Crystalline Hosts Based on the Assembly of Anthracene and Bulky Alcoholic Groups – Host Synthesis, Complex Formation, and X-ray Crystal Structures of Several Inclusion Compounds

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A series of new clathrate host molecules (**1–10**) containing two diarylhydroxymethyl groups attached to different positions (1,5 or 1,8) of a basic anthracene construction unit have been synthesized. Their clathrate formation properties with a variety of organic guests, including amines, alcohols, ketones, and other dipolar aprotic compounds or aromatic hydrocarbons are reported (143 examples of clathrates). The inclusion properties and the clathrate stoichiometries depend in a systematic manner on the structure of the host molecules. The crystal structures of six selected clathrates of different classes of compound have been determined by X-ray diffraction.

Introduction

As a result of their practical uses considerable interest in crystalline inclusion compounds (clathrates) and similar co-crystalline systems has arisen in the past few years.[1] These include chemical and optical separation, stabilization and protection of labile species, topochemistry, and the architecture of new solid materials.[2−4] This interest has stimulated the development of new strategies for crystalline inclusion formation and motivated the design of novel host types.[5] Although a priori the design of a co-crystalline structure still poses insurmountable problems,[6] there are some useful guidelines available for the design of host molecules.[5,7] These include a rigid basic framework, bulky substituents, strategically positioned functional groups and symmetry relations.

Characteristic examples of framework structures are the scissor-type,[8] the roof-shaped,[9] and the dog-bone- or wheel-and-axle-type host molecules.[10] Among the many new species of polar host compounds belonging to one of these basic geometries, molecules containing the hydroxy group, in particular those involving the bulky diarylmethanol moiety, were found to be very effective formers for crystalline inclusion compounds.[10a,11] This, among other things, has given rise to the term "magic diarylmethanol unit"[12] and reference to it as a "clathratogenic" (clathrate-promoting) group.[9a,13] The rigid building blocks or spacer units to be used for the construction of these hosts are generally acetylene[10,11] or simple aromatic rings,[14] or a combination of both groups.[15] On the other hand, apolar pure hydrocarbon hosts composed of more complex aromatic subunits, such as naphthalene or anthracene, have also proven to be highly efficient in the formation of crystalline inclusion compounds due to their π-stacking and spatial shielding effects.[16]

This work reports on the synthesis of several specific compounds, **1**−**10**, that combine both characteristic features, namely the functional and bulky diarylmethanol group as well as the rigid and geometrically defined anthracene construction element. These compounds have two of the characteristic diarylmethanol groups attached to the basic anthracene moiety in the 1,5- (**1**−**5**) or 1,8-positions (**6**−**10**). Moreover, they contain apolar substituents of different size and shape in different positions of the aromatic rings of the diphenylmethanol units, thus enabling a comprehensive evaluation of the host structures. The crystal inclusion (clathrate formation) properties of **1**−**10** and the crystal structures of six clathrate compounds including different hosts and guests of different compound classes are described in detail.

Synthesis

The bis(carbinols) **1**−**5** were synthesized by the reaction of dimethyl anthracene-1,5-dicarboxylate (**11**)[17] with aryllithium reagents. These were prepared by treatment of the appropriate aryl bromides with *n*BuLi under the usual conditions.[18] Analogously, the bis(carbinols) **6**−**10** were synthesized from dimethyl anthracene-1,8-dicarboxylate (**12**),[19] aryl bromides, and *n*BuLi. The dimethyl esters **11** and **12** were obtained according to literature procedures[17][19] from 1,5-dichloro- and 1,8-dichloro-9,10-anthraquinone, respectively. All organolithium reactions gave the bis(carbinols) in rather high yields (52−80%). The inclusion compounds were obtained by recrystallization of the host compound from the guest solvent. The drying con-

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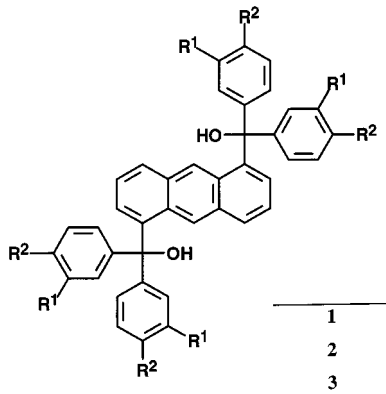
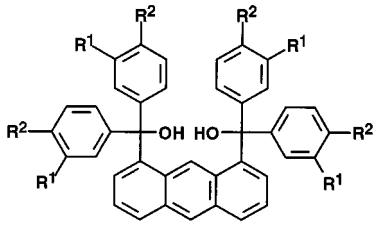


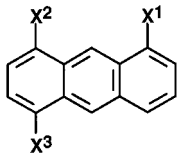
	R^1	R^2
1	H	H
2	CH_3	H
3	H	CH_3
4	H	$C(CH_3)_3$
5	H	C_6H_5



	R^1	R^2
6	H	H
7	CH_3	H
8	H	CH_3
9	H	$C(CH_3)_3$
10	H	C_6H_5

Scheme 1. Host compounds

ditions specified in the Experimental Section (1 h, 15 Torr, room temp.) refer to a "stable clathrate".



	X^1	X^2	X^3
11	$COOCH_3$	H	$COOCH_3$
12	$COOCH_3$	$COOCH_3$	H

Scheme 2. Anthracene starting compounds

Inclusion Properties

In order to study the inclusion behaviour of the potential host compounds **1**−**10** as completely as possible, a broad variety of solvents including amines, alcohols, ketones, nitriles, nitro compounds, and other aprotic dipolar solvents, heterocycles and aromatic hydrocarbons of different constitutions (cf. Table 1) were used for the recrystallization (clathration) experiments. A total of 143 different lattice inclusions are specified, showing the general efficiency of the new host design. Nevertheless, the individual compounds **1**−**10** are rather different in their inclusion ability and demonstrate characteristic levels of selectivity in each case.

The greatest number of inclusions (22) are formed by the phenyl-substituted bis(methanol) **5**, the lowest number (6) by compound **10** which is the positional isomer of the host molecule **5** (1,8- instead of 1,5-substituted anthracene). Similarly, the *m*-tolyl derivative **2** (1,5-substituted anthracene) yields 17 different inclusion compounds, whereas **7** (1,8-positional isomer of the anthracene) resulted only in 7 clathrates. Although the difference is not as marked for the other analagous isomers, as a general rule the 1,5-substituted anthracenes are superior to the 1,8-derivatives in their efficiency to form crystalline inclusion complexes, except for **8** which is a little more effective than **3**.

Another general difference between the inclusions of the 1,5- and the 1,8-disubstituted anthracenes is obvious from the host/guest stoichiometric ratios. Whereas the 1,5-derivatives favour the 1:2 stoichiometric ratio (the 1:1 ratio being the second favourite), the 1,8-derivatives favour the 1:1 host/guest stoichiometric ratio, and the 1:2 ratio is a minor product. In summary, the 1,5-bis(diarylhydroxymethyl)-substituted anthracene hosts **1**−**5** are more inclined to form inclusions with a high guest percentage than the 1,8-analogues **6**−**10**. In one case of the inclusions of the 1,5-disubstituted hosts (**3** · DMF) the stoichiometric ratio host/guest observed is even as high as 1:4 and, on the other hand, for one of the inclusions of the 1,8-disubstituted hosts (**10** · Et_3N) the observed ratio is 3:1. This is perhaps a reference for possible modes of host/guest interaction and the availability of the hydroxy groups for binding in the two compound series.

