

STRUCTURE OF A 1:1 MOLECULAR COMPLEX OF  
TRANS-9,10-DIHYDROXY-9,10-DIPHENYL-9,10-DIHYDROANTHRACENE WITH ETHANOL

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**Summary:** X-ray analysis of the title complex revealed hydrogen-bonded chains comprising two crystallographically independent types of trans-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene molecules, in which the central 1,4-cyclohexadiene rings are respectively flat and very slightly puckered, with the ethanol molecules attached exclusively to the latter type.

The stereochemistry of 9,10-dihydroanthracene (1) and its 9,10-substituted derivatives has been a subject of considerable interest in the last three decades.<sup>1</sup> Unlike the parent 1,4-cyclohexadiene and 1,4-dihydronaphthalene, whose planar structures were resolved only recently after a long controversy,<sup>1,2</sup> 1 has been known to exist in the C<sub>2v</sub> boat-shaped (or folded) conformation through an early X-ray diffraction study.<sup>3</sup> The latest theoretical calculations confirmed that the boat-shaped conformation of 1 corresponds to a shallow potential minimum in both the gaseous phase and the solid state.<sup>4</sup> An X-ray analysis of 9,10-dihydro-1,2,5,6-dibenzanthracene appeared to provide the first example of a planar 9,10-dihydroanthracene skeleton,<sup>5</sup> but further work led to the conclusion that the two 'naphthalene groupings' make angles of 176.5° with the planar central 1,4-cyclohexadiene ring, resulting in an interplanar spacing of 0.18 Å between the groupings.<sup>6</sup>

The effect of single and multiple substitution at the 9- and 10-positions on the equilibrium geometry of 1 has been investigated by theoretical computations,<sup>2b</sup> NMR spectroscopy,<sup>1</sup> and X-ray crystallography.<sup>5,7-11</sup> We now report our determination of the molecular structure of trans-9,10-dihydroxy-9,10-diphenyl-9,10-dihydroanthracene (2) through an X-ray analysis of its 1:1 molecular adduct (3) with ethanol.

Recent work on molecular inclusion has shown that 2, along with other hydroxy host

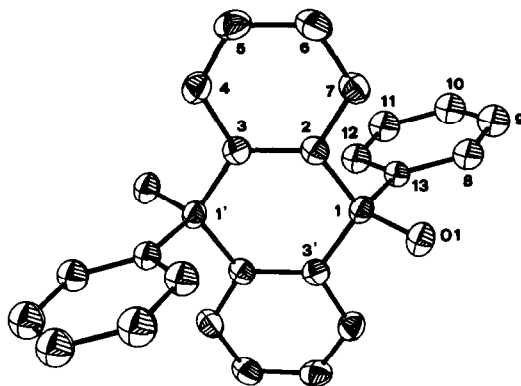
molecules, readily form crystalline adducts with a variety of alcohols.<sup>12</sup> The complexation has been successfully utilized to extract ethanol from its aqueous solution of various concentration, and may be of potential value in deriving inexpensive energy from the fermentation of biomass. Our decision to investigate  $\mathfrak{z}$  was prompted by its unexpected stoichiometry, which poses intriguing questions concerning the mode of molecular association in the crystalline state.

Crystal data.  $C_{26}H_{20}O_2 \cdot C_2H_6O$  ( $\mathfrak{z}$ ), MW = 410.51, triclinic, space group  $P\bar{1}$  (from intensity statistics),  $a = 9.148(5)$ ,  $b = 9.599(4)$ ,  $c = 13.765(6)$  Å,  $\alpha = 114.98(3)$ ,  $\beta = 91.38(4)$ ,  $\gamma = 97.55(4)^\circ$ ,  $V = 1081.9(8)$  Å<sup>3</sup>,  $Z = 2$ ,  $D_c = 1.260$ ,  $D_m$  (flotation in aqueous KI) = 1.28 g cm<sup>-3</sup>, Mo-K $\alpha$  radiation (graphite-monochromatized),  $\lambda = 0.71069$  Å,  $\mu = 0.75$  cm<sup>-1</sup>.

Complex  $\mathfrak{z}$  rapidly turns opaque upon exposure to air. A single crystal (0.42 x 0.40 x 0.34 mm) was sealed in a Lindemann glass capillary partly filled with ethanol at its tip portion. Intensities ( $2\theta_{max} = 45^\circ$ ) were collected on a Nicolet R3m diffractometer system using the  $\omega$ - $2\theta$  variable scan ( $2.02$ - $8.37^\circ$  min<sup>-1</sup>) technique. A total of 2394 unique reflections were processed with the learnt-profile procedure<sup>13</sup> and corrected for Lorentz and polarization factors.

