PERKIN 2

# Roof-shaped hydroxy hosts: synthesis, complex formation and X-ray crystal structures of inclusion compounds with EtOH, nitroethane and benzene

**Edwin Weber,**[*,a] **Thomas Hens,**[a] **Olga Gallardo**[b] **and Ingeborg Csöregh**[*,b]

[a] *Institut für Organische Chemie der Technischen Universität Bergakademie Freiberg, Leipziger Straße 29, D-09596 Freiberg/Sa., Germany*
[b] *Department of Structural Chemistry, Arrhenius Laboratory, Stockholm University, S-10691 Stockholm, Sweden*

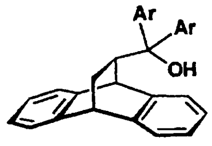
**A series of crystalline host molecules 1 and 2a–e, based on a characteristic 9,10-dihydro-9,10-ethanoanthracene rigid framework and appended diarylmethanol clathratogenic groups, has been synthesized and studied with regard to their inclusion behaviour. These hosts form crystalline inclusion compounds with a variety of uncharged organic molecules, ranging from protic dipolar to apolar compounds (183 different species), but show a preference for amines and aromatic hydrocarbons. The bis-methanols are largely superior to the mono-methanols, except for the 4-chlorophenyl substituted methanol, which has proved to have equal efficiency.**

**The building principles and the mode of complexation of the host compound 2a (*trans*-α,α,α′,α′-tetraphenyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol) with ethanol (protic), nitroethane (aprotic polar) and benzene (aprotic apolar) as guests have been investigated by single crystal X-ray diffraction. The conformation of the host molecule observed in the 1:2 (host:guest) EtOH complex is different from that in the nitroethane (1:1) or benzene (2:1) inclusions. The host–guest contact pattern in 2a·EtOH (1:2) features a huge 16-membered loop of H-bonds involving four functional OH groups of both host and guest, with one intra-host H-bond for each of the two host molecules of the 2:4 (host:guest) aggregate. On the other hand, in the compounds of 2a with the aprotic guest species nitroethane and benzene the host hydroxys are involved in specific intramolecular OH ··· π-aryl contact, thus yielding true lattice-type inclusions, although with different organizations. Accordingly, in 2a·nitroethane (1:1) the polar guest units fill up the voids between the bulky host molecules, while in 2a·benzene (2:1) the host molecules are arranged so as to form tunnels in the crystallographic *c* direction, where the guests are located.**

Molecules (hosts) that recognize and bind to specific substrates (guests) are important for analytical applications and for the development of more effective catalysts, carriers and reagents.[1] Exploring interactions at the supramolecular level is therefore an exciting and challenging aspect of contemporary chemistry.[2]

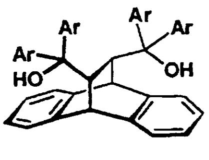
'Coordinatoclathrand'[3] is the name we have given to a particular type of substance which allows specific interactions between host and guest molecules in the crystalline state. Interactions proceed from functional group relationships involving the host and the guest, and they include H-bonds as the main factor. Most of our work in this respect has been focused on the design of carboxylic acid hosts with $CO_2H$ sensor groups strategically attached to particular rigid frameworks[4] which may resemble a pair of scissors,[5] may consist of small-ring compounds,[6] or may involve a roof-shaped skeleton.[7] Recently, we have also demonstrated the diarylmethanol unit to be an efficient 'clathratogenic group'[8] when combined with a rigid structural element such as a molecular axis[9] or a twisted aromatic building block.[10]

Consequently, we have now tested a host design involving both the characteristic roof-shaped 9,10-dihydro-9,10-ethanoanthracene basic skeleton and appended diarylmethanol clathratogenic groups. Preparation of specific compounds of this type (**1a–e**, **2a–c** and **2e**) is described, crystal inclusion properties are discussed, and X-ray crystal structures of three isolated host–guest species are reported, which are inclusion compounds between **2a** and polar protic [**2a**·EtOH (1:2)], polar aprotic [**2a**·nitroethane (1:1)] and apolar aprotic [**2a**·benzene (2:1)] guests.

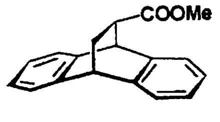


**1**

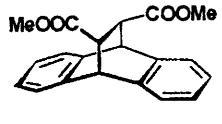
a; Ar = Ph
b; Ar = 4-$MeC_6H_4$
c; Ar = 4-$Bu^tC_6H_4$
d; Ar = 4-$FC_6H_4$
e; Ar = 4-$ClC_6H_4$



**2**



**3**



**4**

## Results and discussion

### Synthesis

Compounds **1** and **2** were synthesized from the roof-shaped esters **3** and **4** *via* addition of organometallic reagents. The