In the case of the 1,5-bis(diarylhydroxymethyl)-substituted anthracene hosts **1**−**5**, for reasons of geometry, the two hydroxy groups may be regarded as individual units capable of binding two guests independently, giving rise to mainly 1:2 host/guest stoichiometric ratio in the inclusion compounds. The two hydroxy groups in the 1,8-disubstituted host analogues, however, are crowded and able to mutually interact, thus reducing the external binding capacity to guest molecules and giving a preferred 1:1 stoichiometric ratio in the inclusion compounds. Sterical crowding is most pronounced in case of **10**, which is a possible reason for the decidedly low inclusion behaviour of this host.

With reference to the guest/solvent class of compounds, there is a clear preference for entrapment of amines, 1,4-dioxane, DMF, and DMSO, and to a lesser extent THF and ketones, while alcohols, nitriles, and aromatic hydrocarbons are included only to a rather low degree. In particular, the simple non-cyclic alcohols such as methanol, ethanol etc., were found to be completely inefficient. The cyclic alcohols are mainly included by the host compound **8**, the nitriles by compound **2**, and the aromatic hydrocarbons equally by **1** and **8**.

On going through the data listed in Table 1 there are more remarkable findings. For example, host compound **2** readily yields crystalline inclusions with primary amines but not with aliphatic secondary and tertiary amines. Host

Table 1. Crystalline inclusion compounds (host/guest stoichiometric ratios)[a]

Guest solvent[b]	Host compound **1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
n$PrNH_2$	–	1:2	–	–	1:1	1:1	1:1	1:2	–	[c]
i$PrNH_2$	–	1:2	1:1	–	1:1	–	1:1	–	–	[c]
n$BuNH_2$	–	1:2	1:1	–	1:1	–	–	2:3	–	2:3
i$BuNH_2$	1:2	1:2	–	1:2	1:1	1:1	1:1	1:2	1:1	[c]
2-$BuNH_2$	1:2	1:2	1:1	1:2	1:1	1:1	–	–	–	[c]
CyclohexylNH_2	1:2	1:2	1:1	1:2	1:1	1:1	[c]	1:2	–	[c]
Et_2NH	1:2	–	1:1	–	1:1	1:1	1:1	1:2	1:1	1:1
nPr_2NH	–	–	1:2	–	–	–	–	–	–	–
nBu_2NH	–	–	1:2	–	1:1	–	–	–	–	–
Et_3N	1:1	–	–	–	1:1	–	–	–	–	3:1
Piperidine	1:2	1:2	1:2	1:2	1:2	1:1	[c]	–	1:1	[c]
Pyridine	1:2	1:2	1:1	1:1	1:2	–	[c]	–	1:1	[c]
2-Picoline	–	[d]	[d]	1:1	1:2	1:1	[c]	–	–	[c]
3-Picoline	–	[d]	[d]	1:1	1:2	1:1	[c]	–	1:1	[c]
4-Picoline	–	[d]	[d]	1:1	1:2	1:1	[c]	–	–	[c]
CyclopentylOH	–	–	[c]	[c]	–	[c]	[c]	1:1	–	[c]
CyclohexylOH	–	–	[c]	[c]	–	[c]	1:2	1:1	–	[c]
CycloheptylOH	–	–	–	–	–	[c]	[c]	1:1	–	[c]
Acetone	1:2	–	–	–	–	1:1	–	1:2	1:1	–
Cyclopentanone	[c]	–	1:2	1:2	1:2	–	1:1	–	1:1	[c]
Cyclohexanone	[c]	1:1	1:2	1:1	1:2	–	1:1	[c]	1:1	[c]
Cycloheptanone	[c]	[d]	[d]	[d]	1:2	–	[c]	[c]	–	[c]
EtOAc	–	1:2	–	–	–	–	–	–	–	–
DMF	1:2	1:2	1:4	1:2	1:2	1:1	–	1:2	1:1	1:2
DMSO	1:2	1:2	1:2	1:2	1:2	1:1	–	1:2	1:1	1:2
Propionitrile	–	1:2	[c]	[c]	[c]	[c]	–	[c]	[c]	–
Butyronitrile	–	1:2	[c]	[c]	[c]	–	–	–	–	–
Benzonitrile	[c]	1:2	–	–	1:1	–	–	1:2	–	–
Nitroethane	1:2	–	[c]	[c]	–	–	–	–	–	–
THF	–	1:2	1:2	1:1	1:2	1:1	–	–	–	[c]
1,4-Dioxane	1:2	1:2	1:2	1:1	1:2	1:1	–	1:2	1:1	[c]
Benzene	1:1	–	–	[d]	–	–	–	1:1	–	[d]
Toluene	1:1	–	–	–	–	–	–	1:1	–	1:1
o-Xylene	1:1	–	–	–	–	–	–	1:1	–	[d]
m-Xylene	1:1	–	–	–	–	1:1	–	1:1	–	[d]
p-Xylene	1:1	–	–	–	–	1:1	–	1:1	–	[d]

[a] See Experimental Section for methods of preparation, drying standard and characterization. – [b] MeOH, EtOH, 1-PrOH, 2-PrOH, 1-BuOH, 2-BuOH, *i*BuOH, *t*BuOH, 2-PentOH and nitromethane, which were also tested as guest solvents, yielded no inclusion compounds. – [c] Difficult to crystallize. – [d] Not tested.

compound **4** is even more specific in this respect, also resisting the inclusion of small primary amines, while compound **5** is found to be a universal host for the inclusion of amines. In the same manner, it seems that host compound **7**, similar to **8**, refuses the inclusion of cyclic amines. Moreover, host compounds **1** and **8**, though different in geometry and the degree of substitution, are equal in the entrapment of the given aromatic hydrocarbons, while **6**, which is the positional isomer of **1**, fails to enclathrate benzene, toluene, and *o*-xylene but demonstrates efficient inclusion of *m*- and *p*-xylene.

This result stimulated guest competition experiments using solvent mixtures of *o*-xylene with either *m*- or *p*-xylene for recrystallization of **6**. In each case the *o*-xylene is discriminated against compared to the other xylenes, which contradicts the known behaviour of certain roof-shaped diol hosts,[9a] thus complementing the isomer separation of xylenes. There is no guest solvent represented in Table 1 which is efficient with each of the hosts, and conversely, there are several cases of guest solvents being included by one particular host only. This is a fact suggesting many other divisions between the solvents shown in Table 1.

Crystal Structures of Inclusion Compounds

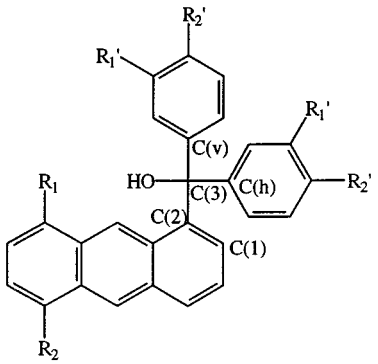
The clathrating abilities of the new type of host compounds are intimately related to their molecular shapes including sterical bulk and arrangement of the functional groups. In order to investigate the building principles of the new clathrate design, and in particular to learn what modes of interaction the new host type uses for the enclathration of polar protic (amines), aprotic dipolar (acetone, DMF, DMSO) and apolar (*p*-xylene) guest molecules, no fewer than six crystal structures of inclusion compounds have been studied in this work, including different types of guest solvents and relevant examples of hosts or combinations of hosts and guests. To this end the crystal structures of the following inclusion compounds: **1** · Et_2NH (1:2), **1** · acetone (1:2), **4** · DMF (1:2), **6** · DMSO (1:1), **6** · *p*-xylene (1:1), and **10** · *n*$BuNH_2$ (2:3) (Table 3) have been solved.

