding dihedral angle being 87.0 (2)°. The relative configurations of the C18–C23 phenyl, the oxazoline and the dioxine rings are determined by the sp^3 state of atom C17, with an average subtended bond angle of 109.5°. The dihedral angle between the dioxine and oxazoline rings is 102.3 (2)°.

The dioxine ring adopts a boat conformation, with atoms O1 and O2 displaced by 0.283 (3) and 0.395 (3) Å, respectively, from the C1/C14/C15/C17 plane. The puckering parameters of this ring are Q_2 = 0.404 (3) Å, Q_3 = −0.047 (4) Å, Q_T = 0.407 (3) Å, φ_2 = 13.0 (6)° and θ = 96.6 (6)°.

In the phenanthrene moiety, the dihedral angles between the benzene rings are within 6.7 (2)°. The phenanthrene system is nearly coplanar with the dioxine ring, due to the Csp^2

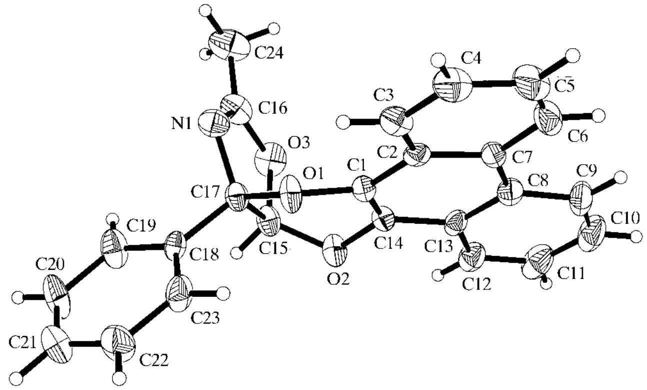


Figure 1
The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii.

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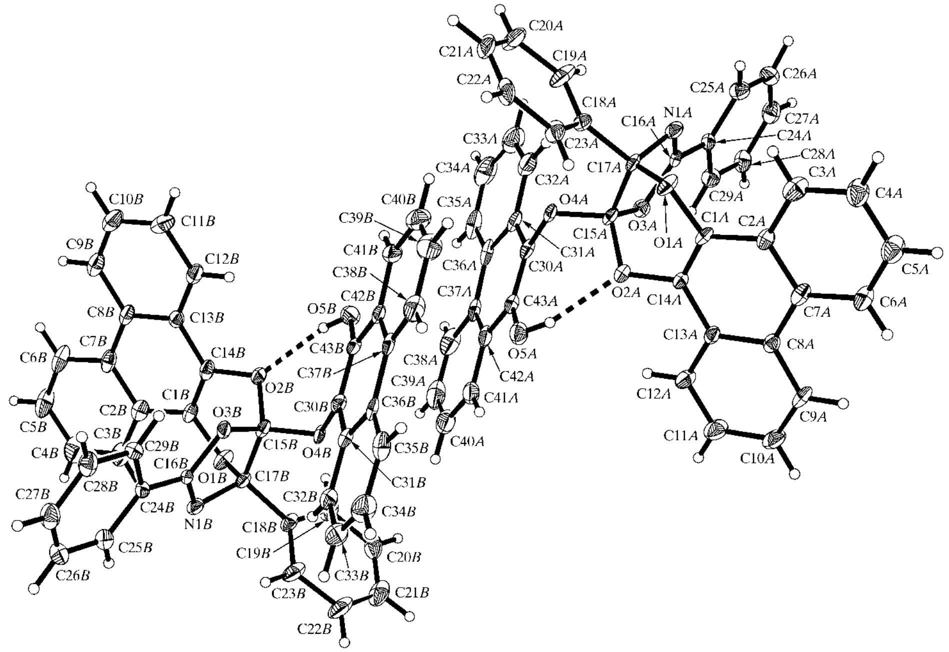

Figure 2

The structure of the two independent molecules of (II), showing 50% probability displacement ellipsoids and the atom-numbering scheme. H atoms are drawn as small spheres of arbitrary radii and the dashed lines denote intramolecular interactions.

character of the shared atoms, *viz*. C1 and C14. The dihedral angle between the phenanthrene system and the dioxine ring is 12.1 (1)°.

