Crystalline inclusion compounds of hosts composed of anthracene, ethylene and crowded alcoholic building blocks

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A series of new clathrate host molecules **1**–**3** (**a**, **b**) have been synthesized, which contain two bulky alcoholic groups attached *via* an acetylene connection element to different positions (1,5, 1,8 or 9,10) of a basic anthracene construction unit. Their clathrate formation properties with organic guests, including amines, dipolar aprotic and apolar compounds, are reported (78 examples of clathrates); these demonstrate a characteristic level of selectivity. The crystal structures of three selected clathrates, containing acetone or tetrahydrofuran as the guest, have been determined by X-ray diffraction. H-bonded 1 : 2 host–guest associates are formed in these clathrates, where each of the host hydroxy groups binds to a guest oxygen, although the host–guest arrangements in the acetone and tetrahydrofuran complexes are different in orientation, being in *endo*- and *exo*-mode relative to the anthracene unit, respectively.

Introduction

Organic crystals having open network structures are intriguing for a variety of fundamental and practical issues[1] such as the potential to accommodate guest molecules with desirable optical properties, to separate small molecules based on size exclusion or chemical affinity, or to provide tailored reaction environments for included molecules[2] to be used in chemical sensor development,[3] chiral separation[4] and topochemical reactions.[5] The building blocks which are assembled in these materials and give rise to the porous host lattice obey a control at the molecular level.[6] In many cases, a rigid and bulkily substituted organic molecule is involved, which shows distinct hydrogen bonding functionality.[7] Characteristic examples are the large family of bis(diarylmethanol) or bis(fluoren-9-ol) substituted aromatic compounds that form a great variety of clathrates or crystalline inclusions.[8]

Recently, 1,5- and 1,8-bis(diarylmethanol) substituted derivatives of anthracene have been described as being very efficient in clathrate formation.[9] Nevertheless, the individual compounds of this type are rather different in their inclusion ability depending on the positions of the substituents attached to the anthracene moiety. As a general rule, the 1,5-substituted anthracenes were found to be more efficient than the 1,8-derivatives in forming crystalline inclusions. Moreover, the 1,5-derivatives favor the 1 : 2 host : guest stoichiometric ratio, whereas a 1 : 1 ratio is more commonly found for the 1,8-substituted anthracenes. A promising structural modification and extension of this design concept emerging from the previous results would be preparation of the molecules that contain linear rigid ethynylene building blocks inserted between the anthracene and the diphenylmethanol groups, including also a 9,10-substituted analog and bridged derivatives having 9-hydroxyfluoren-9-yl instead of diphenylmethanol groups, in order to widen the available network space[10] and to bring into play π-stacking interactions advantageous to cavity stabilization.[11]

Here we report on the synthesis of the compounds **1**–**3** (**a**, **b**) (Scheme 1), describe in detail their crystal inclusion (clathrate formation) properties and present crystal structures of three clathrate compounds, namely **1a**·THF (1 : 2), **1a**·acetone (1 : 2) and **1b**·acetone (1 : 2).

Results and discussion

Synthesis

The host compounds **1**–**3** (**a**, **b**) were synthesized by reaction of the corresponding dibromoanthracene and the aromatic alkynols **4** and **5**, respectively, using Hagihara conditions.[12] The alkynols **4** and **5** were prepared from lithium acetylide ethylenediamine complex and benzophenone or fluoren-9-one in *N*,*N*-dimethylacetamide.[13,14] The inclusion compounds were obtained by recrystallization of the host compounds from the respective guest solvent. The drying conditions specified in the experimental section (1 h, 15 Torr, room temperature) refer to what we consider a "stable clathrate".