1 · Et_2NH (1:2)

The centrosymmetric host molecule **1** (Figure 1a) has normal bond lengths and angles. The axis of one indepen-

dent phenyl ring (henceforth referred to as horizontal) is nearly co-planar with the anthracene moiety, as indicated by the value of 2.2° for the torsion angle C(1)−C(2)−C(3)−C(h) (see Table 2). The other independent phenyl ring, designated as vertical, has its axis approximately normal to the anthracene nucleus; the relevant torsion angle C(1)−C(2)−C(3)−C(v) is −124.7°. Each hydroxy group is hydrogen-bonded to the nitrogen atom of a diethylamine guest molecule (O1···N1 2.813 Å), the ethyl groups of which exhibit disorder, suggestive of some spatial degrees of freedom in the crystal packing.

Table 2. Relevant geometrical data



Complexes	O···X [Å][a]	C(1)−C(2)−C(3)−C(h) [°]	C(1)−C(2)−C(3)−(v) [°]	C(1)−C(2)−C(3)−OH [°]
1 · Et_2NH (1:2)	2.813	−2.2	−124.7	117.2
1 · acetone (1:2)	2.837	5.8	−117.7	125.1
4 · DMF (1:2)	2.804	4.4	−119.3	121.0
6 · DMSO (1:1)	2.722	−2.5	120.6	−121.6
6 · *p*-xylene (1:1)	3.436[b]	2.7	−120.3	118.3
	3.524[b]	4.8	−118.8	121.1
10 · *n*$BuNH_2$ (2:3)	−	6.8	−116.7	122.4
	2.780	0.7	117.3	−122.4

[a] X denotes the acceptor atom in the bond O−H···X. − [b] X represents the center of the phenyl ring that is involved in an O−H···π interaction.

The host molecules are packed in a straight column along the [101] direction. When these parallel columns are arranged side by side, the anthracene moities and the vertical phenyl rings are seen to be concentrated about the [10$\bar{1}$] family of planes, but the horizontal phenyl rings are outwardly extended. A perspective view of the crystal structure of **1** · Et_2NH (1:2) along the *b* axis (Figure 1b) shows that the guest molecules are accommodated in cavities created between the vertical phenyl rings and layers of anthracene moities, with an interlayer spacing of 11.160 Å.

1 · Acetone (1:2)

The host molecule **1** is located at an inversion center and the structure of the 1:2 host/guest complex is similar to that of the previous complex, except that acetone molecules replace the diethylamine molecules as hydrogen-bond acceptors to the host hydroxy groups (Figure 2a). The packing modes of the two complexes are also similar (Figure 2b), but the interlayer spacing is only 7.089 Å in the present complex since the acetone guest molecule has a smaller size.

4 · DMF (1:2)

In many respects this inclusion compound has similar structural features to the previous two complexes. However, here the hydrogen-bonded DMF guest species extent away from the anthracene plane (Figure 3a). The crystal structure is also of a layer-type (Figure 3b), but the separation between adjacent layers is large (10.304 Å), as may be expected in view of the bulk of the *tert*-butyl groups on the substituted phenyl rings and the outstretched attachment of the guest molecules.

6 · DMSO (1:1)

The host molecule **6** has usual dimensions and occupies Wyckoff position 4(c) at (0, *y*, 1/4), with a crystallographic two-fold axis passing through atoms C(20) and C(21) (9,10-positions of the anthracene skeleton) (Figure 4a). As indicated by the relevant torsion angles, −2.5 and 120.6° (Table 2), the phenyl rings at the 1,8-positions of the anthracene nucleus have similar orientations to those in the above mentioned 1,5-substituted compounds.

The DMSO guest molecule exhibits disorder as its S(1) atom lies on another crystallographic two-fold axis in Wyckoff position 4(c) at (1/2, *y*, 1/4). In the model used for refinement, the O(2) atom can occupy either one of two equivalent posi-

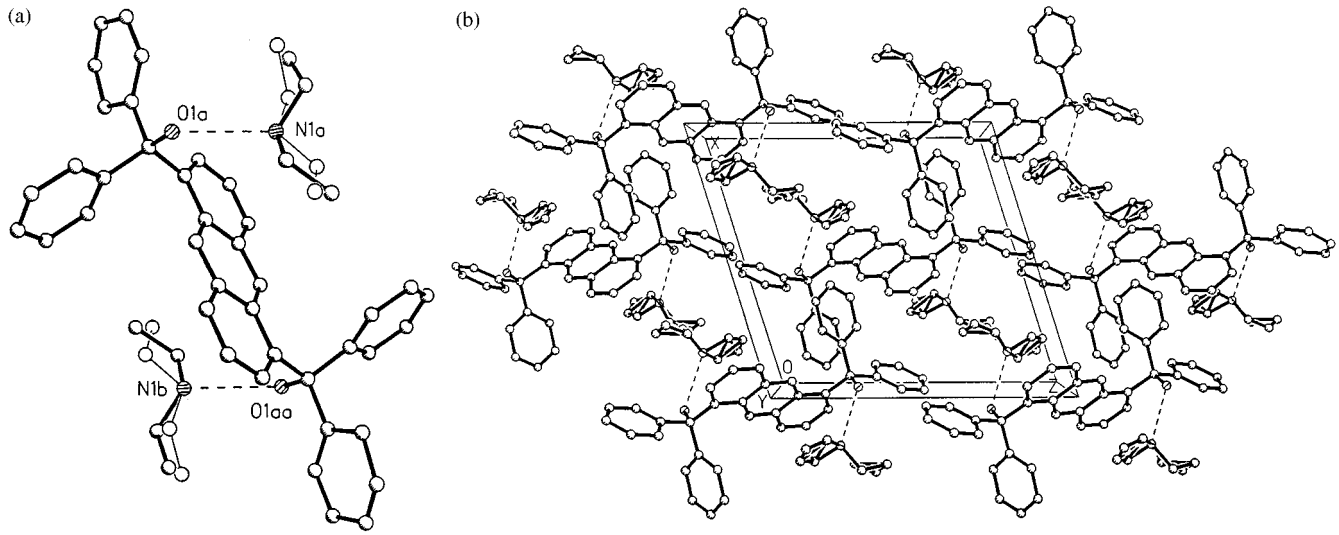


Figure 1. Perspective view (a) and packing structure (b) of **1** · Et_2NH (1:2); the dotted lines indicate hydrogen bonds

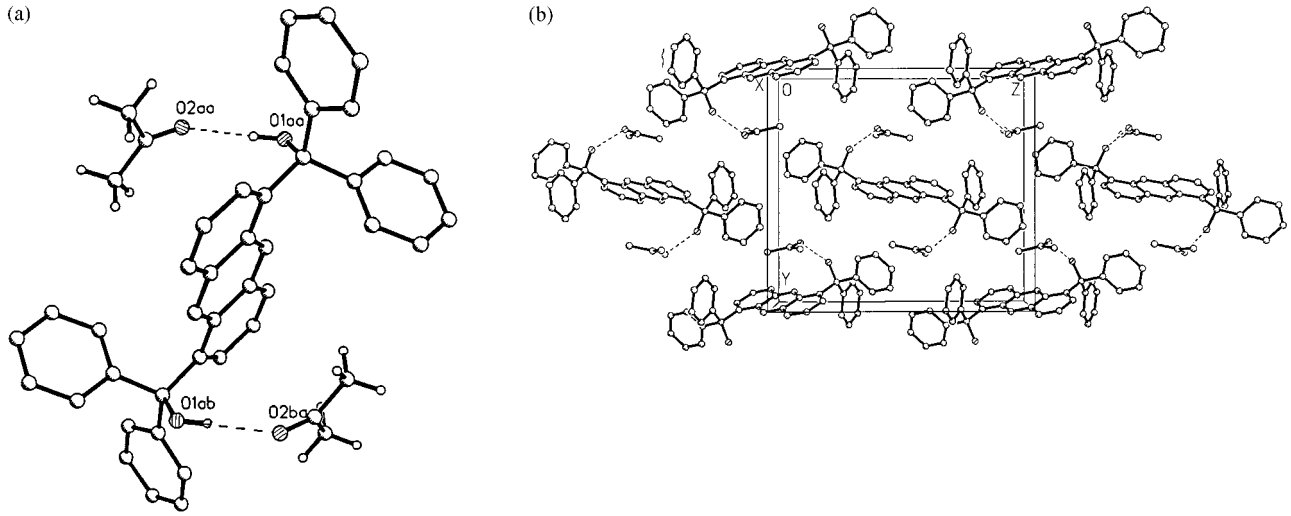


Figure 2. Perspective view (a) and packing structure (b) of **1** · acetone (1:2); the dotted lines indicate hydrogen bonds