As seen in Fig. 1, atoms C15 and C17 are the *R* chiral centres. Since the structure belongs to a chiral space group, only one enantiomorph is present, but the Flack parameter (Flack, 1983) did not allow us to determine the absolute configuration for this light-atom structure.

In the crystal structure of (II), there are two crystallographically independent molecules, *A* and *B*, in the asymmetric unit. The bond lengths and angles of molecules *A* and *B* (Table 2 and Fig. 2) agree with each other and are comparable with those in (I). Molecules *A* and *B* are related by a local inversion centre. In molecule *A* (Fig. 2), atoms C15 and C17 have *S* and *R* chirality, respectively, and in molecule *B*, the atoms have opposite, *R* and *S*, chirality. The centrosymmetric space group also implies that (II) is a racemic mixture of enantiomers with opposite chiralities.

In contrast with (I), the oxazoline ring in molecules *A* and *B* of (II) is planar. This is due to the difference in the substituents attached to the oxazoline ring, especially the bulky substituents attached at C15 and C17 in (II). As a result, the C18–C23 phenyl ring makes a much smaller dihedral angle with the oxazoline ring [72.2 (2)° in molecule *A* and 69.6 (2)° in molecule *B*] compared with that in (I). The other phenyl ring (C24–C29) is nearly coplanar with the oxazoline ring, with corresponding dihedral angles of 6.8 (2) and 4.3 (2)° in molecules *A* and *B*, respectively, facilitating the delocalization of π-conjugation between the two ring moieties.

The dioxine ring of molecules *A* and *B* of (II) tends towards a boat conformation, with atoms O1 and O2 displaced from the C1/C14/C15/C17 plane by 0.449 (3) and 0.462 (2) Å, respectively, in molecule *A*, and by 0.496 (3) and 0.501 (2) Å, respectively, in molecule *B*. The puckering parameters are Q_2 = 0.528 (3) Å, Q_3 = 0.528 (3) Å, φ_2 = 4.3 (4)° and θ_2 = 90.5 (4)° for molecule *A*, and Q_2 = 0.576 (3) Å, Q_3 = 0.576 (3) Å, φ_2 = 0.8 (4)° and θ_2 = 89.8 (4)° for molecule *B*.

The average bond angle subtended at atoms C15 and C17 is 109.5°. The O1—C17—C15—O2 and N1—C17—C15—O3 torsion angles are 4.7 (4) and 2.1 (3)°, respectively, in molecule *A*, and −2.1 (4) and −1.3 (3)°, respectively, in molecule *B*. These imply an eclipsed configuration of the Csp^3 of the atoms shared between the oxazoline and dioxine rings, *viz*. C15 and C17. The dihedral angles between the two rings are 97.3 (2) and 95.5 (2)° in molecules *A* and *B*, respectively.

In both molecules *A* and *B*, the phenanthrene (C1–C14) system is nearly coplanar with the dioxine ring, which is similar to what is observed in compound (I). The dihedral angles between the phenanthrene (C1–C14) system and the dioxine ring are 19.8 (1) and 24.3 (2)° in molecules *A* and *B*, respectively. The relative configuration of another phenanthrene system (C30–C43) and the dioxine ring is determined by the sp^3 state of the joining atom, O4. The C15—O4—C30 bond angles are 117.7 (3) and 117.9 (3)° in molecules *A* and *B*, respectively, and the dihedral angles between the phenanthrene system (C30–C43) and the dioxine ring are 36.4 (1) and 32.5 (1)° in molecules *A* and *B*, respectively.

In molecules *A* and *B* of (II), the H atom of the hydroxy group facilitates an intermolecular hydrogen bond with one of the O atoms of the dioxine moiety. This C5—H5···O1 bond (Table 3) forms a seven-membered ring, *viz*. O2/C15/O4/C30/C43/O5/H5 (Fig. 2).

Experimental

The title compounds, (I) and (II), were isolated from their reaction mixtures (see *Comment*) by column chromatography on silica gel.

Single crystals suitable for X-ray diffraction were obtained by slow evaporation of solutions in acetone–petroleum ether (1:1 *v*/*v*).