**Table 1** Crystalline inclusion compounds (host : guest stoichiometric ratios)[a]

| Guest solvent | Host compound | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | **1a** | **1b** | **1c** | **1d** | **1e** | **2a** | **2b** | **2c** | **2e** |
| $PrNH_2$ | 3:2 | — | 3:2 | — | 1:1 | 1:2 | 1:1 | 1:1 | 1:1 |
| $Pr^iNH_2$ | 3:1 | — | 3:1 | — | 1:1 | 1:2 | 1:1 | 1:1 | 1:1 |
| $BuNH_2$ | — | 1:1 | — | — | 1:1 | 1:2 | 1:1 | 1:1 | 1:1 |
| $Bu^iNH_2$ | — | 1:1 | — | — | — | 1:2 | 1:1 | 1:2 | 1:1 |
| 2-$BuNH_2$ | — | — | — | — | 1:1 | 1:2 | 1:1 | 1:2 | 1:1 |
| c-$HexNH_2$ | — | — | — | — | 1:2 | — | 1:1 | 1:2 | 1:2 |
| $Et_2NH$ | — | — | — | — | 2:1 | — | 1:1 | 1:2 | 1:2 |
| $Pr_2NH$ | — | — | — | — | 2:1 | — | 1:1 | 1:2 | 2:3 |
| $Bu_2NH$ | — | — | — | — | — | — | 1:1 | 1:2 | 2:3 |
| $Et_3N$ | — | — | — | — | 1:1 | 1:1 | 2:1 | 1:1 | 2:1 |
| $Pr_3N$ | — | — | — | — | — | — | 2:1 | 1:1 | 2:1 |
| $Bu_3N$ | — | — | — | — | — | — | 2:1 | — | 1:1 |
| Piperidine | 1:2 | — | 1:2 | — | — | 1:2 | 1:2 | 1:2 | 1:2 |
| Pyridine | — | — | — | — | 1:1 | — | 1:1 | 1:2 | 1:1 |
| 2-Picoline | — | — | — | — | 1:1 | — | 1:1 | 1:2 | 1:1 |
| 3-Picoline | — | — | — | — | 1:1 | — | 1:1 | 1:1 | 1:1 |
| 4-Picoline | — | — | — | — | — | — | 1:1 | 1:1 | 1:1 |
| MeOH | — | — | — | — | — | — | 1:1 | 1:1 | —[c] |
| EtOH | — | — | — | — | — | 1:2 | 3:1 | 1:2 | —[c] |
| $Pr^iOH$ | — | — | — | 3:1 | — | 3:1 | 3:2 | — | —[c] |
| $Bu^iOH$ | — | — | — | 3:1 | — | — | — | — | —[c] |
| 2-BuOH | — | — | — | — | — | — | — | 1:1 | —[c] |
| $Bu^tOH$ | — | — | — | 1:1 | — | 1:2 | — | — | —[c] |
| 2-PentOH | — | — | — | — | — | 1:1 | 1:1 | — | 1:1 |
| c-PentOH | — | — | — | — | 1:1 | 2:1 | 1:1 | — | 1:1 |
| c-HexOH | — | — | — | — | 1:1 | —[b] | —[b] | — | — |
| c-HeptOH | —[b] | — | — | — | 1:1 | —[b] | —[b] | —[b] | 1:1 |
| Acetone | — | — | — | — | 1:1 | 1:1 | 1:1 | 2:1 | — |
| Cyclopentanone | — | — | — | — | — | 1:1 | — | 1:1 | 1:3 |
| Cyclohexanone | — | — | — | — | — | — | — | 1:2 | —[b] |
| 2-Methylbutyraldehyde | — | — | — | — | — | — | — | —[b] | 1:1 |
| AcOEt | —[c] | — | — | — | 1:1 | —[c] | 1:1 | —[c] | — |
| DMF | — | — | — | 1:1 | 1:1 | — | 1:2 | 1:2 | 1:2 |
| DMSO | 1:1 | — | — | — | 1:1 | 1:2 | 1:2 | 1:2 | 1:2 |
| Acetonitrile | — | — | — | — | 1:1 | 1:2 | 1:1 | 1:1 | 1:2 |
| Propionitrile | — | — | — | — | 1:1 | 1:1 | 1:1 | — | 1:2 |
| Butyronitrile | — | — | — | — | 1:1 | 1:1 | — | — | 1:2 |
| Benzonitrile | — | — | — | — | 1:1 | 1:1 | — | — | 1:2 |
| Nitromethane | — | — | — | — | 1:1 | — | 1:1 | 1:1 | 1:1 |
| Nitroethane | — | — | — | — | 1:1 | 1:1 | 1:1 | — | 1:1 |
| THF | — | — | — | — | 1:1 | — | 1:1 | 1:1 | 1:2 |
| 1,4-Dioxane | — | — | 4:1 | — | 1:1 | — | 1:1 | 1:1 | 1:2 |
| Benzene | — | — | — | 1:1 | 1:1 | 2:1 | 1:1 | 1:1 | 1:1 |
| Toluene | — | — | — | 1:1 | 1:1 | 3:1 | 1:1 | 1:1 | 1:1 |
| *o*-Xylene | 1:1 | — | — | 1:1 | 1:1 | 3:1 | 1:1 | 3:1 | 1:3 |
| *m*-Xylene | — | — | — | 1:1 | 1:1 | 3:1 | 1:1 | 3:1 | 1:1 |
| *p*-Xylene | — | — | — | 1:1 | 1:1 | 3:1 | 1:1 | 3:1 | 3:1 |

[a] See Experimental section for methods of preparation, drying standard and characterization. [b] Difficult to crystallize. [c] Not tested.

mono-methanols **1a–e** were prepared in 64–73% yield from **3** by Grignard reactions with the corresponding aryl bromides. The bis-methanols **2a–c** and **2e** were obtained in 36–65% from **4** and aryl bromides, using BuLi.

## Inclusion properties

In order to show the inclusion behaviour of potential host compounds **1** and **2** as completely as possible, we used a broad variety of solvents including amines, alcohols, nitriles, nitro compounds and other aprotic dipolar solvents, heterocycles and aromatic hydrocarbons of different constitutions (*cf.* Table 1) for the recrystallization (clathration) experiments. The capability of the present hosts in forming inclusion compounds is evident from Table 1. A total of 183 different lattice inclusions are specified there, showing the general efficiency of the diarylmethanol-substituted roof framework. Nevertheless, the individual compounds **1a–e**, **2a–c** and **2e** are rather different in their inclusion ability and demonstrate a characteristic level of selectivity.

The greatest number of inclusions by far are formed by the bis-methanols **2**, while the mono-methanols **1** allow considerably fewer inclusions, except for **1e** which is just as efficient as the bis-methanols. One may speculate that intramolecular Cl · · · Cl interactions[11] promote the formation of inclusion lattices in this case. Another general difference between the inclusions of **1** and **2** is obvious from the host : guest stoichiometric ratios. Whereas compounds **1** favour the 1 : 1 stoichiometric ratio, compounds **2** generally form both 1 : 1 and 1 : 2 stoichiometric ratios besides some 2 : 1, 2 : 3, 1 : 3 and 3 : 1 ratios. In other words, the bis-methanols **2** are more inclined to form high host–guest-ratio inclusions than the mono-methanols **1**, corresponding to the number of clathratogenic groups. On the other hand, it is difficult to see a correlation between the nature of substituents on the host aryl groups and stoichiometric host–guest ratios. Nevertheless, a comparison between methyl substituted **2b** and *tert*-butyl substituted **2c** shows that the bulky *tert*-butyl groups provide more lattice space for guests, thus giving rise to a high number of 1 : 2 host–guest ratios at inclusion formation.

With reference to the guest solvent class of compounds, there is a clear preference for entrapment of amines and aromatic hydrocarbons, while alcohols and carbonyl compounds are not

**Table 2** Crystal data, experimental parameters and selected refinement details for **2a**·EtOH (1 : 2), **2a**·nitroethane (1 : 1) and **2a**·benzene (2 : 1)