Inclusion properties

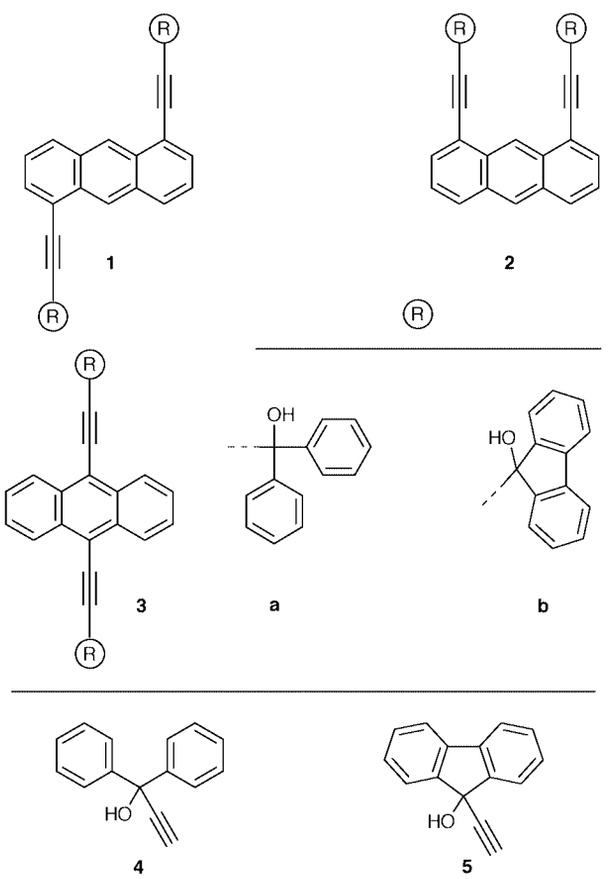
In order to make possible a good comparison between the inclusion properties of the present and the previously described host compounds,[9] the same variety of organic solvents—including amines, alcohols, ketones, nitriles, nitro compounds and other aprotic dipolar solvents, heterocycles and aromatic compounds of different constitutions—were used for the recrystallization (clathrate formation) experiments. A total of 78 different lattice inclusions are specified in Table 1, showing the new compounds to be efficient hosts as well. Nevertheless, the individual compounds **1a**–**3a** and **1b**–**3b** differ in inclusion ability and demonstrate a characteristic level of selectivity differing also from that of the structural analogs previously described.[9]

The differences are mainly in the variety rather than in the absolute number of solvents being included by each of the host compounds, although there is a general preference for the entrapment of DMF, DMSO and 1,4-dioxane, which are included by all the hosts without exception. Also, all host compounds enclathrate cyclohexylamine and diethylamine, while the other amines of Table 1 are not generally included, except by **3b** which is found to be a universal host for the inclusion of

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

Guest solvent[b]	Host compound					
	1a	**1b**	**2a**	**2b**	**3a**	**3b**
Pr^nNH_2	—	1 : 1	—	1 : 1	—	1 : 1
Pr^iNH_2	—	1 : 1	—	1 : 1	1 : 1	1 : 1
Bu^nNH_2	—	—	1 : 1	1 : 1	[c]	1 : 2
Bu^iNH_2	1 : 1	—	1 : 1	[c]	—	1 : 2
2-$BuNH_2$	2 : 3	—	1 : 1	[c]	2 : 3	1 : 2
Hex^cNH_2	1 : 1	1 : 2	1 : 1	1 : 2	1 : 2	1 : 2
Et_2NH	1 : 2	1 : 2	1 : 2	1 : 2	1 : 2	1 : 2
Pr^n_2NH	[c]	[c]	1 : 2	[c]	[c]	1 : 2
Et_3N	—	—	1 : 1	1 : 2	1 : 1	1 : 2
Pr^n_3N	—	—	1 : 1	[c]	[c]	2 : 1
Bu^n_3N	—	—	2 : 1	[c]	[c]	2 : 1
Piperidine	2 : 3	1 : 2	2 : 3	[c]	1 : 2	[c]
Acetonitrile	—	—	—	1 : 1	—	1 : 1
Propionitrile	—	—	—	1 : 1	—	1 : 1
DMF	1 : 2	1 : 2	1 : 1	1 : 2	1 : 2	1 : 2
DMSO	1 : 2	1 : 2	1 : 1	1 : 2	1 : 2	1 : 2
Ethyl acetate	2 : 1	—	—	1 : 1	—	—
Acetone	1 : 2	1 : 2	—	1 : 2	3 : 1	1 : 1
Cyclopentanone	—	—	—	—	1 : 2	—
Cyclohexanone	—	—	—	—	1 : 2	—
THF	1 : 2	1 : 1	1 : 1	—	—	—
1,4-Dioxane	1 : 1	1 : 2	1 : 1	1 : 1	1 : 2	2 : 1
Toluene	—	—	—	3 : 1	—	—

