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5a,6,9,9a-Tetrahydro-4-hydroxy-6,9-methano-5*H*-fluoreno[2,3-*b*]furan-5-one and 5a,6,9,9a-tetrahydro-6,9-methano-4-methoxy-5*H*-fluoreno[2,3-*b*]furan-5-ol

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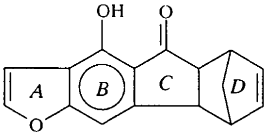
Abstract

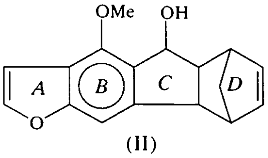
In the title compounds, $C_{16}H_{12}O_3$ and $C_{17}H_{16}O_3$, the six-membered ring of the norbornene moiety adopts a boat conformation and the five-membered rings formed by the methylene bridge adopt envelope conformations; the other rings in the molecules are nearly coplanar. In the solid state, both compounds exhibit O—H···O and C—H···O hydrogen bonds.

Comment

The title compounds, 5a,6,9,9a-tetrahydro-4-hydroxy-6,9-methano-5*H*-fluoreno[2,3-*b*]furan-5-one, (I), and 5a,6,9,9a-tetrahydro-6,9-methano-4-methoxy-5*H*-fluoreno[2,3-*b*]furan-5-ol, (II), were prepared for the purpose of generating new analogues of photodynamic drugs, *i.e.* psoralens (Shim, 1984). Both the title intermediates have been successfully transformed into their respective psoralens (Mal *et al.*, 1998). The X-ray structure determinations were carried out in order to establish the relative stereochemistries.



(I)



(II)

The bond lengths and angles observed in fused rings *A*, *B* and *C* of compounds (I) and (II) agree with each other, and those in the norbornene ring system are comparable with reported values (Beddoes *et al.*, 1993; Chinnakali *et al.*, 1999). The asymmetric unit of (II) consists of two independent molecules [(II*A*) and (II*B*)] which have different orientations of the methoxy group [C3*A*—C4*A*—O2*A*—C17*A* 49.8 (4) and C3*B*—C4*B*—O2*B*—C17*B* −54.9 (4)°].

In the molecules of (I) and (II), the fused rings *A*, *B* and *C* are nearly coplanar. The fused five-membered ring *C* in (II*A*) adopts a flattened envelope conformation, and in (II*B*) it is in the half-chair conformation; asymmetry parameters ΔC_s(C6*A*) = 0.004 (1) and ΔC_2(C13*B*) = 0.005 (1) (Nardelli, 1983).

In both compounds, the six-membered ring (*D*) of the norbornene ring system is a fairly symmetrical boat, with asymmetry parameters ΔC_s(C7—C12) = 0.001 (1) (I), 0.025 (1) (II*A*) and 0.021 (1) (II*B*), and ΔC_s(C8) = 0.012 (1) (I), 0.030 (1) (II*A*) and 0.025 (1) (II*B*); the five-membered rings in the norbornene moiety formed by the methylene bridge adopt envelope conformations. The C7/C9/C10/C12 plane is nearly perpendicular to the five-membered ring *C*, with a dihedral angle of 87.50 (7) in (I), 89.7 (1) in (II*A*) and 89.08 (8)° in (II*B*). In both compounds, the *C*/*D* ring junction is *cis*.

In (I), the hydroxyl- and carbonyl-O atoms are involved in a weak O—H···O intramolecular hydrogen bond. In the crystal, the screw-related molecules are linked by weak C1—H1*A*···O3$(1 + x, \frac{1}{2} - y, \frac{1}{2} + z)$ hydrogen bonds along the *a* direction (Table 2). In (II), the two independent molecules in the asymmetric unit are linked by O3*B*—H3*BA*···O2*A* and O3*A*—H3*AA*···O2*B* intermolecular hydrogen bonds. In the solid state, weak C—H···O contacts are observed for (II*A*) along the *b* direction and for (II*B*) along the *a* direction (Table 4).