| | | | |
|---|---|---|---|
| Crystal data | | | |
| Formula | $C_{42}H_{34}O_2{\cdot}2C_2H_5OH$ | $C_{42}H_{34}O_2{\cdot}C_2H_5NO_2$ | $C_{42}H_{34}O_2{\cdot}0.5C_6H_6$ |
| Formula weight | 662.87 | 645.80 | 609.79 |
| $F(000)$ | 1416 | 1368 | 2584 |
| Space group | $P2_1/c$ (No. 14) | $P2_1/c$ (No. 14) | $I\bar{4}$ (No. 82) |
| $a$/Å | 12.931(1) | 12.094(1) | 23.089(1) |
| $b$/Å | 11.940(1) | 12.063(1) | 23.089(1) |
| $c$/Å | 23.787(2) | 23.773(2) | 12.377(1) |
| $\alpha$/° | 90 | 90 | 90 |
| $\beta$/° | 91.71(1) | 102.37(1) | 90 |
| $\gamma$/° | 90 | 90 | 90 |
| $V$/Å$^3$ | 3671.0(5) | 3387.7(5) | 6598.2(7) |
| $Z$ | 4 | 4 | 8 |
| $D_c$/g cm$^{-3}$ | 1.199 | 1.266 | 1.228 |
| μ/cm$^{-1}$ | 0.699 | 0.749 | 0.684 |
| Approximate crystal size/mm | 0 .342 × 0.360 × 0.556 | 0.209 × 0.446 × 0.380 | 0.143 × 0.190 × 0.347 |
| Intensity measurements | | | |
| Radiation (λ/Å) | Mo-Kα (0.710 69) | Mo-Kα (0.710 69) | Mo-Kα (0.710 69) |
| Temperature/K | 193 ± 1 | 173 ± 1 | 173 ± 1 |
| Scan type | $\omega$–$2\theta$ | $\omega$–$2\theta$ | $\omega$–$2\theta$ |
| Range of $2\theta$/° | 3–55 | 3–55 | 3–60 |
| Range of $hkl$ | −16/16 0/15 0/30 | 0/15 0/15 −30/30 | 0/32 0/32 0/17 |
| No. of collected reflections | 9042 total, 6972 unique | 8636 total, 6540 unique | 5034 total, 4347 unique |
| No. of standard reflections | 4 | 4 | 5 |
| Time interval/min | 90 | 90 | 60 |
| Intensity instability (%) | *ca.* 2.5 | *ca.* 1 | *ca.* 1 |
| Structure refinement | | | |
| No. of reflections included | 3179 with $I > 3\sigma$ | 3124 with $I > 3\sigma(I)$ | 2066 with $I > 2\sigma(I)$ |
| Total no. of refined parameters[a] | 459 | 430 | 422 |
| Linear agreement factor $R = \Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert$ | 0.042 | 0.060 | 0.048 |
| Weighted agreement factor $wR = [\Sigma w\lvert\Delta F\rvert^2/\Sigma w\lvert F_o\rvert^2]^{\frac{1}{2}}$ | 0.050 | 0.077 | 0.051 |
| Weighting: $w = k/[\sigma^2(F) + g\lvert F\rvert^2]$ with $g$ | 0.0004 | 0.0057 | 0.0006 |
| Weighted agreement factor including all unique non-zero reflections $wR_{tot}$ | 0.059 | 0.084 | 0.059 |
| Final $\Delta\rho_{max}/\Delta\rho_{min}$/e Å$^{-3}$ | 0.34/−0.21 | 0.56/−0.45 | 0.26/−0.20 |

[a] Blocked full-matrix refinements have been performed (see the text).

**Table 3** Selected torsion angles (°) for **2a**·EtOH (1 : 2), **2a**·nitroethane (1 : 1) and **2a**·benzene (2 : 1) with e.s.d.s in parentheses

| Torsion angle | **2a**·EtOH (1 : 2) | **2a**·nitroethane (1 : 1) | **2a**·benzene (2 : 1) |
|---|---|---|---|
| C(13)–C(10)–C(11)–C(26) | −89.7(3) | 112.0(4) | −111.5(4) |
| C(11)–C(10)–C(13)–O(13) | 30.1(3) | 49.5(4) | −45.5(5) |
| C(11)–C(10)–C(13)–C(14) | −87.4(3) | 171.9(3) | −167.4(4) |
| C(11)–C(10)–C(13)–C(20) | 148.5(2) | −69.2(4) | 74.5(5) |
| C(10)–C(11)–C(26)–O(26) | 34.8(3) | 37.6(4) | −42.5(5) |
| C(10)–C(11)–C(26)–C(27) | −83.6(3) | 159.7(3) | −163.3(4) |
| C(10)–C(11)–C(26)–C(33) | 152.4(2) | −81.6(4) | 76.7(5) |
| C(10)–C(13)–O(13)–H(O13) | 31.7 | 48.8 | −45.2 |
| C(11)–C(26)–O(26)–H(O26) | −172.1 | 67.5 | −51.1 |
| O(13)–C(13)–C(14)–C(15) | 143.5(3) | 174.5(4) | −173.2(4) |
| O(13)–C(13)–C(20)–C(21) | −43.1(3) | 22.2(5) | −24.0(6) |
| O(26)–C(26)–C(27)–C(28) | −34.6(3) | −4.1(5) | 2.0(6) |
| O(26)–C(26)–C(33)–C(34) | −52.8(3) | 27.6(5) | −25.1(5) |

so easily included. In particular, the unbranched alcohols, *e.g.* PrOH and BuOH, were found to be inefficient. There is also one more remarkable finding: the mono-methanol **1a** readily yields a crystalline inclusion compound with *o*-xylene but fails to enclathrate *m*- and *p*-xylene. This result stimulated guest-competition experiments using solvent mixtures of *o*-xylene with either benzene, toluene and *m*- or *p*-xylene for recrystallization of **1a**. In each case *o*-xylene is clearly favoured.

In order to investigate the building principles of the new clathrate design, and in particular to learn what modes of interaction the new host type uses for enclathration of polar protic and apolar guest molecules, we have studied the crystal structures of **2a**·EtOH (1:2), **2a**·nitroethane (1:1) and **2a**·benzene (2:1).

## X-Ray analysis: structure description of 2a·EtOH (1:2), 2a·nitroethane (1:1) and 2a·benzene (2:1)

Illustrations of the crystallographic asymmetric units, with crystallographic atomic numbering of the inclusion compounds formed by the host **2a** with the respective guest are shown in Fig. 1. Stereo packing diagrams are presented in Figs. 2–4. Crystal data and selected experimental and refinement details are given in Table 2.

### Molecular structures

A noteworthy feature of these three structures is the conformational flexibility of the host molecule. The geometry of the host unit **2a** is similar (conformation 1) in the inclusions with nitroethane or benzene and differs from that of the