[a] See Experimental for methods of preparation, drying standard, and characterization. [b] MeOH, EtOH, Pr^nOH, Bu^nOH, $Pent^cOH$, Hex^cOH, butyronitrile, benzonitrile, nitromethane, nitroethane, pyridine, 2-picoline, 3-picoline, 4-picoline, *o*-xylene, *m*-xylene and *p*-xylene, which were also tested as guest solvents, yielded no inclusion compounds. [c] Difficult to crystallize.



Scheme 1

amines. Another remarkable finding is obvious from the inclusions with acetonitrile and propionitrile, which are formed only with **2b** and **3b**, while ethyl acetate gives inclusions only with **1a** and **2b**. Moreover, the only inclusion compounds with cyclopentanone and cyclohexanone are formed by **3a**, whereas **2b** selectively yields the single inclusion compound with toluene.

With reference to the stoichiometric host–guest ratios of the inclusion compounds listed in Table 1, the following preferences emerge: The present 1,5- and also the 9,10-substituted anthracenes do favor the 1 : 2 stoichiometric ratio, with the 1 : 1 ratio being rather secondary. By way of contrast, the 1,8-derivatives favor the 1 : 2 host : guest stoichiometric ratio, with the 1 : 2 ratio being minor. In other words, the 1,5- and the 9,10-disubstituted anthracene hosts **1** (**a**, **b**) and **3** (**a**, **b**) for geometric reasons are more inclined than the 1,8-analogs **2** (**a**, **b**) to bind two guests independently, giving rise to the predominance of the 1 : 2 (host–guest) inclusion compounds. On the other hand, the two hydroxy groups in the 1,8-disubstituted host analogs are rather well prepared for mutual interaction, thus reducing the external binding capacity for guest molecules, which accounts for the preferential 1 : 1 stoichiometric ratio. Nevertheless, this general behavior is less pronounced for the present host compounds than for the previously described host analogs lacking the ethynylenic spacer units.[9] Hence, insertion of acetylenic spacer elements between the anthracene and the bulky alcoholic groups has a moderate effect on the structural dictates coming from the positioning of the substituents. Moreover, bridging of the phenyl rings in **1a**–**3a** to give the fluorene moieties in **1b**–**3b** does not decisively affect the stoichiometric host–guest ratios or the general capacity to form inclusion compounds, but to some extent it affects the individual inclusion behavior, as shown in Table 1.

X-Ray structural studies

Crystallographic data and details of the structure refinement calculations of the inclusion compounds **1a**·THF (1 : 2), **1a**·acetone (1 : 2), and **1b**·acetone (1 : 2) are given in Table 2. Figs. 1(a)–(c) show perspective views of the stoichiometric host–guest units. Stereo packing illustrations are presented in Figs. 2–4. Conformational features of the host molecules and geometric parameters of selected intermolecular interactions are listed in Tables 3 and 4. Since acetone is the guest component both in the inclusion compounds with **1a**, **1b** and a previously studied non-acetylenic host analog,[9] the present compounds are complementary examples making possible a reasonable series of comparisons.