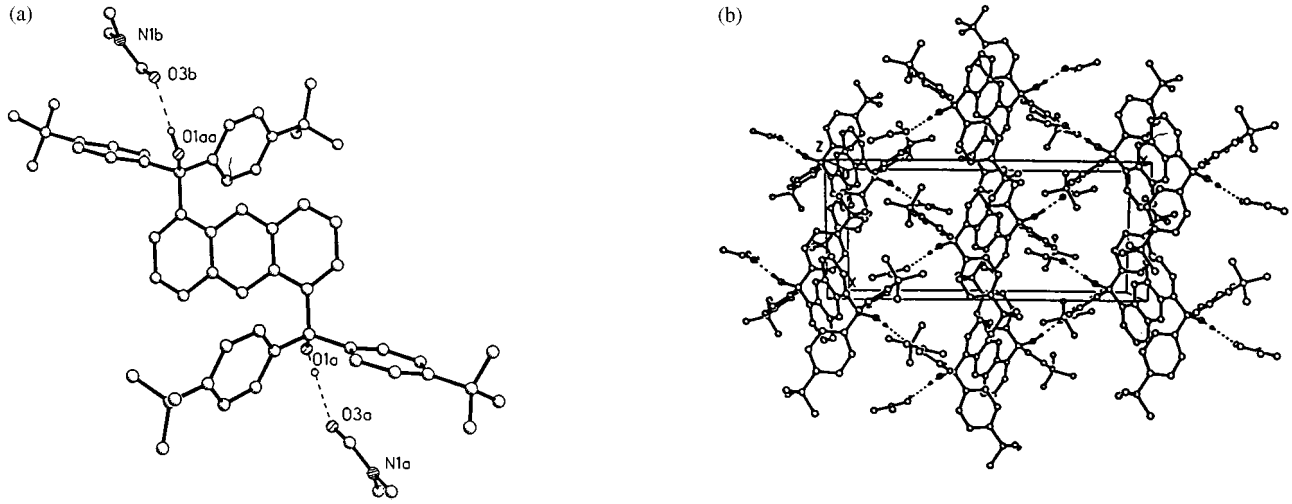


Figure 3. Perspective view (a) and packing structure (b) of **4** · DMF (1:2); the dotted lines indicate hydrogen bonds

tions. Consequently, the DMSO molecule takes the appearance of dimethyl sulfone in forming two half-weighted acceptor O···H−O hydrogen bonds with the hydroxy groups of the host molecules on both sides, so that a one dimension infinite host/guest column extending in the [0 1 0] direction is

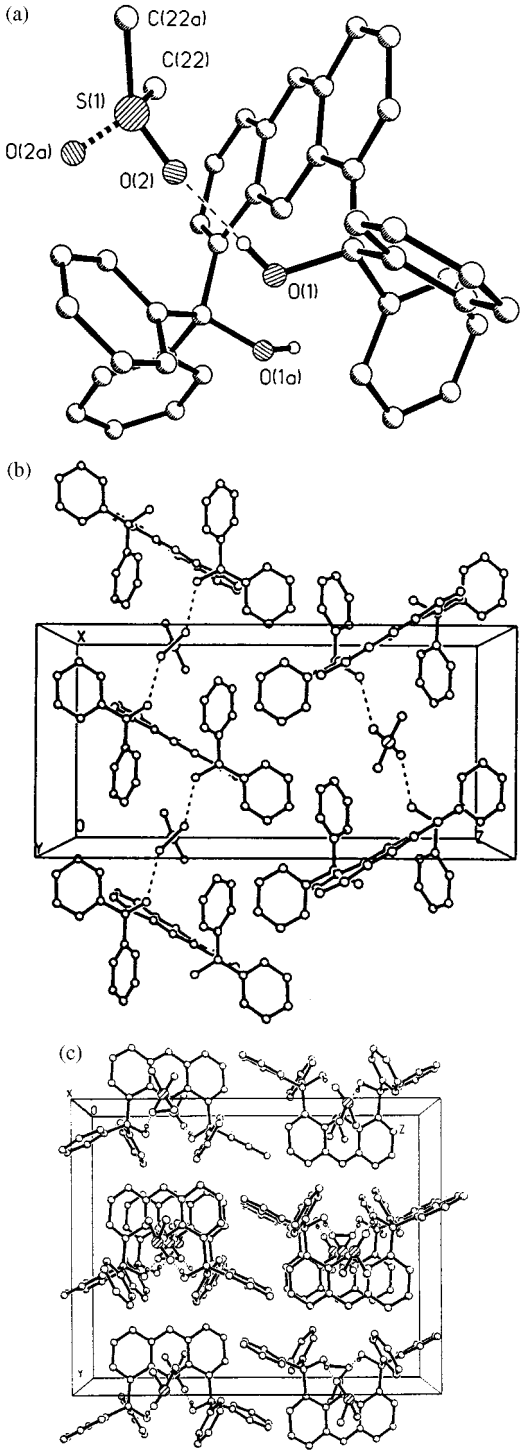


Figure 4. Host/guest interaction (a), packing structure viewed along *b* (b), and viewed along *a* (c) of **6** · DMSO (1:1); the dotted lines indicate hydrogen bonds

generated (Figure 4b). When this crystal structure is viewed along the *b* axis (Figure 4c), it can be described as a packing of infinite columns in which the guest molecules are embedded in the cavities formed by the crab-like host molecules.

6 · *p*-Xylene (1:1)

In this crystal structure the host molecule features intramolecular donor-hydrogen bonding from the hydroxy group of each Ph_2COH moiety to a phenyl ring of the other Ph_2COH unit (Figure 5a and Table 2). A similar behaviour involving intramolecular OH···π-aryl contacts[20] was recently reported in connection with apolar guest inclusion compounds of roof-shaped diol hosts.[9a] Two independent *p*-xylene guest molecules each occupying a site of $\bar{1}$ symmetry are arranged in two separate columns running parallel to the [1 0 0] direction. The parallel, alternate arrangement of these two columns constitutes a guest layer oriented parallel to the [0 0 1] family of planes, with an intercolumnar spacing of $b/2 = 5.460$ Å. The alternate host and guest layers are in a sandwich-like packing arrangement (Figure 5b), in which there is only van der Waals interactions between the molecules.

10 · *n*BuNH$_2$ (2:3)

Analogous to **6** in the above mentioned complexes, the hydroxy groups of the present host compound (**10**) also adopt an almost *endo* conformation. The aromatic rings of the biphenylyl residues are crowded against each other, giving rise to a highly twisted structure of connected aromatic units (Figure 6a), as can be seen from a comparison of their relevant torsion angles (Table 2). Two independent *n*-butylamine guest molecules are accommodated by the host lattice in totally different modes. One of them is linked to a hydroxy group of the host molecule by an O−H···N hydrogen bond of length 2.780 Å. The second amine molecule is located around an inversion center at (0, 0, 1/2) and accordingly is highly disordered, such that it cannot be located accurately due to its diffuse electron density. In contrast to host molecules **1**, **4**, and **6** in their inclusion compounds, only one of the two hydroxy groups of host molecule **10** is involved in hydrogen bonding, whereas the other remains unbound. As shown in Figure 6b, the guest molecules are arranged in a straight column along the [1 0 0] direction and accommodated between a "pseudo-channel type" lattice built by two columns of host molecules, with two longer, extended $-C_6H_4-C_6H_5$ groups per host molecule lining the walls of the channel.