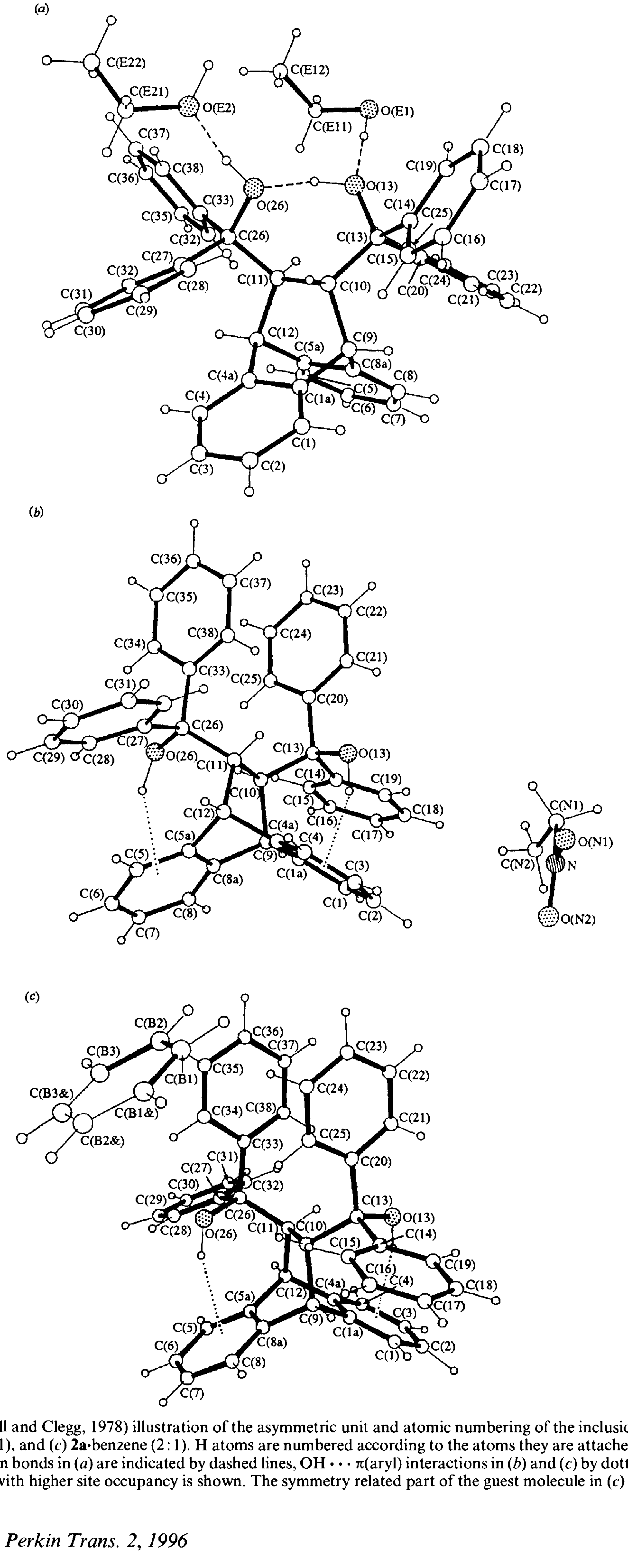


**Fig. 1** PLUTO (Motherwell and Clegg, 1978) illustration of the asymmetric unit and atomic numbering of the inclusion compounds: (*a*) **2a**·EtOH (1 : 2), (*b*) **2a**·nitroethane (1 : 1), and (*c*) **2a**·benzene (2 : 1). H atoms are numbered according to the atoms they are attached to. O atoms are shaded; N atoms hatched. The hydrogen bonds in (*a*) are indicated by dashed lines, OH · · · π(aryl) interactions in (*b*) and (*c*) by dotted lines. For the $NO_2$ group in (*b*) only the disorder site with higher site occupancy is shown. The symmetry related part of the guest molecule in (*c*) is drawn by thinner lines.

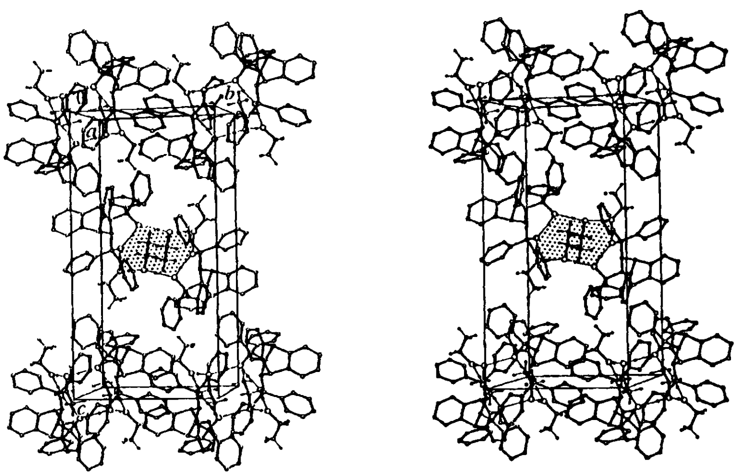


**Fig. 2** Stereo packing diagram of the inclusion compound **2a**·EtOH (1 : 2). An example of an H-bonded ring system, involving host and guest, is specified by dotting. H-bonds are drawn as thin lines. The H atoms of the host molecule that do not participate in hydrogen bonding are omitted for clarity.

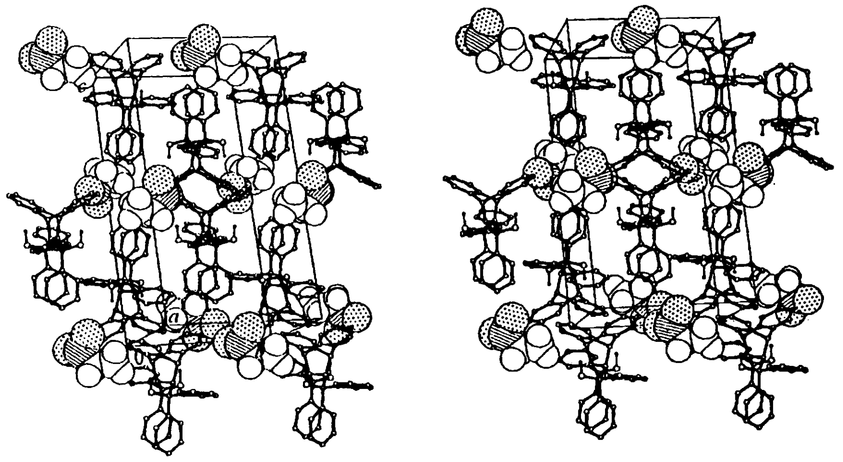


**Fig. 3** Stereo packing diagram of the inclusion compound **2a**·nitroethane (1 : 1). The guest molecules are drawn as space filling-models (O atoms shaded, N atoms hatched). For the $NO_2$ group only the disorder site with higher site occupancy is shown. The H atoms of the host molecule are omitted for clarity.

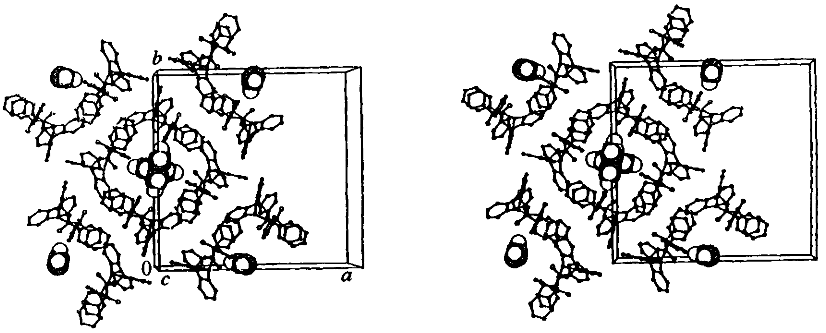


**Fig. 4** Stereo packing diagram of the inclusion compound **2a**·benzene (1 : 1). The guest molecules are drawn as space-filling models. The H atoms of the host molecule are omitted for clarity.

inclusion with ethanol (conformation 2) in the spatial arrangement of the diarylmethanol groups with respect to the dihydroanthracene moiety. The conformational transformation can be seen as rotation of the diary methanol groups of conformation 1 around C(10)–C(13) and C(11)–C(26) bonds so that the intramolecular hydrogen bonding between the OH groups as a part of the hydrogen bond pattern in **2a**·EtOH (1 : 2) inclusion is established for conformation 2 (see section below, on packing relations and host–guest interactions). Selected torsion angles for all three inclusions are shown in Table 3. Both OH groups in conformation 1 seem to be engaged in intramolecular hydrogen bonding involving the π-electron cloud of the nearest benzo ring of the dihydroanthracene moiety. Recently, crystallographic evidence of inter-[12a,b] and intramolecular[12c] hydrogen bonding between OH groups and aromatic π-electrons has been reported. The alcoholic hydrogen atoms in our compounds lie above the periphery of the π-cloud of the respective ring, as was also observed for similar intramolecular interactions in [tris(dimethylphenylsilyl)methyl]-methylsilanol.[12c] The distance from the OH hydrogen atom to the nearest carbon atom of the relevant phenyl group is: 2.09 Å from O(13)H to C(1a) and 2.17 Å from O(26)H to C(5a) in **2a**·nitroethane (1 : 1), and 2.18 Å from O(13)H to C(1a) and 2.21 Å from O(26)H to C(5a) in **2a**·benzene (2 : 1). The distance between the corresponding OH hydrogen atom and the mean plane of the ring is 2.08 Å for O(13)H and 2.12 Å for O(26)H in