Molecular structures. The host molecules **1a** and **1b**, differing only in the attached R groups (Scheme 1), exhibit inversion (C_i) symmetry, which perfectly coincides with the crystallographic centrosymmetry in the present inclusion crystals. Accordingly, the host molecule is located on the crystallographic inversion center in all three compounds, and the unique part of the structures comprises half of the host and one guest molecule (Figs. 1a–c). The rigid, flat 1,5 diethynyl-substituted anthracene moiety of **1a** and **1b** has similar geometry in the studied co-crystals, whereas the orientation of the OH functionality and also of the whole R group, seems to be a soft parameter which may be seriously affected by the host–guest interaction modes and/or the crystal packing forces (see below). The tetrahydrofuran (THF) and acetone guests are polar, non-protic molecules, which are hydrogen bonded to the host alcoholic functions in similar ways. The THF guest in **1a**·THF (1 : 2) has a near half-chair (or twist) conformation with an approximate two-fold rotation axis going through atom C(2T). This conclusion is based on the ring puckering parameters $Q_T = 0.393(2)$ Å and $\varphi_2 = 16.8(3)°$ (following Cremer and Pople),[15,16] and on the fact that the ΔC_2 parameter with location at C(2T) has the lowest value [0.0065(7) Å][15,17] among the asymmetry parameters. The acetone guest skeletons are planar within 0.019 [in **1a**·acetone (1 : 2)] and 0.016 Å [in **1b**·acetone (1 : 2)]. The bond

Table 2 Crystal data and selected details of the refinement calculations for compounds **1a**·THF (1 : 2), **1a**·acetone (1 : 2) and **1b**·acetone (1 : 2)[a]

Compound	**1a**·THF (1 : 2)	**1a**·acetone (1 : 2)	**1b**·acetone (1 : 2)
Crystal data			
Empirical formula	$C_{44}H_{30}O_2$·2(C_4H_8O)	$C_{44}H_{30}O_2$·2(C_3H_6O)	$C_{44}H_{26}O_2$·2(C_3H_6O)
Formula mass	734.89	706.84	702.80
T/K	100(2)	295(2)	100(2)
Radiation used	Mo-Kα	Cu-Kα	Mo-Kα
λ/Å	0.71073	1.5418	0.71073
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_1/n$	$P\bar{1}$
Unit cell dimensions			
a/Å	8.924(1)	11.5927(3)	8.400(1)
b/Å	9.155(1)	12.8758(5)	8.880(1)
c/Å	11.963(2)	14.0251(4)	13.450(2)
α/°	90.53(2)	90.0	82.33(2)
β/°	92.12(2)	105.162(2)	71.63(2)
γ/°	96.56(2)	90.0	76.64(2)
V_c/Å^3	970.2(2)	2020.59(11)	924.4(2)
Z (formula)	1	2	1
D_c/g cm^{-3}	1.2578(3)	1.1618(1)	1.2626(1)
μ/mm^{-1}	0.078	0.57	0.079
F(000)	390	748	370
Reflections collected	7552	3302	5935
Independent reflections	3477	3302	3331
R_{int}	0.037	—	0.022
Refinement			
No. of parameters refined	276	268	265
R [$I > 2\sigma(I)$]	0.0358	0.0583	0.0348
No. of reflections with $I > 2\sigma(I)$	2387	2366	2689
R (F^2)	0.0583	0.0784	0.0462
wR^b (F^2)	0.0915	0.1919	0.1002
No. of F^2 used[c]	3477	3290	3328
S (Goodness-of-fit on F^2)	0.901	1.059	1.052
Largest diff. peak and hole/e Å^{-3}	0.16 and −0.19	0.47 and −0.38	0.21 and −0.20

[a] Esd's, where given, are in parentheses. [b] The weights of the F^2 values were assumed as $w = [\sigma^2(F_o^2) + (c_1P)^2 + (c_2P)^2]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$, and the constants c_1 and c_2 had the values 0.056 and 0.0 for **1a**·THF (1 : 2), 0.0947 and 0.5215 for **1a**·acetone (1 : 2), and 0.0660 and 0.047 for **1b**·acetone (1 : 2), respectively. Moreover, the F_c values of **1a**·acetone (1 : 2) were multiplied by $\mathbf{k}[1 + 0.001\mathbf{x}F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$, where **x** is the extinction coefficient (=0.01904), refined by least squares method, and **k** is the overall scale factor (=1.09450). [c] Twelve reflections have been excluded from the final refinement calculation of the **1a**·acetone (1 : 2) compound due to potential systematic errors. Furthermore, three strong low-θ reflections [1 0 0, 0 1 1 and 1 0 1], having considerably higher values for F_c than F_o, in all probability depending on extinction effects, have been excluded from the final refinement of **1b**·acetone (1 : 2).

distances and angles mostly conform to generally accepted values, and no extreme value was observed.