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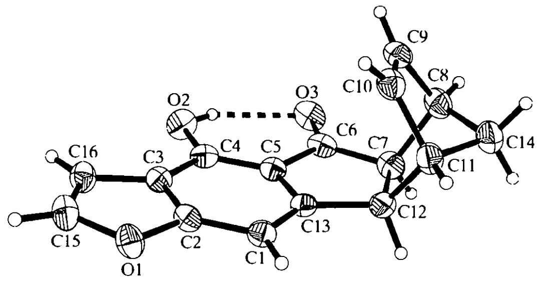

Fig. 1. The structure of (I) showing 50% probability displacement ellipsoids and the atom-numbering scheme.

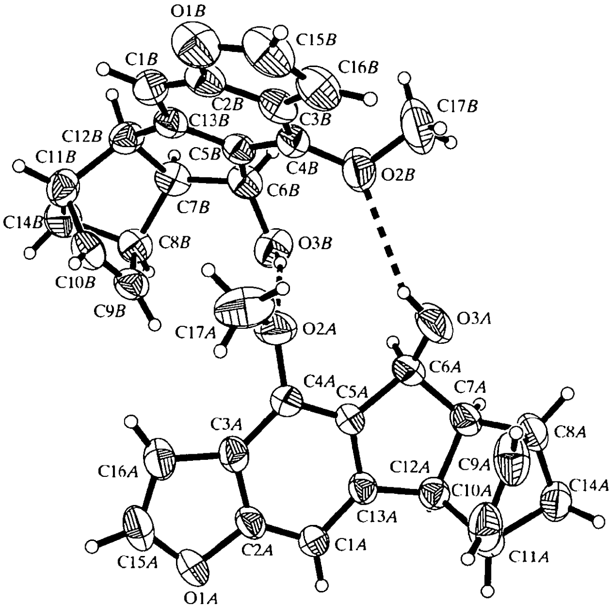

Fig. 2. The structure of (II) showing 50% probability displacement ellipsoids and the atom-numbering scheme. One of the two H atoms attached to the C14*A* and C14*B* atoms are hidden.

Experimental

Compound (I) was prepared in good yield by condensation of methyl phenylsulfonylfuran-3-carboxylate with bicyclopentadiene in the presence of ^{t}BuOLi (*tert*-butyloxylithium) (Mal *et al.*, 1998). It was recrystallized from a 1:2 mixture of dichloromethane and acetone by slow evaporation; m.p. 401 K. Compound (II) was prepared in two steps from (I) by *o*-methylation followed by sodium borohydride reduction in methanol. Recrystallization of (II) was performed in the manner described for (I); m.p. 391 K.

Compound (I)

Crystal data

$C_{16}H_{12}O_3$
$M_r = 252.26$
Monoclinic
$P2_1/c$
$a = 6.3760\,(1)$ Å
$b = 18.1210\,(2)$ Å
$c = 10.6546\,(1)$ Å
$\beta = 107.4075\,(1)°$
$V = 1174.65\,(3)$ Å^3
$Z = 4$
$D_x = 1.426$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4438 reflections
$\theta = 2.25$–28.31°
$\mu = 0.098$ mm^{-1}
$T = 293\,(2)$ K
Plate
$0.44 \times 0.32 \times 0.08$ mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
7571 measured reflections
2875 independent reflections

1750 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.066$
$\theta_{\rm max} = 28.31°$
$h = -8 \rightarrow 8$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.059$
$wR(F^2) = 0.159$
$S = 0.913$
2875 reflections
174 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0859P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$

$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.019 (5)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (I)*

O1—C2	1.375 (2)	O3—C6	1.232 (2)
O1—C15	1.383 (2)	C9—C10	1.315 (3)
O2—C4	1.353 (2)	C15—C16	1.329 (3)
C8—C14—C11	94.01 (16)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2*A*···O3	0.82	2.09	2.795 (2)	144
C1—H1*A*···O3$^{\rm i}$	0.93	2.48	3.288 (2)	146

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

Compound (II)