**Table 4** The geometry of hydrogen bonds and possible C–H ··· O interactions for **2a**·EtOH (1 : 2), **2a**·nitroethane (1 : 1) and **2a**·benzene (2 : 1). The e.s.d.s, where given, are in parentheses[a]

| Atoms involved | Symmetry | Distance/Å |  |  | Angle/° |
|---|---|---|---|---|---|
|  |  | Donor ··· Acceptor | Donor–H | H ··· Acceptor | Donor–H ··· O |
| **2a**·EtOH (1 : 2) |  |  |  |  |  |
| O(13)–H(O13) ··· O(26) | $x, y, z$ | 2.545(2) | 1.05 | 1.51 | 169 |
| O(26)–H(O26) ··· O(E2) | $x, y, z$ | 2.633(3) | 0.95 | 1.70 | 167 |
| O(E1)–H(OE1) ··· O(13) | $x, y, z$ | 2.720(3) | 1.00 | 1.72 | 180 |
| O(E2)–H(OE2) ··· O(E1) | $-x + 1, -y + 2, -z$ | 2.690(3) | 1.00 | 1.69 | 180 |
| C(34)–H(34) ··· O(E2) | $x, y, z$ | 3.459(4) | 1.00 | 2.55 | 151 |
| C(11E)–H(112) ··· O(13) | $x, y, z$ | 3.268(4) | 1.00 | 2.99 | 97 |
| **2a**·nitroethane (1 : 1) |  |  |  |  |  |
| O(13)–H(O13) ··· centroid(1)[b] | $x, y, z$ | 3.352(3) | 1.02 | 2.38 | 159 |
| O(26)–H(O26) ··· centroid(2)[c] | $x, y, z$ | 3.397(3) | 1.12 | 2.41 | 146 |
| C(3)–H(3) ··· O(N1) | $-x, -y + 1, -z$ | 3.43 | 1.00 | 2.67 | 133 |
| C(8)–H(8) ··· O(N1) | $x, y - 1, z$ | 3.50 | 1.00 | 2.52 | 165 |
| C(3)–H(3) ··· O(N1′) | $-x, -y + 1, -z$ | 3.37 | 1.00 | 2.42 | 158 |
| C(3)–H(3) ··· O(N2′) | $-x, -y + 1, -z$ | 3.42 | 1.00 | 2.76 | 124 |
| **2a**·benzene (2 : 1) |  |  |  |  |  |
| O(13)–H(O13) ··· centroid(1)[b] | $x, y, z$ | 3.310(4) | 0.91 | 2.42 | 168 |
| O(26)–H(O26) ··· centroid(2)[c] | $x, y, z$ | 3.354(3) | 0.98 | 2.40 | 163 |
| C(2)–H(2) ··· O(26) | $y + 1, -x + 1, -z$ | 3.280(6) | 1.08 | 2.42 | 135 |

[a] The carbon-bonded H atom positions in all three inclusions and the disordered nitro group positions in **2a**·nitroethane (1 : 1) are not refined. [b] Centroid means the geometrical centre of the benzo ring C(1a)–C(1)–C(2)–C(3)–C(4)–C(4a). [c] Centroid means the geometrical centre of the benzo ring C(5a)–C(5)–C(6)–C(7)–C(8)–C(8a).

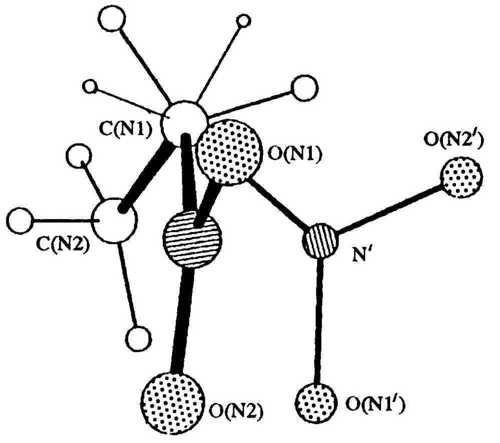


**Fig. 5** View of the guest molecule in **2a**·nitroethane (1 : 1) showing the major disorder positions of the nitro group. The primed atom positions belong to the disorder model with the lower site occupancy (see the text).

**2a**·nitroethane (1 : 1), and 2.16 Å for O(13)H and 2.18 Å for O(26)H in **2a**·benzene (2 : 1). Both hydrogen bonds in the two inclusions are directed essentially towards the centre of the ring (Table 4) with O(13)–H and O(26)–H bonds making angles of 56 and 51° with the respective phenyl planes in the inclusion with nitroethane and 60 and 55° in the inclusion with benzene. The OH groups show rather vigorous thermal motion, suggesting weak attractive forces for this type of interaction. Conformation 1 seems to be additionally stabilized by a weak charge-transfer effect between the $\pi$-electron clouds of the benzo rings C(20)–C(21)–C(22)–C(23)–C(24)–C(25) and C(33)–C(34)–C(35)–C(36)–C(37)–C(38). The dihedral angle between the least-squares planes through these two rings is 6.4(2) and 6.4(1)°, and the distance between their geometrical centres is 3.547(3) and 3.566(3) Å for **2a**·nitroethane (1 : 1) and **2a**·benzene (2 : 1), respectively. The tricyclic dihydroanthracene moiety has the usual 'roof' shape with a dihedral angle of 119.3(1), 120.7(1) and 124.8(2)° in **2a**·EtOH (1 : 2), **2a**·nitroethane (1 : 1) and **2a**·benzene (2 : 1), respectively, between the two phenyl ring planes. We have noted, in earlier X-ray studies of compounds containing the basic dihydroethanoanthracene moiety,[7,8] that the two sides of the ethano bridge [the C(9)–C(10) and C(11)–C(12) bonds] are always elongated due to the strain in the molecule, whereas the C(10)–C(11) bond distance in between them conforms to the expected value of 1.541 ± 3 Å[13] for such bonds. The ethano bridge in the earlier studied compounds was either connected to carboxy groups[7a–d] or amide substituents[7e] or was fused to a planar succinimide ring.[8] Substitution on the ethano bridge with the bulky diarylmethanol groups gives rise to additional strain in the molecule as indicated by the observed bond lengths. Accordingly, not only the two side bonds mentioned above, but all three bonds of the ethano bridge together with those linking the diarylmethanol groups to the ethano bridge are elongated in the host **2a**. The average lengths of the elongated bonds in the ethano bridge and bonds from the basic skeleton to diarylmethanol groups, with r.m.s.d.s in square brackets, are 1.576[5] and 1.573[5] Å, respectively.