Compound (I)

Crystal data

$C_{24}H_{17}NO_3$
$M_r = 367.39$
Orthorhombic, $P2_12_12_1$
$a = 9.7633$ (4) Å
$b = 10.9896$ (4) Å
$c = 16.6210$ (7) Å
$V = 1783.35$ (12) Å^3
$Z = 4$
$D_x = 1.368$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 3641 reflections
$\theta = 2.4–28.3°$
$\mu = 0.09$ mm^{-1}
$T = 213$ (2) K
Slab, colourless
0.34 × 0.26 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
8619 measured reflections
1795 independent reflections
1254 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.104$
$\theta_{\rm max} = 25°$
$h = -7 \rightarrow 11$
$k = -13 \rightarrow 12$
$l = -17 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.122$
$S = 0.96$
1795 reflections
255 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.20$ e Å^{-3}
Extinction correction: *SHELXTL*
Extinction coefficient: 0.016 (3)

Table 1
Selected bond distances (Å) for (I).

O1—C1	1.381 (4)	O3—C16	1.375 (5)
O1—C17	1.441 (4)	O3—C15	1.431 (5)
O2—C14	1.384 (4)	N1—C16	1.264 (5)
O2—C15	1.393 (5)	N1—C17	1.459 (5)

Compound (II)

Crystal data

$C_{43}H_{27}NO_5$
$M_r = 637.66$
Triclinic, $P\overline{1}$
$a = 12.4812$ (3) Å
$b = 14.3317$ (1) Å
$c = 18.5727$ (3) Å
$\alpha = 102.607$ (1)°
$\beta = 99.511$ (1)°
$\gamma = 94.529$ (1)°
$V = 3174.64$ (9) Å^3

$Z = 4$
$D_x = 1.334$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5405 reflections
$\theta = 2.8–28.4°$
$\mu = 0.09$ mm^{-1}
$T = 213$ (2) K
Slab, yellow
0.5 × 0.4 × 0.1 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
19 415 measured reflections
14 575 independent reflections
4506 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.088$
$\theta_{\rm max} = 28.4°$
$h = -10 \rightarrow 16$
$k = -19 \rightarrow 19$
$l = -24 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.073$
$wR(F^2) = 0.194$
$S = 0.75$
14 575 reflections
883 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.41$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.41$ e Å^{-3}

Table 2
Selected bond distances (Å) for (II).

O1*A*—C1*A*	1.398 (4)	O1*B*—C1*B*	1.395 (4)
O1*A*—C17*A*	1.437 (4)	O1*B*—C17*B*	1.436 (4)
O2*A*—C14*A*	1.397 (4)	O2*B*—C15*B*	1.396 (4)
O2*A*—C15*A*	1.401 (4)	O2*B*—C14*B*	1.407 (4)
O3*A*—C16*A*	1.385 (4)	O3*B*—C16*B*	1.377 (4)
O3*A*—C15*A*	1.412 (4)	O3*B*—C15*B*	1.417 (4)
N1*A*—C16*A*	1.273 (4)	N1*B*—C16*B*	1.278 (4)
N1*A*—C17*A*	1.459 (4)	N1*B*—C17*B*	1.453 (4)

Table 3
Hydrogen-bonding geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5*A*—H5*AA*···O2*A*	0.82	1.95	2.704 (3)	152
O5*B*—H5*BA*···O2*B*	0.82	1.95	2.725 (3)	156

In both compounds, the H atoms were fixed geometrically and treated as riding on their parent C atoms, with aromatic C—H = 0.93 Å and methylene C—H = 0.96 Å, and, for (II), O—H = 0.82 Å. For compound (I), due to the absence of any significant anomalous scatterers, the 1333 Friedel equivalents were merged before the final refinement and the absolute configuration was arbitrarily chosen. The structure of (II) contains solvent-accessible voids of 72.0 Å^3. There is no significant residual peak density within the voids, which is probably an indication of a loss of solvent and a reason for the poor quality of the data.

For both compounds, data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT* and *SADABS* (Sheldrick, 1996); 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: SK1563). Services for accessing these data are described at the back of the journal.

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