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9,10-Diphenyl-9,10-epidioxyanthracene and 9,10-dihydro-10,10-dimethoxy-9-phenylanthracen-9-ol

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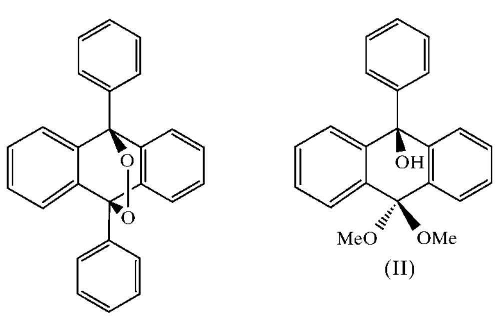
9,10-Diphenyl-9,10-epidioxyanthracene, $C_{26}H_{18}O_2$, (I), was accidentally used in a photooxygenation reaction that produced 9,10-dihydro-10,10-dimethoxy-9-phenylanthracen-9-ol, $C_{22}H_{20}O_3$, (II). In both compounds, the phenyl rings are approximately orthogonal to the anthracene moiety. The conformation of the anthracene moiety differs as a result of substitution. Intramolecular C—H···O interactions in (I) form two approximately planar *S*(5) rings in each of the two crystallographically independent molecules. The packing of (I) and (II) consists of molecular dimers stabilized by C—H···O interactions and of molecular chains stabilized by O—H···O interactions, respectively.

Comment

9,10-Diphenylanthracene endoperoxide, (I), is a well known chemical source that releases singlet oxygen when heated in benzene and other solvents (Wasserman & Scheffer, 1967). During the course of our investigation of the singlet oxygen reactions of indolizine derivatives (Tian *et al.*, 2001), we refluxed (I) with an indolizine sample in toluene–methanol, with the aim of inducing singlet oxygen reactions, and obtained (II), a phenylanthracene derivative, as one of the products. We have structurally analyzed both (I) and (II), and the results are presented here.



(I) (II)

The asymmetric unit of (I) consists of two crystallographically independent molecules, *viz*. *A* and *B*, related by a local pseudo-twofold rotation axis. The bond lengths and angles of molecules *A* and *B* (Fig. 1 and Table 1) agree with each other and are within normal ranges (Allen *et al.*, 1987).

In both molecules, within the C1–C14 anthracene moiety, the C1—C6—C7—C8—C13—C14 ring exhibits a boat conformation, with atoms C7 and C14 displaced by 0.627 (4) and 0.644 (4) Å, respectively, from the C1/C6/C8/C13 plane in molecule *A*; the corresponding displacements in molecule *B* are 0.659 (4) and 0.644 (4) Å. The two fused benzene rings, C1–C6 and C8–C13, make dihedral angles with the C1/C6/C8/C13 plane of 21.8 (2) and 19.5 (2)° in molecule *A*, and 26.1 (2) and 23.4 (2)° in molecule *B*. The C1/C6/C8/C13 plane is orthogonal to the C7/O2/O1/C14 plane, with the dihedral angle between the two planes being 89.7 (2) and 89.9 (2)° in molecules *A* and *B*, respectively.

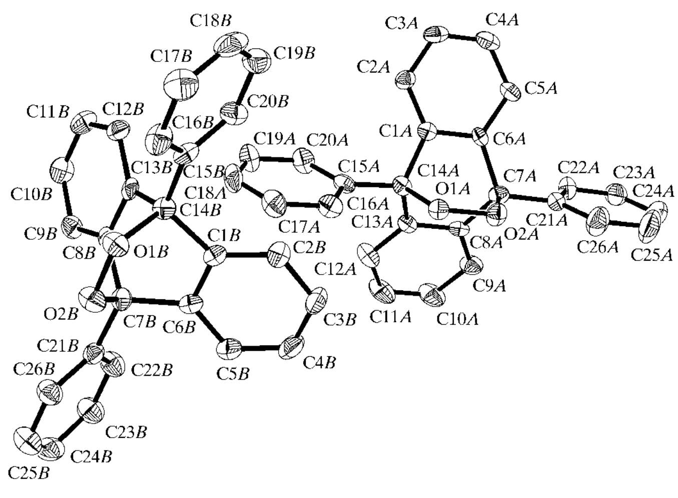


Figure 1
A view of the structure of (I), showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme. All H atoms have been omitted for clarity.