The guest molecules in all three inclusions are disorded to some extent. The atomic displacement parameters indicate larger mobility for the atoms of the alcohol guests than for those of the host. The larger displacement parameters for the atoms of the guest units in the two aprotic guest inclusions indicate their weaker fixation in the crystal lattice. For the nitro group in **2a**·nitroethane (1 : 1) two major disorder sites were realized (Fig. 5). The dihedral angle formed by the planes through the two disorder positions of the $NO_2$ group is 59.9(5)°. The loose attachment of the guest molecules gives rise to decrease of the observed bond lengths values from the ideal ones.

### Packing relations and host–guest interactions

The host molecule **2a** equipped with two alcoholic OH groups has potential capability for both intra- and inter-molecular hydrogen bonding of the O–H ··· O type. Nevertheless, strong inter-host hydrogen bonding is not observed in any of the present inclusions, though intramolecular hydrogen bonding is found in **2a**·EtOH (1 : 2). The host–guest interaction pattern in this inclusion compound is characterized by 16-membered hydrogen-bonded loops (Table 4) which are located around the centre of symmetry. Each loop includes four guest and two host molecules. As subunits of this pattern, two seven-membered intramolecular hydrogen-bonded rings involving both OH groups of the the same host are observed. The O(13)–H $\cdots$ O(26) bond length is shorter than both intermolecular O(E2)–H $\cdots$ O(26) and O(E1)–H $\cdots$ O(13) bonds (Table 4). Perhaps this property meets the second empirical hydrogen-bond rule,[14] which suggests that in crystal structures intramolecular hydrogen bonds formed between similar donors and acceptors usually occur in preference to intermolecular hydrogen bonds, when donor and acceptor groups are positioned to allow such an interaction. Although the validity of this rule has been proved for six-membered H-bonded rings only, seven-membered rings may be treated similarly. Intermolecular C–H $\cdots$ O contacts shorter than 3.6 Å of possible electrostatic nature[15] further enhance the host–guest interaction (Table 4). The 2:4 host–guest associates are then held together in the crystal by ordinary van der Waals forces.

The weak interaction between the host molecule and the two aprotic guests, namely the polar nitroethane and the apolar benzene, yields true lattice-type inclusions, although with different organizations. In the inclusion with nitroethane, the polar guests fill up the voids between the host molecules. Weak electrostatic interactions of C–(H) $\cdots$ O type[15] from the host to the oxygen atoms of the guest seem to supplement the ordinary van der Waals forces and may thus also contribute to the stabilization of the crystal structure. In the inclusion with benzene, the host matrix contains tunnels in the crystallographic *c* direction and is held together by weak C–(H) $\cdots$ O interactions besides the ordinary van der Waals forces. The guests are located in the tunnels within the host matrix in a strictly stoichiometric host : guest ratio without any interaction stronger than the weak van der Waals forces.

## Conclusions

Amalgamation of the well-known 9,10-dihydro-9,10-ethanoanthracene building block and potential diarylmethanol clathrate-promoting (clathratogenic) groups has produced new crystalline inclusion hosts with novel structures. They form crystalline inclusions with a variety of uncharged organic molecules, ranging from protic dipolar to apolar compounds (183 different species, Table 1), but with a clear preference for amines and simple aromatic hydrocarbons, while previous hosts based on the characteristic tetracyclic framework and different kinds of polar groups, *e.g.* $CO_2H$ instead of $Ar_2COH$,[5a] favour alcohols. The structural versatility of the new host type is demonstrated by the crystal structures of **2a**·EtOH (1:2), **2a**·nitroethane (1:1) and **2a**·benzene (2:1), showing that host **2a** is able to form inclusion compounds with very different characteristics, *e.g.* H-bonded complexes involving both hydroxy groups of the host and uncomplexed lattice type clathrates with a different organization. The conformational flexibility of the host molecule may be rationalized in terms of a compromise between the requirements of compact packing (the major factor) and other factors tending to lower the free energy, particularly, hydrogen bonds. Therefore the present compounds are a substantial improvement upon the basic roof-shaped organic host type.

## Experimental

### General methods and materials

Melting points were determined with a Reichert hot-stage apparatus and are uncorrected. $^{13}C$ NMR spectra (63 MHz) and $^1H$ NMR spectra (250 MHz) were recorded with a Bruker WM-250 instrument using $CDCl_3$ as solvent ($SiMe_4$ as internal standard, $\delta$ in ppm). Mass spectra were obtained from an AEI MS 50 and a Kratos (FAB) instrument. Microanalyses were carried out by the Microanalytical Laboratory of the Institut für Organische Chemie und Biochemie, Universität Bonn. For column chromatography, silica gel (0.04–0.06 mm) was used. The solvents were dried by standard procedures. 1-Bromo-4-*tert*-butylbenzene,[16] methyl 9,10-dihydro-9,10-ethanoanthracene-11-carboxylate **3**[17] and *trans*-dimethyl 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylate **4**[18] were prepared according to literature procedures.

### General procedure for the synthesis of (mono-methanols 1a–e)

To a Grignard solution prepared from Mg (165 mmol) and the respective aryl halide (160 mmol) in dry $Et_2O$ (100 cm$^3$) was added dropwise at 0 °C a solution of monoester **4** (20 mmol) in dry THF (100 cm$^3$). The solution was refluxed for 5 h, cooled and quenched with saturated aqueous $NH_4Cl$. The work-up involved separation of the organic layer, washing with water, drying over $Na_2SO_4$ and evaporation under reduced pressure. Specific details for each compound including purification are given below.

**α,α-Diphenyl-9,10-dihydro-9,10-ethanoanthracene-11-methanol 1a.** From bromobenzene and **3**; the orange precipitate which formed was recrystallized from AcOEt and then from toluene to yield colourless crystals (5.2 g, 67%), mp 191–192 °C (Found: C, 89.4; H, 6.3. $C_{29}H_{24}O$ requires C, 89.66; H, 6.23%); $\delta_C$(250 MHz; $CDCl_3$) 30.22, 44.43, 45.38, 47.27, 80.27, 123.00, 123.75, 124.03, 124.28, 125.22, 125.44, 125.69, 125.93, 126.28, 126.41, 126.63, 126.76, 128.01, 128.56, 140.36, 143.73, 144.46, 145.54, 146.55 and 147.54; $\delta_H$(200 MHz; $CDCl_3$) 1.77 (1 H, s, OH), 1.90–2.15 (2 H, m, ethano-$CH_2$), 3.38–3.50 (1 H, m, ethano-CH), 4.38 (1 H, d, bridgehead), 4.48 (1 H, t, bridgehead) and 7.18–7.85 (18 H, m, Ar); *m*/*z* 388.183 (EI).