Structure solution was achieved by direct methods based on negative quartets.<sup>14</sup> In subsequent refinement, the phenyl rings were treated as rigid groups (hexagons of edge 1.395 Å), and the remaining C and O atoms were varied anisotropically. All H atoms except that belonging to the ethanolic OH group were included in structure factor calculations. Convergence for 2014 observed data [ $|F_o| > 3\sigma|F_o|$ ] and 199 variables was reached at  $R = 0.086$ . All computations were performed with the SHELXTL program package.<sup>15</sup> The weighting scheme employed was  $w = [\sigma^2(|F_o|) + 0.0008|F_o|^2]^{-1}$ . Positional and thermal parameters (atom numbering given in Figure 1), bond distances, and bond angles have been deposited at the Cambridge Crystallographic Data Centre.

Figure 1. Perspective view of the molecular structure of  $\mathfrak{z}$  in  $\mathfrak{z}$ . Atom labelling in the asymmetric unit of molecule I is shown; for molecule II, change O1 to O2, single prime to double prime in the superscript, and add 13 to the numbering of each C atom.



The present structure is unusual in that it contains two molecules of  $\underline{2}$  occupying non-equivalent sites of symmetry  $\bar{1}$ ; molecules  $\underline{I}$  and  $\underline{II}$  are centered at  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ , respectively (Figure 2). These crystallographically distinct molecules are alternately linked by  $O(1)\cdots H-O(2)$  hydrogen bonds [ $2.767(8) \text{ \AA}$ ] to form infinite zigzag chains extending along the  $\underline{c}$  axis, with ethanol molecules attached laterally via acceptor hydrogen bonds [ $O(3)\cdots H-O(1) = 2.894(9) \text{ \AA}$ ]. The ethanol molecule does not partake in donor hydrogen bonding, and in this respect the mode of molecular association differs from that observed in the 1:2 complex of 2,5-bis(2,4-dimethylphenyl)hydroquinone with ethanol.<sup>16</sup>

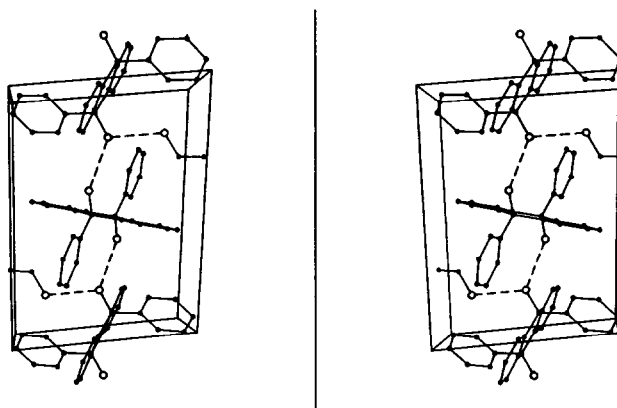
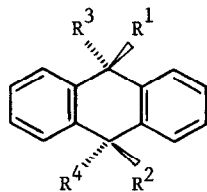


Figure 2. Stereodrawing of the molecular packing in  $\underline{3}$ . Hydrogen bonds are indicated by broken lines. The origin of the unit cell lies at the upper left corner, with  $\underline{a}$  pointing from left to right,  $\underline{b}$  towards the reader, and  $\underline{c}$  downwards.

Molecules  $\underline{I}$  and  $\underline{II}$  have very similar dimensions, except that the C-O bond in  $\underline{I}$  [ $O(1)-C(1) = 1.426(6) \text{ \AA}$ ] is significantly shorter than that in  $\underline{II}$  [ $O(2)-C(14) = 1.461(7) \text{ \AA}$ ], which correlates well with the mode of hydrogen bonding. The 1,4-cyclohexadiene ring of  $\underline{I}$

Table 1. Structures of some 9,10-substituted 9,10-dihydroanthracenes

	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Central ring	Ref.
$\underline{1}$	H	H	H	H	folded, $\delta = 145^\circ$	5
$\underline{4}$	t-Bu	H	H	H	folded, $\delta = 146.6^\circ$	7
$\underline{5}$	Me	Et	H	H	folded, $\delta = 152^\circ$	8
$\underline{6}$	Me	H	H	i-Pr	folded, $\delta = 129^\circ$	9
$\underline{7}$	SiMe <sub>3</sub>	SiMe <sub>3</sub>	H	H	deformed-boat	10
$\underline{8}$	SiMe <sub>3</sub>	H	H	SiMe <sub>3</sub>	deformed-chair	10
$\underline{9}$	Cl	Cl	Cl	Cl	$\underline{I}$ and $\underline{II}$ both planar	11
$\underline{2}$	OH	Ph	Ph	OH	$\underline{I}$ very slightly pucked, this work $\underline{II}$ planar	



$\delta$  = dihedral angle  
between benzene rings

deviates slightly but significantly from planarity (rms  $\Delta = 0.033 \text{ \AA}$ , chair-like distortion), and its mean plane makes a dihedral angle of  $176^\circ$  with an adjacent benzene ring. On the other hand, the carbon skeleton of the 9,10-dihydroanthracene moiety of II attains planarity well within experimental error.

The diversity in structure of 9,10-substituted 9,10-dihydroanthracenes is illustrated in Table 1, showing that the conformational preference of the central ring depends on the degree and pattern of substitution as well as the steric bulk of the substituents. However, it remains an open question as to whether disubstitution at the 9-position would be sufficient to flatten the central ring.

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