Conclusions

The attachement of two potential diarylmethanol clathrate-promoting (clathratogenic) groups[9a,13] to the 1,5- or 1,8-positions of anthracene has produced new crystalline inclusion hosts with novel structures. They form crystalline inclusions with a variety of uncharged molecules, ranging from protic dipolar to apolar compounds (142 different

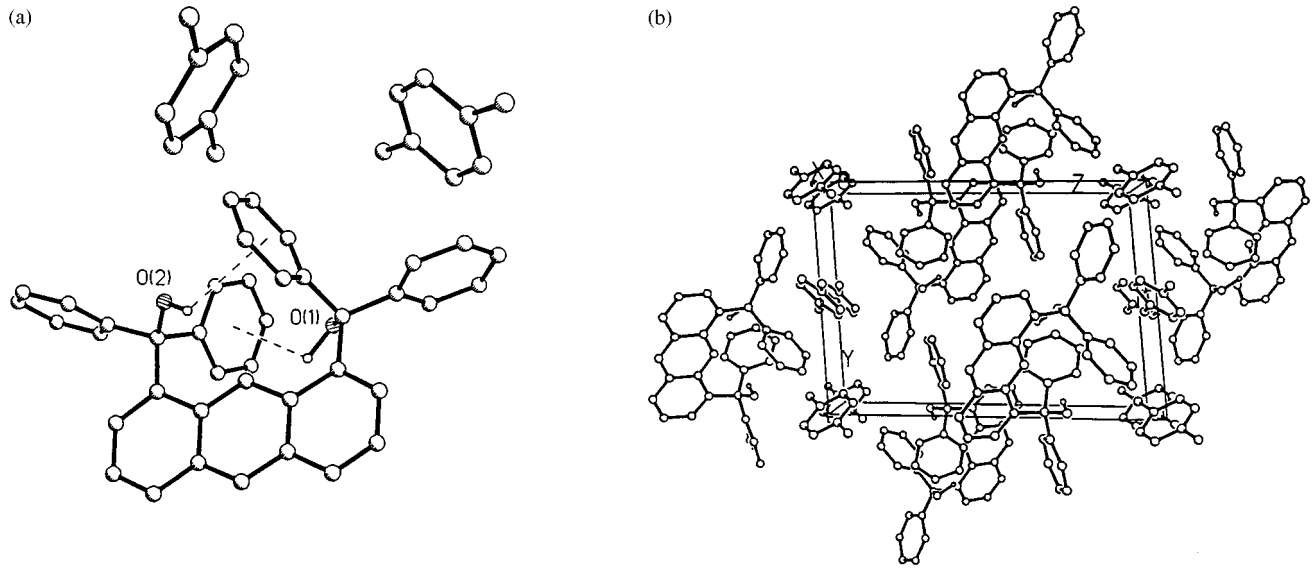


Figure 5. Perspective view (a) and packing structure (b) of **6** · *p*-xylene (1:1); the dotted lines indicate OH···π(aryl) interactions

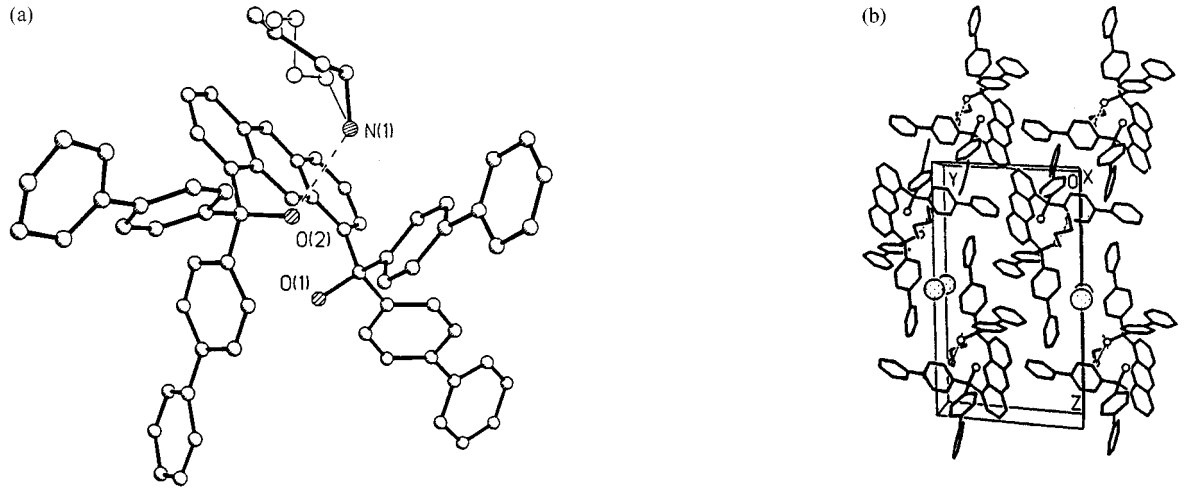


Figure 6. Perspective view (a) and packing structure (b) of **10** · nBuNH$_2$ (2:3); the dotted lines indicate hydrogen bonds and the disordered guest molecules in (b) are shown as large spheres

species, Table 1), but with a clear preference for amines and particular dipolar aprotic solvents (DMF, DMSO), while alcohols were found to be almost inefficient. This general behaviour is in keeping with previous hosts featuring two diarylmethanol clathratogenic groups,[9a] but in its individual and specific inclusion property the present hosts differ. In particular the present hosts show only a moderate ability to include apolar hydrocarbons or nitro compounds and nitriles. On the other hand, they are more selective in these fields since they capture only a smaller variety of guest molecules.

The structural versatility of the new host type is demonstrated by the crystal structures of **1** · Et_2NH (1:2), **1** · acetone (1:2), **4** · DMF (1:2), **6** · DMSO (1:1), **6** · *p*-xylene (1:1), and **10** · nBuNH$_2$ (2:3) showing that the hosts, dependening on their constitution and the bulk of substituents, are able to form inclusion compounds with very different characteristics, e.g. H-bonded complexes involving both hydroxy groups of the host, and others that use only one hydroxy group and uncomplexed lattice type clathrates with a different organization.

In the future, a promising structural extension of this design concept would be the preparation of host molecules that contain linear rigid ethynyl building blocks inserted between the anthracene and the diarylmethanol groups,[21] in order to widen the available lattice space.[1a,10] Moreover, considering fluorescence, host compounds comprising the anthracene moiety are potential candidates for operating as fluoroclathrands for uses of chemical sensing.[21] Preliminary results give rise to concrete hopes in this direction.

Experimental Section

General: ^{1}H NMR (internal standard TMS): Bruker AC 200. − ^{13}C NMR (internal standard TMS): Bruker AC 200 und WM 250. − IR: Perkin−Elmer FT-IR 1600. − MS: A.E.I. MS 50 and Kratos

FAB-MS Concept 1H. − Melting points: Kofler melting point microscope (uncorrected). − Elemental analyses: Heraeus CHN rapid analyzer. − Column chromatography: Silica gel (63−100 μm), Woelm. − Organic solvents were purified by standard procedures.

General Procedure. − Synthesis of Host Compounds 1−5: The solid diester **11**[17] (2.94 g, 10 mmol). was added in portions to a stirred solution of the corresponding aryllithium compound (80 mmol), prepared from the respective aryl bromide (80 mmol) and *n*BuLi (1.6 M in hexane, 53.3 mL, 85 mmol) in diethyl ether (75 mL), at 0°C and under argon The suspension was diluted with 100 mL of dry THF, stirred for 2 h at 0°C, slowly warmed to room temp. and stirred for 48 h. Then the reaction was quenched with ice. The aq. layer was extracted with diethyl ether, and the combined organic layers were washed with water, dried (Na_2SO_4), and concentrated. Inclusion compounds (solvates; for composition see Table 1), where obtained, were desolvated on heating the recrystallized material (clathrate) in vacuo (0.01 Torr) for 12 h at 120°C. Details for purification and data of the individual compounds are given below.