**α,α-Bis(4-methylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11-methanol 1b.** From 4-bromotoluene and **3**; chromatography of the light yellow oil on $SiO_2$ [eluent: light petroleum (bp 40–60 °C)–$Et_2O$ 5:1] yielded a colourless powder (5.3 g, 64%), mp 167–169 °C (Found: C, 89.3; H, 6.9. $C_{31}H_{28}O$ requires C, 89.38; H, 6.77%); $\delta_C$(250 MHz; $CDCl_3$) 20.88, 21.07, 30.33, 44.60, 45.51, 47.29, 80.14, 123.09, 123.81, 124.06, 124.39, 125.13, 125.36, 125.72, 125.94, 126.43, 126.78, 128.79, 129.34, 135.75, 136.11, 140.64, 143.97, 144.10, 144.75, 144.94 and 145.69; $\delta_H$(200 MHz; $CDCl_3$) 1.52 (1 H, s, OH), 1.77–2.00 (2 H, m, ethano-$CH_2$), 2.25 (3 H, s, $CH_3$), 2.45 (3 H, s, $CH_3$), 3.27 (1 H, dd, ethano-CH), 4.25 (1 H, d, bridgehead), 4.35 (1 H, t, bridgehead) and 6.95–7.65 (16 H, m, Ar); *m*/*z* 416.2130 (EI).

**α,α-Bis(4-*tert*-butylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11-methanol 1c.** From 1-bromo-4-*tert*-butylbenzene and **3**, the oily residue was stirred with pentane and cooled (refrigerator); the precipitate which formed was recrystallized from AcOEt to yield colourless crystals (6.4 g, 64%), mp 209 °C (Found: C, 88.4; H, 7.9. $C_{37}H_{40}O$ requires C, 88.75; H, 8.05%); $\delta_C$(250 MHz; $CDCl_3$) 30.33, 31.36, 31.53, 34.24, 34.46, 44.58, 45.43, 47.63, 80.05, 123.05, 123.76, 123.97, 124.34, 124.83, 124.88, 125.14, 125.39, 125.63, 125.86, 126.36, 126.69, 140.60, 143.82, 143.89, 144.54, 144.72, 145.66, 148.71 and 149.13; $\delta_H$(200 MHz; $CDCl_3$) 1.24 (9 H, s, Bu$^t$), 1.48 (1 H, s, OH), 1.68–1.96 (2 H, m, ethano-$CH_2$), 3.22 (1 H, dd, ethano-CH), 4.19 (1 H, d, bridgehead), 4.30 (1 H, t, bridgehead) and 7.06–7.55 (16 H, m, Ar); *m*/*z* 523.3 (M + Na$^+$, FAB).

**α,α-Bis(4-fluorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11-methanol 1d.** From 4-bromofluorobenzene and **3**; recrystallization from toluene gave a 1:1 solvent inclusion compound which decomposed on heating at 100 °C and 15 Torr for 24 h to yield a colourless powder (5.7 g, 68%), mp 106 °C; $\delta_C$(250 MHz; $CDCl_3$) 30.25, 44.39, 45.40, 47.39, 79.77, 114.63, 115.05, 115.26, 115.68, 123.05, 123.87, 124.18, 124.32, 125.36, 125.84, 126.12, 126.58, 126.84, 126.99, 127.07, 127.23, 140.06, 142.30, 142.37, 143.21, 143.28, 143.64, 144.22, 145.54, 158.89, 159.21, 163.77 and 164.09; $\delta_H$(200 MHz; $CDCl_3$) 1.58 (1 H, s, OH), 1.66–1.96 (2 H, m, ethano-$CH_2$), 3.17 (1 H, dd, ethano-CH), 4.12 (1 H, d, bridgehead), 4.32 (1 H, t, bridgehead) and 6.60–7.58 (16 H, m, Ar); *m*/*z* 447.2 (M + Na$^+$, FAB).

**α,α-Bis(4-chlorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11-methanol 1e.** From 4-bromochlorobenzene and **3**; recrystallization from AcOEt gave colourless crystals (6.6 g, 73%), mp 124–125 °C (Found: C, 76.0; H, 4.9. $C_{29}H_{22}Cl_2O$ requires C, 76.15; H, 4.85%); $\delta_C$(250 MHz; $CDCl_3$) 30.20, 44.38, 45.35, 47.10, 79.79, 123.09, 123.90, 124.23, 124.36, 124.91, 126.20, 126.72, 126.98, 127.11, 128.31, 128.92, 132.48, 132.87, 139.99, 143.62, 144.13, 144.85, 145.59 and 145.82; $\delta_H$(250 MHz; $CDCl_3$) 1.77 (1 H, s, OH), 1.84–1.95 (2 H, m, ethano-$CH_2$), 3.16 (1 H, dd, ethano-CH), 4.12 (1 H, d, bridgehead), 4.32 (1 H, t, bridgehead) and 7.05–7.53 (16 H, m, Ar); *m*/*z* 456.1042 (EI).

### General procedure for the synthesis of bis-methanols 2a–c and 2e

To a stirred solution of the respective aryl halide (120 mmol) in dry $Et_2O$ (100 $cm^3$) was dropped at 0 °C and under argon a solution of BuLi (80 $cm^3$, 128 mmol; 1.6 mol $dm^{-3}$ in hexane). Stirring was continued at 0 °C for an additional 2 h, and a solution of diester **4** (20 mmol) in dry $Et_2O$ (100 $cm^3$) was added during 0.5 h. After stirring for 2 h at room temperature, the mixture was refluxed for 3 h, then cooled, quenched and worked up as before. Specific details for each compound including purification are given below.

***trans*-α,α,α′,α′-Tetraphenyl-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol 2a.** From bromobenzene and **4**; chromatography of the viscous yellow oil on $SiO_2$ [eluent petroleum ether (bp 40–60)–$Et_2O$ 2:1] yielded 5.5 g (48%) of colourless powder, mp 159–160 °C (Found: C, 88.5; H, 6.3. $C_{42}H_{34}O_2$ requires C, 88.39; H, 6.00%); $\delta_C$(250 MHz; $CDCl_3$) 48.09, 48.48, 80.42, 123.96, 124.97, 125.50, 126.15, 126.38, 126.44, 127.79, 128.01, 141.47, 144.43, 146.09 and 147.79; $\delta_H$(200 MHz; $CDCl_3$) 1.35 (2 H, s, OH), 3.95 (2 H, s, ethano), 4.37 (2 H, s, brigehead), 6.49–6.52 (2 H, d, Ar) and 6.75–7.35 (26 H, m, Ar); *m*/*z* 553.2 ($M^+$ − OH, FAB).

***trans*-α,α,α′,α′-Tetrakis(4-methylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol 2b.** From 4-bromotoluene and **4**; recrystallization from acetone gave a 1:1 solvent inclusion compound which decomposed on heating at 120 °C and 15 Torr for 8 h to yield a colourless powder (4.5 g, 36%), mp 246–248 °C (Found: C, 88.2; H, 7.0. $C_{46}H_{42}O_2$ requires C, 88.14; H, 6.75%); $\delta_C$(250 MHz; $CDCl_3$) 21.01, 48.23, 48.45, 80.37, 124.03, 125.10, 125.39, 126.01, 126.27, 126.46, 128.44, 128.76, 135.33, 136.72, 141.80, 143.62, 144.75 and 145.40; $\delta_H$(200 MHz; $CDCl_3$) 1.28 (2 H, s, OH), 2.12 (6 H, s, $CH_3$), 2.31 (6 H, s, $CH_3$), 3.88 (2 H, s, ethano), 4.37 (2 H, s, bridgehead), 6.48–6.64 (6 H, m, Ar) and 6.90–7.35 (18 H, m, Ar); *m*/*z* 649.3 (M + $Na^+$, FAB).