Host–guest interactions and packing relations. All three crystal structures consist of hydrogen bonded 1 : 2 host–guest associates (Table 4) held together by ordinary van der Waals' interactions, *i.e.* by relatively weak forces. In such a case the requirement of dense packing plays a crucial role in the crystallization process. So, the observed distinctly different orientation of the diarylmethanol groups of host **1a** in its THF and acetone inclusion compounds (Figs. 1a–b), is certainly a consequence of the requirement of close packing. The acetone guest takes a position above (or below) the central anthracene moiety in **1a**·acetone (1 : 2), roughly parallel with the C(11)···C(16) phenyl ring, whereas the THF ring, located on the other side of the linear ethynyl chain, forms a propeller-like arrangement with the two phenyl rings of the diarylmethanol group in **1a**·THF (1 : 2). The dihedral angle formed by the least-squares (LS) planes through the C(11)···C(16) phenyl ring and the acetone skeleton in **1a**·acetone (1 : 2) is 11.3(2)°, and the average distance between these structural elements is about 3.7 Å. On the contrary, the best LS plane through the THF ring makes the dihedral angles of 126.88(5) and 94.95(5)° with the LS planes through the C(11)···C(16) and C(17)···C(22) phenyl rings, respectively, in **1a**·THF (1 : 2).

Interestingly enough, the orientation of the host OH groups and the positioning of the acetone guests are comparable in the two studied acetone inclusion compounds, despite the difference in the host R groups. Thus, the acetones are located centrosymmetrically above and below the anthracene rings, with an O(1A)···C(1) distance of 3.768(4) Å to **1a**, and 3.370(2) Å to **1b**. The dihedral angle between the anthracene LS plane and that of the acetone guest is 75.0(2)° in **1a**·acetone (1 : 2) and 62.0(1)° in **1b**·acetone (1 : 2). Moreover, the acetone LS plane forms an angle of 47.23(5)° with the fluorene plane, which is near to 46.2°, the arithmetic average value of the two dihedral angles, 11.3(2) and 81.1(2)°, formed by the acetone guest with the two phenyl rings [C(11)···C(16) and C(17)···C(22) rings, respectively] in **1a**·acetone (1 : 2).

The requirement of dense packing of the hydrogen bonded 1 : 2 host–guest associates led to arrangements with relatively low crystal symmetries [triclinic $P\bar{1}$ for **1a**·THF (1 : 2) and **1b**·acetone (1 : 2), and monoclinic $P2_1/n$ for **1a**·acetone (1 : 2)]. It is interesting to note that the packing with the higher symmetry has the lowest density and packing density[18] as well. The calculated packing coefficients[18,19] for the triclinic structures are 70.0% [**1a**·THF (1 : 2)] and 69.0% [**1b**·acetone (1 : 2)] and they have no solvent-accessible free space, whereas the monoclinic [**1a**·acetone (1 : 2)] compound has only 63.9% calculated packing density and about 22.0 Å^3 free space per unit cell. It is important to stress, however, that both triclinic structures have been studied at low temperature [100(2) K], whereas the data for the monoclinic **1a**·acetone (1 : 2) were collected at room temperature [295(2) K]. Investigation of the inter-associate contact distances indicates that the **1a**·THF (1 : 2) structure is held together by ordinary van der Waals' interactions only, whereas

Table 3 Selected conformational features of the host molecules **1a** and **1b**[a]