1,1,1′,1′-Tetraphenyl-1,1′-(anthracene-1,5-diyl)dimethanol (1): Phenyllithium (from bromobenzene and *n*BuLi) was used. The solid residue was treated with hot MeOH, cooled to room temp. and filtered. Recrystallization from DMSO and decomposition of the clathrate yielded 2.8 g (52%) of a colorless powder. − M.p. 288°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3540 cm^{-1} (ss, OH), 3049 (s, Ar−H), 1733 (s), 1445 (s, Ar), 1162 (s, C−O), 756 (ss), 704 (ss, monosubst. Ar). − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 6.65 (d, ^3J = 7.2 Hz, 2 H, Ar−H), 6.93 (s, 2 H, OH), 7.12−7.38 (m, 22 H, Ar−H), 7.52 (d, ^3J = 8.3 Hz, 2 H, Ar−H), 8.78 (s, 2 H, Ar−H). − $C_{40}H_{30}O_2$ (HR MS): calcd. 542.2238; found 542.2237. − $C_{40}H_{30}O_2$: calcd. C 88.53, H 5.57; found C 88.48, H 5.69.

1,1,1′,1′-Tetrakis(3-methylphenyl)-1,1′-(anthracene-1,5-diyl)-dimethanol (2): 3-Tolyllithium (from 3-bromotoluene and *n*BuLi) was used. Storage of the concentrated etheral extract at 4°C overnight gave an off-white precipitate. Recrystallization from DMF and decomposition of the clathrate yielded 3.8 g (64%) of colorless crystals. − M.p. > 320°C. − IR (KBr): $\tilde{\nu}$ = 3252 cm^{-1} (br, OH), 3070−2900 (w, Ar−H, C−H), 1670 (ss, Ar), 1102 (s, C−O), 769 (s), 707 (s, 1,3-disubst. Ar). − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.24 (s, 12 H, CH_3, 6.64 (d, ^3J = 7.2 Hz, 2 H, Ar−H), 6.83 (s, 2 H, OH), 6.91−7.25 (m, 18 H, Ar−H), 7.53 (d, ^3J = 8.4 Hz, 2 H, Ar−H), 8.79 (s, 2 H, Ar−H). − ^{13}C NMR (50.32 MHz, [D$_6$]DMSO): δ = 21.39 (CH_3), 81.98 (C−OH), 123.95, 124.95, 126.89, 127.32, 127.46, 128.01, 128.43, 128.93, 129.45, 131.67, 136.62, 142.63, 147.78, (13 C, CH resp. C_q). − $C_{44}H_{38}O_2$ (HR MS): calcd. 598.2862; found 598.2870. − $C_{44}H_{38}O_2$: calcd. C 88.26, H 6.40; found C 88.01, H 6.67.

1,1,1′,1′-Tetrakis(4-methylphenyl)-1,1′-(anthracene-1,5-diyl)-dimethanol (3): 4-Tolyllithium (from 4-bromotoluene and *n*BuLi) was used. The oily residue was treated with hot MeOH and cooled to room temp. to give a pale yellow solid Recrystallization from dioxane and decomposition of the clathrate yielded 3.75 g (63%) of a light yellow powder. − M.p. > 320°C. − IR (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (s, OH), 3020 (m, Ar−H), 2965 (m, C−H), 1506 (ss, Ar), 1170 (s, C−O), 805 (s, 1,4-disubst. Ar), 742 (ss, Ar). − ^{1}H NMR (200 MHz), [D$_6$]DMSO): δ = 2.26 (s, 12 H, CH_3), 6.65 (d, *J* = 6.9 Hz, 2 H, Ar−H), 6.78 (s, 2 H, OH), 7.00−7.28 (m, 18 H, Ar−H), 7.53 (d, ^3J = 8.7 Hz, 2 H, Ar−H), 8.82 (s, 2 H, Ar−H). − ^{13}C NMR (50.32 MHz, [D$_6$]DMSO): δ = 20.63 (CH_3), 81.82 (C−OH), 123.95, 125.35, 127.52, 128.24, 128.42, 128.93, 129.33, 131.78, 135.52, 145.01(10 C, CH resp. C_q). − $C_{44}H_{38}O_2$ (HR MS): calcd. 598.2862; found 598.2873. − $C_{44}H_{38}O_2$: calcd. C 88.26, H 6.40; found C 87.96, H 6.56.

1,1,1′,1′-Tetrakis(4-*tert*-butylphenyl)-1,1′-(anthracene-1,5-diyl)-dimethanol (4): 4-*tert*-Butylphenyllithium (from 4-*tert*-butylbromobenzene and *n*BuLi) was used. The oily residue was digested with MeOH to give a yellow solid. Recrystallization from toluene yielded 4.05 g (53%) of a colorless powder. − M.p. > 320°C. − IR (KBr): $\tilde{\nu}$ = 3481 cm^{-1} (s, OH), 3049 (w, Ar−H), 2961 (ss), 2856 (s, C−H), 1507 (ss, Ar), 1268 (s, C−O), 839 (s, 1,4-disubst. Ar). − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 1.22 (s, 36 H *t*-Bu), 6.34 (s, 2 H, OH), 6.70 (d, ^3J = 7.0 H, 2 H, Ar−H), 7.07 (d, d, ^3J = 7.0/8.4 Hz, 2 H, Ar−H), 7.21 (m, 16 H, Ar−H), 7.51 (d, *J* = 8.4 Hz, 2 H, Ar−H), 8.78 (s, 2 H, Ar−H). − ^{13}C NMR (62.89 MHz, [D$_5$]pyridine): δ = 31.01 (CH_3), 34.05 (C_q), 82.63 (C−OH), 124.67, 127.41, 127.98, 129.36, 129.76, 129.95, 132.58, 135.52, 143.35, 145.92, 149.06 (11 C, CH resp. C_q). − $C_{56}H_{62}O_2$ (FAB-MS, *m*NBA): calcd. 766.47; found 766.4. − $C_{56}H_{62}O_2$: calcd. C 85.87, H 8.30; found C 85.73, H 8.14.

1,1,1′,1′-Tetra(4-biphenylyl)-1,1′-(anthracene-1,5-diyl)dimethanol (5): 4-Biphenyllithium (from 4-bromobiphenyl and *n*BuLi) was used. Quenching of the reaction with aq. NH_4Cl gave a pale yellow solid. Recrystallization from DMF and decomposition of the clathrate yielded 5.34 g (63%) of pale yellow crystals. − M.p. > 320°C. − IR (KBr): $\tilde{\nu}$ = 3209 cm^{-1} (s, br, OH), 3026 (s, Ar−H), 1660 (ss), 1483 (s, Ar), 835 (s, 1,4-disubst. Ar), 744 (s), 694 (s, monosubst. Ar). − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 6.81 (d, ^3J = 7.2 Hz, 2 H, Ar−H), 6.98 (s, 2 H, OH), 7.19 (dd, ^3J = 7.2/8.3 Hz, 2 H, Ar−H), 7.25−7.67 (m, 38 H, Ar−H), 8.91 (s, 2 H, Ar−H). − $C_{64}H_{46}O_2$ (FAB-MS, Ei 270°C): calcd. 846.3486; found 846.4. − $C_{64}H_{46}O_2$: calcd. C 90.75, H 5.47; found C 90.69, H 5.69.