***trans*-α,α,α′,α′-Tetrakis(4-*tert*-butylphenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol 2c.** From 1-bromo-4-*tert*-butylbenzene and **4**; treatment of the oily residue with light petroleum (bp 40–60 °C) to dissolve byproducts, filtration and recrystallization from EtOH gave a 1:2 solvent inclusion compound which decomposed on heating at 150 °C and 15 Torr for 24 h to yield **2b** (6.2 g, 39%) as a colourless powder, mp 287–289 °C (Found: C, 87.95; H, 8.3. $C_{58}H_{66}O_2$ requires C, 87.61; H, 8.37%); $\delta_C$(250 MHz; $CDCl_3$) 31.33, 31.48, 34.31, 48.58, 50.51, 79.42, 122.36, 124.49, 124.56, 125.00, 125.15, 125.64, 126.53, 127.27, 142.29, 143.19, 144.91, 145.22, 149.15 and 149.47; $\delta_H$(200 MHz; $CDCl_3$) 1.27 (18 H, s, $Bu^t$), 1.32 (18 H, s, $Bu^t$), 1.76 (2 H, s, OH), 3.73 (2 H, s, ethano), 4.28 (2 H, s, bridgehead), 6.22 (2 H, d, Ar), 6.71 (2 H, t, Ar) and 6.92–7.28 (20 H, m, Ar); *m*/*z* 817.5 (M + $Na^+$, FAB).

***trans*-α,α,α′,α′-tetrakis(4-chlorophenyl)-9,10-dihydro-9,10-ethanoanthracene-11,12-dimethanol 2e.** From 4-bromochlorobenzene and **4**; chromatography of the orange coloured solid on $SiO_2$ [eluent: light petroleum (bp 40–60 °C)–$Et_2O$ 3:1] yielded a colourless powder (9.1 g, 65%), mp 244 °C (Found: C, 71.5; H, 4.4). $C_{42}H_{30}Cl_4O_2$ requires C, 71.20; H, 4.27%); $\delta_C$(250 MHz; $CDCl_3$) 46.84, 47.61, 80.01, 124.78, 125.04, 126.30, 126.62, 127.21, 127.27, 127.79, 128.53, 132.42, 132.61, 140.77, 143.77 and 146.85; $\delta_H$(200 MHz; $CDCl_3$) 1.15 (2 H, s, OH), 3.98 (2 H, s, ethano), 4.46 (2 H, s, bridgehead) and 6.55–7.50 (24 H, m, Ar); *m*/*z* 729.1 (M + $Na^+$, FAB).

### Crystalline inclusion compounds

The host compound was dissolved under heating in a minimum amount of the respective guest solvent. The solution was allowed to cool slowly. The crystals which formed were collected by suction filtration and dried (1 h, 15 Torr, room temperature). The host:guest stoichiometric ratios were determined by $^1H$ NMR integration. Data for each compound are given in Table 1.

### Crystal structure determination

**Data collection and processing.** Low temperature X-ray measurements were performed on a STOE/AED2 diffractometer with graphite-monochromatized Mo-Kα radiation, using the $\omega$–$2\theta$ scan technique. The crystals of all three compounds were colourless and transparent. Suitable crystals used for data collection were irregularly shaped. Lattice constants were determined by least-squares fitting of the setting angles of carefully centred reflections: 50 reflections in the range $31 < 2\theta < 42°$ for **2a**·EtOH (1:2), 59 reflections in the range $20 < 2\theta < 34°$ for **2a**·benzene (2:1) and 38 reflections in the range $25 < 2\theta < 39°$ for **2a**·nitroethane (1:1). Background, decay, Lorentz and polarization corrections were applied, but no allowance was made for the small effects of absorption.

**Structure analysis and refinement.** All the structures were solved by the automatic direct methods routine of the SHELXS86[19] program. The coordinates of all non-hydrogen atoms were provided by the best E-maps, though this procedure was not straightforward for **2a**·nitroethane (1:1). The occurrence of some high peaks in the region of the difference electron density map ($\Delta\rho$) of this inclusion compound where the nitro group of the guest molecule was supposed to be located, was interpreted as possible multiple positioning for it. When modelling disorder locations, two different nitro group orientations were accepted. In the final stage of the refinement their occupation factors were refined to 0.69 and 0.31. Furthermore, the systematic absences in the case of **2a**·benzene (2:1) structure yield eight different *I*-centred space groups. The symmetry of the diffraction pattern and analysis of statistical distribution of intensities allowed us to determine the Laue class and to recognize the space group as acentric. Thus, the number of possible space groups was reduced to two, namely, $I4$ (No. 79) and $I\bar{4}$ (No. 82). The final decision on $I\bar{4}$ came from the complete structure determination. Completion and refinement of the initial structural models for all three structures were made by difference Fourier syntheses and blocked full-matrix least-squares calculations based on $|F|$ [in two blocks for **2a**·EtOH (1:2) and **2a**·benzene (2:1) and in three blocks for **2a**·nitroethane (1:1)], by means of the software package SHELX76.[20] The blocked full-matrix least-squares procedure had to be used because the maximum number of parameters that could be refined in one cycle was limited to 400. The non-hydrogen atoms with full site occupancy were treated anisotropically. The disordered nitro sites in the guest molecule of **2a**·nitroethane (1:1) were treated isotropically and, in order to preserve chemically reasonable geometry, were held riding on the C(N1) atom throughout subsequent calculations. In order to retain acceptable geometry for the guest molecule in **2a**·benzene (2:1), which has shown some extent of disorder, two 'side' C atoms (the crystallographic asymmetric unit contains only one half of the guest molecule, *i.e.* three C atoms) were held riding on the central one. In **2a**·EtOH (1:2) the CE(21)–CE(22) distance in the EtOH molecule during the last stages of refinement was restrained inside reasonable limits as well. The positions of the hydrogens in the polar groups, namely the OH groups of the host in all three inclusions, and of the ethanol in **2a**·EtOH (1:2) as well, were located from $\Delta\rho$ maps. The remaining (C)–H hydrogens were either taken from $\Delta\rho$ maps and held fixed during the subsequent calculations, or were generated after each cycle of the refinement (C–H = 1.00) using geometric evidence. In the case of the guest molecule in **2a**·nitroethane (1 : 1), the nitro group site occupancy was taken into account when calculating (C)–H hydrogens positions. In the final stages of the refinement 9, 1 and 7 intense low-angle reflections for compounds **2a**·EtOH (1 : 2), **2a**·nitroethane (1 : 1) and **2a**·benzene (2 : 1), respectively, with $|F_o| \ll |F_c|$ were assumed to be affected by secondary extinction and were therefore discarded from the refinement. Crystal data and selected experimental and refinement details are given in Table 2.

**Supplementary data.** The tables of final fractional atomic coordinates, bond lengths and angles involving all the non-hydrogen and hydrogen atoms, and details of the calculations of the weighted least-squares-planes, ring puckering coordinates and asymmetry parameters have been deposited as supplementary data at the Cambridge Crystallographic Data Centre.† Lists of the observed and calculated structure factors and the anisotropic displacement parameters for the non-hydrogen atoms may be obtained directly from the authors (O. G.).

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