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7a,13b-Ethylenedioxy-1-hydroxy-7a,13b-dihydrodibenzo[*a*,*kl*]xanthene

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Key indicators

Single-crystal X-ray study
T = 294 K
Mean σ(C–C) = 0.002 Å
R factor = 0.045
wR factor = 0.136
Data-to-parameter ratio = 19.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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The title compound, $C_{22}H_{16}O_4$, is composed of six rings bridged *via* two chiral C atoms. A couple of enantiomers cocrystallize to give a racemic crystal in which the O—H···O hydrogen bonds connect the enantiomers alternately to form a chain. π–π interactions play an important role in crystal packing to control the parallel arrangement of the chains.

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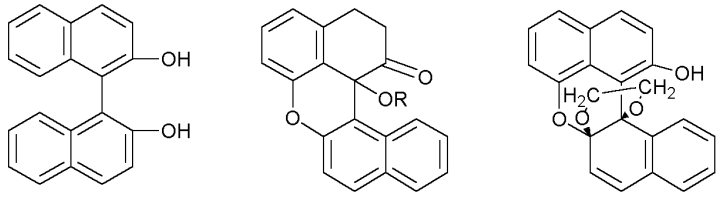
Comment

Copper–amine complexes can be used as functional model compounds of phenol oxidases in biomimetic type synthesis of structurally complicated compounds (Mahadevan *et al.*, 2000). The oxidation of 1,1′-binaphthol, (I), in alcoholic solvents led to an interesting Domino reaction (Tan *et al.*, 2001). When the reaction was carried out in glycol, a yellow compound was formed. Mass spectrum and elemental analysis indicated its formula to be $C_{22}H_{16}O_4$, suggesting that the solvent $HOCH_2CH_2OH$ entered the product *via* elimination of four H atoms from (I) and glycol molecules.



(I) (II*a*) R = Me (II*b*) R = CH_2CH_2OH (III)

Considering the similar reaction in methanol has led to formation of the ketone (II*a*), *i.e.* 1-oxo-13c-methoxy-1,13c-dihydrodibenzo[*a*,*kl*]xanthene, we presumed that the product obtained from glycol was ketone (II*b*), *i.e.* 1-oxo-13c-(2-hydroxy-ethoxy)-1,13c-dihydrodibenzo[*a*,*kl*]xanthene. The IR spectrum of 1603 cm^{-1} was believed to be the vibration of the carbonyl group with a hydrogen-bond effect from the hydroxyl group. However, the ^{13}C NMR remained confused because the chemical shift of the carbonyl group was much less than the usual range of the carbonyl group of α,β-unsaturated ketones (180–213 p.p.m.). In order to further clarify the molecular structure, X-ray single-crystal analysis was performed. The structural analysis showed a ketal structure (III), *i.e.* 7a,13b-ethylenedioxy-1-hydroxy-7a,13b-dihydrodibenzo[*a*,*kl*]xanthene, which was in accordance with NMR and IR spectra.

As shown in Fig. 1, the molecule of (III) is built up by six fused rings: (*A*) C3–C8; (*B*) C1–C3/C8–C10; (*C*) C7/C8/C9/O2/C11/C20; (*D*) C11–C14/C16–C19; (*F*) C11/C20/O3/C22/C21/

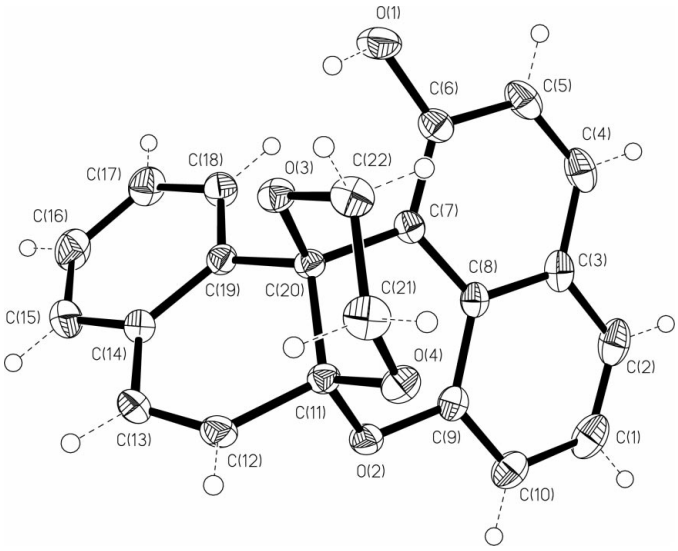


Figure 1
View of the structure of (III) showing the atomic numbering scheme and displacement ellipsoids (50% probability level).