Crystal data

$C_{17}H_{16}O_3$
$M_r = 268.30$
Triclinic
$P\overline{1}$
$a = 9.8318\,(1)$ Å
$b = 9.9472\,(2)$ Å
$c = 14.2471\,(3)$ Å
$\alpha = 73.852\,(8)°$
$\beta = 86.554\,(9)°$
$\gamma = 78.916\,(1)°$
$V = 1313.38\,(4)$ Å^3
$Z = 4$
$D_x = 1.357$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 4108 reflections
$\theta = 1.49$–28.30°
$\mu = 0.092$ mm^{-1}
$T = 293\,(2)$ K
Parallelepiped
$0.36 \times 0.22 \times 0.18$ mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
10 634 measured reflections
6190 independent reflections
2899 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$
$\theta_{\rm max} = 28.30°$
$h = -12 \rightarrow 12$
$k = -12 \rightarrow 12$
$l = 0 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.058$
$wR(F^2) = 0.159$
$S = 0.906$
6190 reflections
366 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0678P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: *SHELXTL* (Sheldrick, 1997)
Extinction coefficient: 0.018 (2)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

O1*A*—C15*A*	1.372 (3)	O1*B*—C15*B*	1.371 (4)
O1*A*—C2*A*	1.378 (3)	O1*B*—C2*B*	1.382 (3)
O2*A*—C4*A*	1.386 (3)	O2*B*—C17*B*	1.363 (3)
O2*A*—C17*A*	1.393 (3)	O2*B*—C4*B*	1.388 (3)
O3*A*—C6*A*	1.423 (3)	O3*B*—C6*B*	1.423 (3)
C9*A*—C10*A*	1.324 (4)	C9*B*—C10*B*	1.324 (3)
C15*A*—C16*A*	1.330 (3)	C15*B*—C16*B*	1.331 (4)
C8*A*—C14*A*—C11*A*	93.23 (18)	C11*B*—C14*B*—C8*B*	94.0 (2)
C17*A*—O2*A*—C4*A*—C3*A*	49.8 (4)		
C17*B*—O2*B*—C4*B*—C3*B*	−54.9 (4)		

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*B*—H3*BA*···O2*A*	0.82	2.20	2.990 (3)	163
O3*A*—H3*AA*···O2*A*	0.82	2.48	2.978 (3)	120
O3*A*—H3*AA*···O2*B*	0.82	2.48	3.215 (3)	149
C8*A*—H8*AA*···O1*A*$^{\rm i}$	0.98	2.52	3.481 (3)	168
C15*A*—H15*A*···O3*A*$^{\rm ii}$	0.93	2.54	3.349 (4)	146
C15*B*—H15*B*···O3*B*$^{\rm iii}$	0.93	2.49	3.386 (4)	161

Symmetry codes: (i) $x, y-1, z$; (ii) $x, 1+y, z$; (iii) $x-1, y, z$.

For both crystals, the data collection covered a hemisphere of reciprocal space by a combination of three sets of exposures, each with a different φ angle (0, 88 and 180°) for the crystal; the crystal-to-detector distance was 3 cm and the detector swing angle was −20°. The frame exposure time was 30 s for (I) and 10 s for (II). Crystal decay was monitored by repeating 30 initial frames at the end of data collection and analysing the intensity of duplicate reflections; it was found to be negligible. Both structures were solved by direct methods and refined by full-matrix least-squares techniques. After checking their presence in a difference map, all the H atoms were placed in geometrically calculated positions and a riding model was used for their refinement; rotating-group refinement was used for the methyl and OH groups.

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1407). Services for accessing these data are described at the back of the journal.

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6,11-Dihydroxy-1,4-methano-1,4,4a,12a-tetrahydronaphthacene-5,12-dione

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Abstract

The title compound, $C_{19}H_{14}O_4$, exists in the quinol form. The six-membered and five-membered rings of the norbornene moiety adopt boat and envelope conformations, respectively. The hydroxyl groups are involved in O—H···O intramolecular hydrogen bonds.

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