The C7/O2/O1/C14 plane is approximately coplanar with the C15–C20 and C21–C26 phenyl rings, with the dihedral angles between the plane and the rings being 5.3 (2) and 2.3 (2)° in molecule *A*, and 4.6 (2) and 1.6 (1)° in molecule *B*. This coplanarity is maintained by intramolecular C16—H16···O1 and C26—H26···O2 interactions, which form O1—C14—C15—C16—H16 and O2—C7—C21—C26—H26 *S*(5) rings (Etter *et al.*, 1990) in both molecules (Fig. 1 and Table 2). The dihedral angles differ between molecules *A* and *B* because atom O1 in molecule *A* facilitates an intermolecular C17*B*—H17*B*···O1A^{i} interaction (see Table 2 for geometric parameters and symmetry code), which connects molecules *A* and *B* from different asymmetric units into dimers.

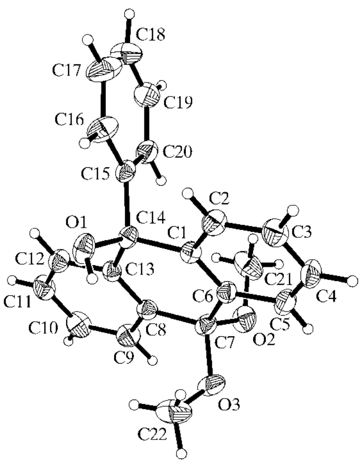


Figure 2
A view of the structure of (II), showing displacement ellipsoids at the 50% probability level and the atom-numbering scheme. All H atoms have been omitted for clarity.

In contrast to (I), the anthracene moiety of (II) is planar to within ±0.042 (3) Å (Fig 2). An intramolecular C16—H16···O1 interaction (Table 3), similar to the intramolecular interactions in (I), forms an O1—C14—C15—C16—H16 *S*(5) ring. This ring deviates slightly from planarity, having an O1—C14—C15—C16 torsion angle of 21.8 (3)°. In (II), the two methoxy groups attached to atom C7 are coplanar. Both the C21/O2/C7/O3/C22 plane and the C15–C20 phenyl ring are orthogonal to the anthracene moiety, with dihedral angles of 89.8 (2) and 81.3 (1)°, respectively. The packing comprises molecular chains along the *b* direction (Fig. 3), stabilized by O1—H1O1···O3[ii] interactions (see Table 3 for geometric parameters and symmetry code).

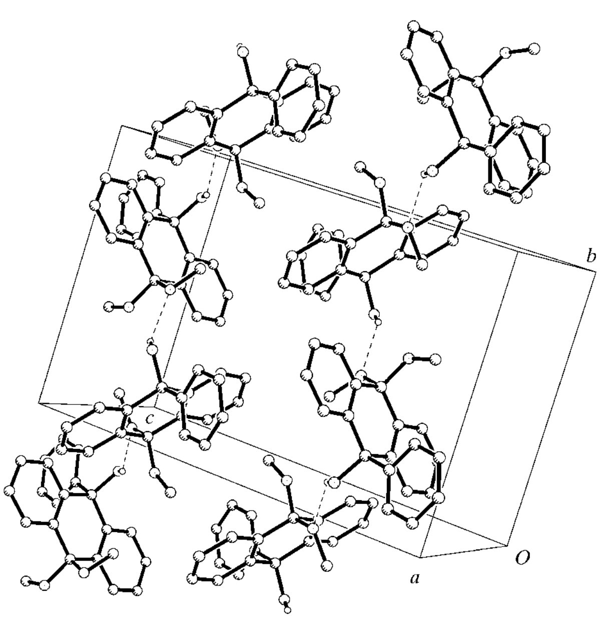


Figure 3
Packing diagram of (II), showing chains parallel to the *b* direction. All H atoms attached to C atoms have been omitted for clarity. Dashed lines denote intermolecular O—H···O interactions.

