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2,3,6,7-Tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene bis(1,4-dioxane) solvate

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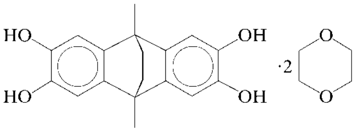
2,3,6,7-Tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene crystallizes with 1,4-dioxane to give a bis-solvate, $C_{18}H_{18}O_4 \cdot 2C_4H_8O_2$. The bis(catechol) molecule is located on a twofold axis and the two aromatic rings form a dihedral angle of 130.61 (4)°. Hydrogen bonds are formed between the hydroxyl groups and either a neighbouring bis(catechol) molecule or the ether-O atom of a dioxane molecule.

Comment

The condensation product of hexane-2,5-dione with catechol in sulfuric acid was at first considered, erroneously, to have an indano–indane structure (Niederl & Nagel, 1940). On the basis of NMR spectral (Le Goff, 1962) and chemical (Davidson & Musgrave, 1963) data, a dihydroethanoanthracene structure was suggested, but this compound appears to have been practically neglected in subsequent chemical literature, notwithstanding its potential interest as a building block for the preparation of synthetic receptors. In the course of our studies on catechol derivatives, we determined the crystal structure of this compound, 2,3,6,7-tetrahydroxy-9,10-dimethyl-9,10-dihydro-9,10-ethanoanthracene, subsequently denoted bis(catechol), as a bis(1,4-dioxane) solvate, (I). Dihydroanthracene and also dihydroethanoanthracene are rather common building blocks, but no structure comprising the tetrahydroxydihydroethanoanthracene unit has been reported. The crystal structures of very few molecules based on the tetrahydroxydihydroanthracene skeleton, which lack the dimethylene bridge and can be viewed as comprising two catechol rings linked in 4,5-positions by two C atoms, are known. A search of the Cambridge Structural Database (Allen & Kennard, 1993) gave only two hits, in which the bridges are substituted differently from those in (I) and the hydroxyl groups are replaced by methoxy ones (Benetollo *et al.*, 1990; Guy *et al.*, 1996).



(I)

The asymmetric unit of (I) comprises half a bis(catechol) and one 1,4-dioxane molecule, the bis(catechol) molecule admitting a twofold symmetry axis. The two catechol rings form a dihedral angle of 130.61 (4)°, whereas the dihedral angles between the catechol rings and the central plane defined (with an r.m.s. deviation of 0.004 Å) by atoms C7, C8, C9 and their symmetry-related counterparts are equal to 114.64 (4)°. The geometry thus appears somewhat distorted with respect to the ideal case of three dihedral angles of 120°. It is to be noted that the molecules with different bridges mentioned above are much flatter, with a dihedral angle between the aromatic rings of about 151.7° (Benetollo *et al.*, 1990).

Two kinds of hydrogen bonds involving the hydroxyl groups are present in (I). The two H atoms are very close to the aromatic mean plane, with deviations of 0.059 (3) and 0.156 (3) Å for H1 and H2, respectively. H1 is bound to the ether atom O3 of the dioxane molecule, whereas H2 is bound to the hydroxyl atom O1 of a neighbouring bis(catechol)

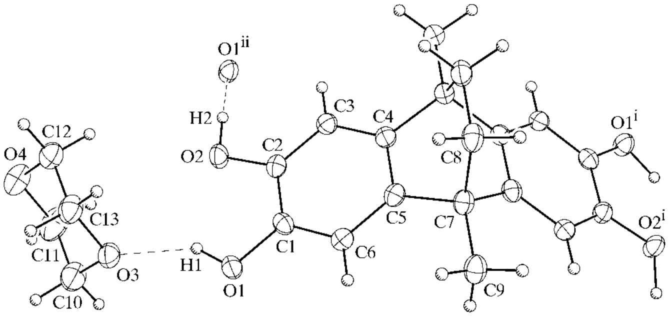


Figure 1
The title molecule, (I), with the atomic numbering scheme. H atoms are drawn as small spheres of an arbitrary radius and hydrogen bonds are shown as dashed lines. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: (i) $-x, y, \frac{1}{2}-z$; (ii) $x, -y, \frac{1}{2}+z$.

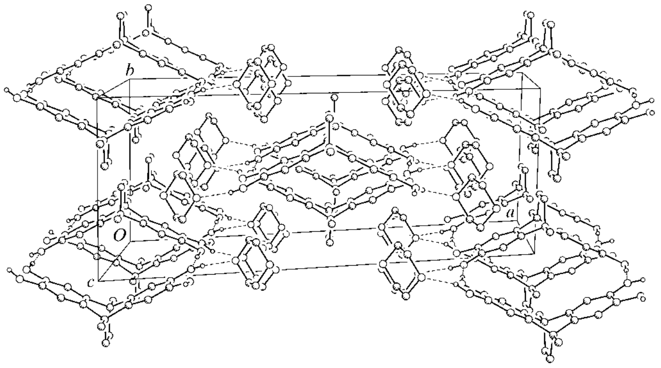


Figure 2
The packing arrangement of (I). H atoms have been omitted for clarity, except for those involved in hydrogen bonds. Hydrogen bonds are shown as dashed lines.

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molecule. The latter results in the formation of ribbons of alternate up and down bis(catechol) molecules, directed along the *c* axis. In projection on the *ab* plane, these ribbons present a lozenge shape. The hydrogen-bonded dioxane molecules are located on both sides of these ribbons and are located between adjacent ribbons, one above and the other below along the *b* axis.

Experimental

The title compound was synthesized as reported previously (Davidson & Musgrave, 1963) and recrystallized from 1,4-dioxane.

Crystal data

$C_{18}H_{18}O_4 \cdot 2C_4H_8O_2$
$M_r = 474.53$
Monoclinic, $C2/c$
$a = 25.6848$ (18) Å
$b = 9.7131$ (10) Å
$c = 10.5531$ (13) Å
$\beta = 111.630$ (6)°
$V = 2447.4$ (4) Å^3
$Z = 4$

$D_x = 1.288$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7056 reflections
$\theta = 3.3$–25.7°
$\mu = 0.10$ mm^{-1}
$T = 100$ (2) K
Parallelepiped, colourless
0.30 × 0.20 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
7056 measured reflections
2312 independent reflections
1723 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.063$
$\theta_{\rm max} = 25.7°$
$h = -31 \rightarrow 31$
$k = -11 \rightarrow 11$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.113$
$S = 1.06$
2312 reflections
155 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0361P)^2 + 1.9711P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.20$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.26$ e Å^{-3}

The hydroxyl H atoms were found on a difference Fourier map and introduced as found, in spite of O—H bonds slightly longer than usual. All other H atoms were introduced at calculated positions (CH 0.93, CH_2 0.97, CH_3 0.96 Å). All H atoms were treated as riding atoms with a displacement parameter equal to 1.2 (OH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom.

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O3	1.00	1.84	2.6745 (18)	138
O2—H2···O1$^{\rm i}$	1.09	1.58	2.6644 (18)	172

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

Data collection: *KappaCCD Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97; molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL*, *PARST*97 (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1094). Services for accessing these data are described at the back of the journal.

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