General Procedure. Synthesis of Host Compounds 6−10: A slightly modified procedure as described for **1**−**5** applies. Unlike **11**,[17] the diester **12**[19] (2.94 g, 10 mmol) was used as a solution in dry THF (100 mL), and subsequent dilution with dry THF was not applicable. Inclusion compounds, where obtained, were decomposed as before. Details for purification and data of the individual compounds are given below.

1,1,1′,1′-Tetraphenyl-1,1′-(anthracene-1,8-diyl)dimethanol (6): Phenyllithium (from bromobenzene and *n*BuLi) was used. Recrystallization from DMSO and decomposition of the clathrate yielded 4.3 g (80%) of a pale yellow powder. − M.p. 314−316°C. − IR (KBr): $\tilde{\nu}$ = 3573 cm^{-1} (s, OH), 3050−3000 (w, Ar−H), 1489 (s), 1445 (s, Ar), 1154 (s, C−O), 761 (ss), 700 (ss, monosubst. Ar). − ^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.30 (s, 2 H, OH), 6.62 (dd, ^3J = 7.1 Hz, ^4J = 1.2 Hz, 2 H, Ar−H), 7.10−7.37 (m, 22 H, Ar−H), 7.89 (dd, ^3J = 8.4, ^4J = 1.2 Hz, 2 H, Ar−H), 8.47 (s, 1 H, Ar−H), 8.58 (s, 1 H, Ar−H). − ^{13}C NMR (50.32 MHz, $CDCl_3$): δ = 82.62 (C−OH), 124.16, 127.17, 127.54, 127.88, 128.07 (5 CH), 128.24 (C_q), 128.51, 128.96 (2 CH), 132.03, 142.03, 146.74 (3 C_q). − $C_{40}H_{30}O_2$ (HR MS): calcd. 542.2238; found 542.2255. − $C_{40}H_{30}O_2$: calcd. C 88.53, H 5.57; found C 88.53, H 5.60.

1,1,1′,1′-Tetrakis(3-methylphenyl)-1,1′-(anthracene-1,8-diyl)dimethanol (7): 3-Tolyllithium (from 3-bromotoluene and *n*BuLi) was used. The oily residue was purified by column chromatography [SiO_2, eluent: petroleum ether (40−60°C)/diethyl ether (1:1), R_f = 0.79] to yield 3.2 g (53%) of an off-white powder. − M.p. 248°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3585 cm^{-1} (ss, OH), 3038 (w, Ar−H), 2948−2856 (m, C−H), 1603 (ss, Ar), 1481 (s, C−O) 790 (s), 746 (s, 1,3-disubst. Ar). − ^{1}H NMR (250 MHz, [D$_6$]DMSO): δ = 2.24 (s, 6 H, CH_3), 2.27 (s, 6 H, CH_3), 4.49 (s, 2 H, OH), 5.90 (s, 1 H, Ar−H), 6.47 (s, 1 H, Ar−H), 6.56 (d, ^3J = 7.9 Hz, 2 H, Ar−H), 8.68−7.35 (m, 20 H, Ar−H). − ^{13}C NMR (50.32 MHz, [D$_6$]DMSO): δ = 21.52 (CH_3), 81.84 (C−OH), 123,90, 125.04, 127.09, 127.24, 128.22, 128.30, 128.49, 129.44, 131.81, 136.23,

Table 3. Structure determination summary of crystalline inclusion compounds

	1 · Et_2NH (1:2)	**1** · acetone (1:2)
Molecular formula	$C_{40}H_{30}O_2 \cdot 2\,[NH(C_2H_5)_2]$	$C_{40}H_{30}O_2 \cdot 2\,[(CH_3)_2CO]$
Molecular weight	688.9	658.8
Color	colorless	colorless
Habit	prism	prism
Crystal size [mm]	0.28 × 0.40 × 0.36	0.28 × 0.32 × 0.34
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (No. 14)	$P2_1/n$ (No. 14)
Unit cell		
a [Å]	13.318(2)	8.434(2)
b [Å]	10.967(1)	14.177(3)
c [Å]	14.267(2)	15.710(3)
α [°]	90	90
β [°]	107.539(8)	90.45(3)
γ [°]	90	90
Volume [Å^3]	1986.7(6)	1878.2(7)
Z	2	2
Calcd. density [g·cm^{-3}]	1.115	1.165
F(000)	740	700
Radiation, λ [Å]	0.71073	0.71073
Absorpt. coeff. [cm^{-1}]	0.70	0.73
Transmission factors	0.851 to 0.920	0.812 to 0.865
Unique data measured	2573	2446
Obsvd. reflections	1133 $\lvert F_o\rvert \geq 3\sigma\,(\lvert F_o\rvert)$	1182 $\lvert F_o\rvert \geq 3\sigma\,(\lvert F_o\rvert)$
Parameters refined	233	228
R/R_w [%]	7.6/9.0	6.3/7.8
S	1.54	1.23
Largest and mean Δ/σ	0.000, 0.000	0.096, 0.002
Res. el. dens. [e·Å^{-3}]	0.44/−0.25	0.22/−0.23

	4 · DMF (1:2)	**6** · DMSO (1:1)
Molecular formula	$C_{56}H_{62}O_2 \cdot 2\,[(CH_3)_2NCHO]$	$C_{40}H_{30}O_3 \cdot (CH_3)_2SO$
Molecular weight	913.2	620.77
Color	colorless	pale yellow
Habit	rectangular	rectangular
Crystal size [mm]	0.28 × 0.34 × 0.44	0.20 × 0.40 × 0.50
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$ (No. 14)	*Pbcn* (No. 60)
Unit ccll		
a [Å]	8.946(3)	9.712(3)
b [Å]	20.608(9)	16.176(5)
c [Å]	15.716(4)	20.451(6)
α [°]	90	90
β [°]	104.33(0)	90
γ [°]	90	90
Volume [Å^3]	2807(2)	3213.0(15)
Z	2	4
Calcd. density [g·cm^{-3}]	1.081	1.283
F(000)	988	1312
Radiation, λ [Å]	0.71073	0.71073
Absorpt. coeff. [cm^{-1}]	0.66	1.41
Transmission factors	0.844 to 0.935	0.913 to 0.935
Unique data measured	3529	3700
Obsvd. reflections	1580	1262
Parameters refined	308	131
R/R_w [%]	7.6/8.4	6.9/9.8
S	1.23	1.30
Largest and mean /	0.002, 0.000	0.001, 0.000
Res. el. dens. [e·Å^{-3}]	0.38/−0.27	0.44/−0.36

	6 · *p*-xylene (1:1)	**10** · *n*$BuNH_2$ (2:3)
Molecular formula	$C_{40}H_{30}O_2 \cdot C_8H_{10}$	$C_{64}H_{46}O_2 \cdot 1.5\,(n\text{-}C_4H_9NH_2)$
Molecular weight	648.8	956.7
Color	colorless	colorless
Habit	prism	cuboid
Crystal size [mm]	0.25 × 0.35 × 0.50	0.28 × 0.44 × 0.44
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
Unit cell		
a [Å]	10.358(4)	11.679(2)
b [Å]	10.919(4)	12.630(3)

Table 3. (continued)

	6 · *p*-xylene (1:1)	**10** · *n*BuNH$_2$ (2:3)
c [Å]	16.075(7)	19.930(4)
α [°]	84.01(1)	91.61(3)
β [°]	79.18(1)	94.38(3)
γ [°]	84.11(1)	111.82(3)
Volume [Å^3]	1770(1)	2617(1)
Z	2	2
Calcd. density [g·cm^{-3}]	1.218	1.170
F(000)	688	1018
Radiation, λ [Å]	0.71073	0.71073
Absorpt. coeff. [cm^{-1}]	0.073	0.069
Transmission factors	0.910 to 1.000	0.734 to 0.805
Unique data measured	6207	6982
Obsvd. reflection	2337	2637
Parameters refined	283	533
R/R_w [%]	9.4/12.0	8.2/8.5
S	2.03	3.09
Largest and mean Δ/σ	0.000, 0.000	0.015, 0.003
Res. el. dens. [e·Å^{-3}]	40.79/−0.48	0.41/−0.41

143.57, 147.35, (12 C, CH resp. C_q). − $C_{44}H_{38}O_2$ (HR MS): calcd. 598.2862; found 598.2856. − $C_{44}H_{38}O_2$: calcd. C 88.26, H 6.40; found 88.39, H 6.28.