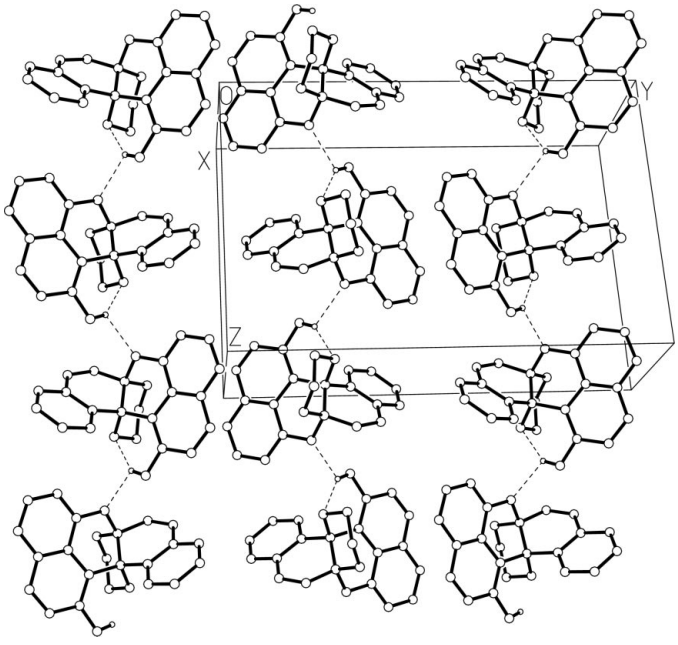


Figure 2
Two-dimensional layer dominated by π–π interactions between O—H···O hydrogen-bonded chains.

O4. The least-squares planes through them form the dihedral angles: (*A*)/(*B*) 1.56 (3), (*B*)/(*C*) 5.28 (4), (*A*)/(*C*) 6.31 (4), (*C*)/(*D*) 64.73 (4); (*D*)/(*E*) 10.79 (4), (*C*)/(*F*) 78.99 (3) and (*D*)/(*F*) 70.47 (4)°. The significant parameters of the puckered rings are (Cremer & Pople, 1975): ring (*C*) Q_T = 0.442 (1) Å, sofa with a local pseudo-mirror running along the C8···C11 direction; ring (*D*) Q_T = 0.401 (1) Å, twist with two pseudo-twofold axes, one running through the midpoints of the C11—C20 and C13—C14 bonds, the other through the C12···C19 atoms; ring (*F*) Q_T = 0.565 (1) Å, distorted chair. The rings (A), (*B*) and (*E*) are actually planar, and (*A*) and (*B*) are nearly coplanar with a dihedral angle of 1.56 (3)°.

According to the structure of (III), there should theoretically be four stereoisomers, (7a-*R*, 13b-*R*), (7a-*R*, 13b-*S*), (7a-*S*, 13b-*R*) and (7a-*S*, 13b-*S*)], because of two chiral centers in this molecule. However, the X-ray structure shows only two enantiomers, (7a-*R*, 13b-*S*) and (7a-*S*, 13b-*R*)], and the other two were not found. Maybe the formation of the (7a-*S*, 13b-*S*) and (7a-*R*, 13b-*R*) isomers is unfavorable in energy.

The hydroxyl is involved as donor in a three-centre (bifurcated) hydrogen bond: O1—H1O···O3 (intramolecular) and O1—H1O···O2^{i} (intermolecular) as shown in Table 1 (symmetry code given in this Table). The intermolecular hydrogen bonds link two enantiomers alternately to form a racemic chain as shown in Fig. 2. Such chains are arranged side-by-side, controlled by π–π interactions formed between rings (*A*) and (*B*) belonging to adjacent chains with centroid-to-centroid distance of 3.9 Å, to generate a wavelike two-dimensional layer (Fig. 2). The whole crystal is stacked up by such overlaid layers.