Experimental

Compound (I) was prepared by methylene blue-sensitized photo-oxygenation of 9,10-diphenylanthracene and was separated by column chromatography on silica gel with petroleum ether and ethyl acetate eluants. Compound (II) was obtained accidentally by refluxing a toluene–methanol solution of 1-(4-methoxybenzoyl)-2-phenylindolizine with (I). Compound (II) was also separated by column chromatography on silica gel with petroleum ether and ethyl acetate as eluants. Single crystals of (I) and (II) were obtained by slow evaporation of their petroleum ether/ethyl acetate solutions.

Compound (I)

Crystal data

$C_{26}H_{18}O_2$
M_r = 362.40
Monoclinic, $P2_1/c$
a = 19.8390 (12) Å
b = 10.4950 (6) Å
c = 18.0130 (10) Å
β = 95.0160 (10)°
V = 3736.1 (4) Å^3
Z = 8
D_x = 1.289 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3581 reflections
θ = 2.3–28.3°
μ = 0.08 mm^{-1}
T = 293 (2) K
Cylinder, colorless
0.46 × 0.20 × 0.16 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
18 226 measured reflections
6575 independent reflections
3917 reflections with $I > 2\sigma(I)$
R_{int} = 0.069
θ_{max} = 25.0°
$h = -20 \rightarrow 23$
$k = -12 \rightarrow 12$
$l = -18 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.091
$wR(F^2)$ = 0.218
S = 1.06
6575 reflections
505 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0783P)^2 + 6.3806P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.35 e Å^{-3}

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

O1*A*—C14*A*	1.476 (5)	O1*B*—C14*B*	1.478 (5)
O1*A*—O2*A*	1.485 (4)	O1*B*—O2*B*	1.483 (4)
O2*A*—C7*A*	1.477 (5)	O2*B*—C7*B*	1.471 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C16*A*—H16*A*···O1*A*	0.93	2.31	2.678 (5)	103
C16*B*—H16*B*···O1*B*	0.93	2.30	2.667 (6)	103
C17*B*—H17*B*···O1*A*[i]	0.93	2.58	3.299 (6)	134
C26*A*—H26*A*···O2*A*	0.93	2.33	2.689 (7)	102
C26*B*—H26*B*···O2*B*	0.93	2.29	2.666 (6)	103

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

Compound (II)

Crystal data

$C_{22}H_{20}O_3$
M_r = 332.38
Monoclinic, $P2_1/c$
a = 8.9181 (10) Å
b = 11.3071 (12) Å
c = 17.0624 (19) Å
β = 90.552 (2)°
V = 1720.5 (3) Å^3
Z = 4
D_x = 1.283 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3446 reflections
θ = 2.9–28.3°
μ = 0.08 mm^{-1}
T = 293 (2) K
Slab, colorless
0.36 × 0.26 × 0.20 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
T_{min} = 0.970, T_{max} = 0.983
8361 measured reflections
3015 independent reflections
2366 reflections with $I > 2\sigma(I)$
R_{int} = 0.024
θ_{max} = 25.0°
$h = -10 \rightarrow 10$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.060
$wR(F^2)$ = 0.133
S = 1.13
3015 reflections
284 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.042P)^2 + 1.1659P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C16—H16···O1	0.96 (3)	2.32 (3)	2.700 (4)	103 (2)
O1—H1O1···O3^{ii}	0.78 (3)	2.31 (3)	2.902 (2)	133 (3)

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

The H atoms of (I) were fixed geometrically and treated as riding on their parent C atoms, with C—H distances of 0.96 Å and U_{iso}(H) values of $1.5U_{eq}$(C). For (II), the H atoms attached to atoms C21 and C22 were fixed geometrically and treated as riding atoms, with C—H distances of 0.93 Å and U_{iso}(H) values of $1.2U_{eq}$(C). The remaining H atoms were located in difference maps and were refined isotropically [C—H = 0.91 (3)–0.99 (2) Å]. A rotating group refinement was used for the methyl groups. Owing to the large number of weak data at higher angles, the maximum 2θ value was limited to 50° for both (I) and (II).

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, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1608). Services for accessing these data are described at the back of the journal.

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