1,1,1′,1′-Tetrakis(4-methylphenyl)-1,1′-(anthracene-1,8-diyl)dimethanol (8): 4-Tolyllithium (from 4-bromotoluene and *n*BuLi) was used. The oily residue was treated with hot MeOH and cooled (4°C, overnight) to give a yellow solid. Recrystallization from toluene and decomposition of the clathrate yielded 3.8 g (64%) of a pale yellow powder. − M.p. 295°C (dec.). − IR (KBr): $\tilde{\nu}$ = 3582 cm^{-1} (ss, OH), 3021 (m, Ar−H), 2918 (s, C−H), 1508 (ss, Ar), 812 (ss, 1,4-disubst. Ar). − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 2.27 (s, 12 H, CH$_3$), 5.46 (s, 2 H, OH), 6.55−7.30 (m, 18 H, Ar−H), 7.22 (dd, ^3J = 7.9/7.9 Hz, 2 H, Ar−H), 7.89 (d, ^3J = 7.9 Hz, 2 H, Ar−H), 8.48 (s, 1 H, Ar−H), 9.53 (s, 1 H, Ar−H). − ^{13}C NMR (62.89, CDCl$_3$): δ = 21.76 (CH$_3$), 83.07 (C−OH), 124.82, 128.37, 128.69, 128.96, 129.01, 129.25, 129.56, 132.90, 137.43, 143.00, 144.82, (11 C, CH resp. C_q). − $C_{44}H_{38}O_2$ (HR MS): calcd. 598.2862; found 598.2873. − $C_{44}H_{38}O_2$: calcd. C 88.26, H 6.40; found C 88.19, H 6.36.

1,1,1′,1′-Tetrakis(4-*tert*-butylphenyl)-1,1′-(anthracene-1,8-diyl)dimethanol (9): 4-*tert*-Butylphenyllithium (from 4-*tert*-butylbromobenzene and *n*BuLi) was used. The oily residue was treated with petroleum ether (40−60°C) to give a pale yellow solid. Recrystallization from xylene yielded 4.65 g (61%) of a colorless powder. − M.p. 305−307°C. − IR (KBr): $\tilde{\nu}$ = 3588 cm^{-1} (s, OH), 3089−3007 (w, Ar−H), 2957 (ss), 2884 (s, C−H), 1505 (ss, Ar), 1268 (s, C−O), 828 (ss, 1,4-disubst. Ar). − ^{1}H NMR (200 MHz, CDCl$_3$): δ = 1.35 (s, 36 H, *t*-Bu), 1.93 (s, 2 H, OH), 6.60 (dd, ^3J = 7.4 Hz, ^4J = 1.0 Hz, 2 H, Ar−H), 7.02−7.38 (m, 18 H, Ar−H), 7.88 (dd, ^3J = 8.4 Hz, ^4J = 1.0 Hz, 2 H, Ar−H), 8.37 (s, 1 H, Ar−H), 8.45 (s, 1 H, Ar−H). − ^{13}C NMR (62.89 MHz, CDCl$_3$): δ = 32.10 (CH$_3$), 35.15 (C_q) 82.74 (C−OH), 124.34, 124.93, 125.39, 128.39, 128.93, 129.10, 129.49, 132.92, 136.55, 143.17, 144.63, 150.42, 150.51 (13 C, CH resp. C_q). − $C_{56}H_{62}O_2$ (FAB-MS, *m*NBA + NaOAc): calcd. 766.4796; found 766.4. − $C_{56}H_{62}O_2$: calcd. C 85.87, H 8.30; found C 85.61, H. 8.23.

1,1,1′,1′-Tetrakis(4-biphenylyl)-1,1′-(anthracene-1,8-diyl)dimethanol (10): 4-Biphenyllithium (from 4-bromobiphenyl and *n*BuLi) was used. The oily residue was treated with hot MeOH and cooled to give a pale yellow solid. Recrystallization from toluene and decomposition of the clathrate yielded 5.58 g (66%) of a colorless powder. − M.p. 263−264°C. − IR (KBr): $\tilde{\nu}$ = 3585 cm^{-1} (s, OH), 3026 (ss, Ar−H), 1484 (s, Ar), 834 (s, 1,4-disubst. Ar), 747 (ss), 695 (ss, mono-subst. Ar). − ^{1}H NMR (200 MHz, [D$_6$]DMSO): δ = 6.59 (s, 2 H, OH), 6.70−8.00 (m, 43 H, Ar−H), 8.55 (s, 1 H, Ar−H). − ^{13}C NMR (62.89 MHz, [D$_6$]DMSO): δ = 81.95 (C−OH), 125.30, 125.94, 126.63, 127.18, 128.19, 128.38, 128.57, 128.82, 128.90, 131.92, 138.20, 140.11, 143.59, 146.62 (14 C, CH resp. C_q). − $C_{64}H_{46}O_2$ (FAB-MS, *m*NBA + NaOAc): calcd. 846.3486; found 869.4. − $C_{64}H_{46}O_2$: calcd. C 90.75, H 5.47; found C 90.55, H 5.47.

Crystalline Inclusion Compounds: The corresponding host compound was dissolved under heating in a minimum amount of the respective guest solvent. After keeping for 12 h at room temp., the crystals which formed were collected, washed with diethyl ether or methanol, and dried (1 h, 15 Torr, room temp.). Host−guest stoichiometric ratios were determined by ^{1}H-NMR integration. Data for each compound are given in Table 1.

Crystallography: Information concerning the crystallographic data and structure determination of the six compounds is summarized in Table 3. Intensities were collected in the variable ω-scan technique[23] with a Siemens *P*4 diffractometer using Mo-K_α radiation (λ = 0.71073 Å) at 294 K, and empirical adsorption correction based on ψ-scan data[24] was applied. All calculations were performed with an IBM-compatible PC using the SHELXTL-PLUS program package.[25] The structures were solved by direct phase determination. The ethyl groups of the Et$_2$NH guest molecule in **1** · Et$_2$NH, the DMSO molecule in **6** · DMSO and the butyl residue of the butylamine molecules in **10** · *n*BuNH$_2$ were found to be twofold disordered, and their scattering power was represented by half-carbon or half-oxygen atoms, respectively. These disordered atoms and the terminal phenyl groups in latter complex were subjected to isotropic refinement, while all of the other non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms except those of the hydroxy groups and disordered carbon atoms were generated geometrically (C−H distance fixed at 0.96 Å), and the hydrogen atoms of the hydroxy groups were generated based on the scheme of hydrogen bonding. All hydrogen atoms were allowed to ride on their respective parent atoms; they were assigned appropriate isotropic temperature factors and included in the structure-factor calculations. Analytic expressions of atomic scattering factors were employed, and anomalous dispersion cor-

rections were incorporated.[26] The refinement of the coordinates and anisotropic thermal parameters of the non-hydrogen atoms was carried out by the full-matrix least-squares method. The final *R* indices and other parameters are listed in Table 3.[27]

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[27] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-114557−114562. Copies of the data can be obtained free of charge on application to, CCDC, 12 Union Road, Cambrigde CB2 1EZ, UK [Fax: int. code + 44-1223/336-033, E-mail: deposit@ccdc.cam.ac.uk].

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