The chiral compounds with structure (III) can behave as potential chiral ligand in synthesis of nonlinear materials (Chemla & Zyss, 1987), and as synthetic intermediates of fused multicyclic compounds.

Experimental

The title compound, (III), was synthesized from 1,1′-bi-naphthol, (I), in glycol in the presence of dioxygen under the catalysis of $CuCl_2$–ethanolamine complex. (III) was obtained as the main product with isolated yield of 58%. The single-crystal used for X-ray analysis was recrystallized from acetone. Elemental analysis calculated for $C_{22}H_{15}O_4$ (%): C 76.97, H 4.37; found: C 76.82, H 4.51. M.p.: 463–465 K. ν_{max}: 3389 (*br*, OH), 1603 (*s*), 1465, 1085, 826. δ_H (500 MHz in $CDCl_3$/ TMS): 3.68 (*dd*, ^3J = 11.7, ^4J = 3.3 Hz, 1H, CH_2), 3.83 (*dd*, ^3J = 11.7, ^4J = 3.3 Hz, 1H, CH_2), 3.91 (*dd*, ^3J = 11.7, ^4J = 3.3 Hz, 1H, CH_2), 4.31 (*dd*, ^3J = 11.7, ^4J = 3.3 Hz, 1H, CH_2), 6.14 (*d*, *J* = 9.8 Hz, 1H, 8–H), 6.96 (*d*, *J* = 7.8 Hz, 1H, 4–H), 6.94 (*d*, *J* = 9.8 Hz, 1H, 9–H), 7.16 (*m*, 1H, 11–H), 7.21–7.25 (*m*, 2 × 1H, 5–H, 10–H or 13–H), 7.27 (*d*, *J* = 6.5 Hz, 1H, 10–H or 13–H), 7.30 (*d*, *J* = 9.1 Hz, 1H, 3–H), 7.32 (*m*, 1H, 12–H), 7.47 (*d*, *J* = 8.5 Hz, 1H, 6–H), 7.88 (*d*, *J* = 9.1 Hz, 1H, 2–H), 8.29 (*s*, 1H, OH). δ_C (125 MHz): 60.06 (CH_2), 63.66 (CH_2), 76.64 (13-b), 94.54, 106.02, 112.34, 119.30, 121.05, 121.72, 124.11, 126.75, 128.66, 128.95, 129.20 (2 × 1C), 129.97, 130.41, 131.42, 133.51, 133.68, 147.43, 154.06. FAB–MS *m*/*z* (%) 345 (M^+ + 1, 48), 344 (M^+, 100), 284 (64), 283 (M^+ − OCH_2CH_2OH, 40).

Crystal data

$C_{22}H_{16}O_4$
M_r = 344.35
Monoclinic, $P2_1/n$
a = 7.317 (1) Å
b = 17.787 (4) Å
c = 12.422 (2) Å
β = 98.70 (3)°
V = 1598.1 (5) Å^3
Z = 4
D_x = 1.431 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 4616 reflections
θ = 4.5–30°
μ = 0.10 mm^{-1}
T = 294 (2) K
Block, yellow
0.36 × 0.25 × 0.20 mm

Data collection

Bruker Smart CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min} = 0.965$, $T_{max} = 0.981$
11 347 measured reflections
4616 independent reflections
3271 reflections with $I > 2\sigma(I)$
$R_{int} = 0.019$
$\theta_{max} = 30.0°$
$h = -9 \rightarrow 10$
$k = -25 \rightarrow 11$
$l = -17 \rightarrow 17$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.136$
$S = 1.01$
4616 reflections
239 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0825P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.34$ e Å^{-3}
$\Delta\rho_{min} = -0.22$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O3	0.88 (2)	1.97 (2)	2.7404 (14)	144.3 (19)
O1—H1O···O2^{i}	0.88 (2)	2.51 (2)	3.0838 (15)	123.3 (17)

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

The H atoms were placed in calculated positions and refined using a riding model, except for H10, which was located in a difference electron-density map and was refined with an isotropic displacement parameter.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT+* (Bruker, 1999); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXL* (Bruker, 1998); software used to prepare material for publication: *SHELXL*.

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