	1a		**1b**
	in **1a**·THF (1:2)	in **1a**·acetone (1:2)	in **1b**·acetone (1:2)
Selected torsional angles/°			
C(8)–C(9)–C(10)–O(1)	104(2)	36(6)	−37(2)
C(8)–C(9)–C(10)–C(11)	−133(2)	−85(6)	85(2)
C(8)–C(9)–C(10)–C(17)	−11(2)	152(6)	
C(8)–C(9)–C(10)–C(22)			−162(2)
C(9)–C(10)–C(11)–C(12)	173.3(1)	−176.6(2)	−62.1(2)
C(9)–C(10)–C(11)–C(16)	−7.8(2)	6.2(3)	116.1(1)
C(9)–C(10)–C(17)–C(18)	−73.9(2)	60.0(3)	
C(9)–C(10)–C(17)–C(22)	103.6(2)	−120.2(3)	
C(9)–C(10)–C(22)–C(17)			−116.2(1)
C(9)–C(10)–C(22)–C(21)			66.2(2)
O(1)–C(10)–C(11)–C(12)	−63.9(2)	62.6(3)	59.3(2)
O(1)–C(10)–C(17)–C(18)	168.6(1)	177.7(2)	
O(1)–C(10)–C(22)–C(21)			−58.1(2)
C atoms are co-planar to within/Å			
Anthracene moiety	0.024	0.037	0.044
C(11)···C(16) phenyl ring	0.007	0.009	0.015
C(17)···C(22) phenyl ring	0.015	0.011	0.014
Fluorene moiety			0.113
Dihedral angle between the LS-planes/°			
Anthracene and C(11)···C(16) ring	103.14(5)	93.72(8)	98.15(4)
Anthracene and C(17)···C(22) ring	100.15(4)	50.30(7)	101.37(4)
Anthracene and fluorene moieties			99.40(4)
C(11)···C(16) and C(17)···C(22) rings	99.35(5)	91.25(8)	4.33(4)

[a] Calculated using the PARST program (see ref. 15). Esd's, where given, are in parentheses.

Table 4 Distances and angles[a] in O–H···O bonds and possible C–H···O interactions in the crystal structures of **1a**·THF (1:2), **1a**·acetone (1:2) and **1b**·acetone (1:2)

		Distance/Å			Angle/°
Atoms	Symmetry	D···A	D–H	H···A	D–H···A
1a·THF (1:2)					
O(1)–H(10)···O(1T)	x, y, z	2.722(2)	0.98	1.83	149
1a·acetone (1:2)					
O(1)–H(10)···O(1A)	x, y, z	2.767(3)	0.87	1.90	175
C(13)–H(13)···O(1)	$-x,-y,-z-1$	3.470(4)	0.93	2.64	149
1b·acetone (1:2)					
O(1)–H(10)···O(1A)	x, y, z	2.809(1)	0.85	1.97	170
C(1)–H(1)···O(1A)	x, y, z	3.370(2)	0.95	2.56	143
C(21)–H(21)···O(1A)	x, y, z	3.535(2)	0.95	2.74	141
C(4)–H(4)···O(1)	$-x+1,-y+1,-z+1$	3.510(2)	0.95	2.69	145

[a] Esd's where given, are in parentheses. The H atom positions were not refined (see the text). D, donor; A, acceptor.

in the acetone inclusion compounds possible C–H···O interactions (Table 4) seem to supplement the van der Waals' type packing forces.

Conclusions

Structural modification of prototype bis(diphenylmethanol) anthracene host compounds, either by insertion of a connective acetylene group between the basic anthracene unit and each of the two bulky substituents at different positions of the anthracene framework (**1a**–**3a**), or by bridging the two phenyl rings in each of the diphenylmethanol structural elements to yield plane fluorenol units (**1b**–**3b**), does not change fundamentally the original property of forming crystalline inclusion compounds.[9] Nevertheless, the different host molecules exhibit varying individual inclusion behaviour. In particular, alcohols were found totally inefficient guest components here, while amines, dipolar aprotic solvents (DMF, DMSO) and 1,4-dioxane showed a clear preference. Common to the 1,5- and the 9,10-substituted anthracenes is the favored 1:2 host:guest stoichiometric ratio in their inclusion compounds, unlike the 1,8-substituted anthracenes where the 1:1 stoichiometry is preferred. This general behavior, although not as distinct as before,[9] is certainly in keeping with the prototype hosts lacking the acetylene structural connections.

The presently studied inclusion compounds are formed by discrete 1:2 host–guest hydrogen bonded associates where each of the host hydroxy groups binds to a guest oxygen atom. Nevertheless, the host–guest arrangements are different in these complexes, with acetone and THF being in *endo*- and *exo*-orientation relative to the anthracene units, respectively, irrespective of the nature of the substituents (bridged or

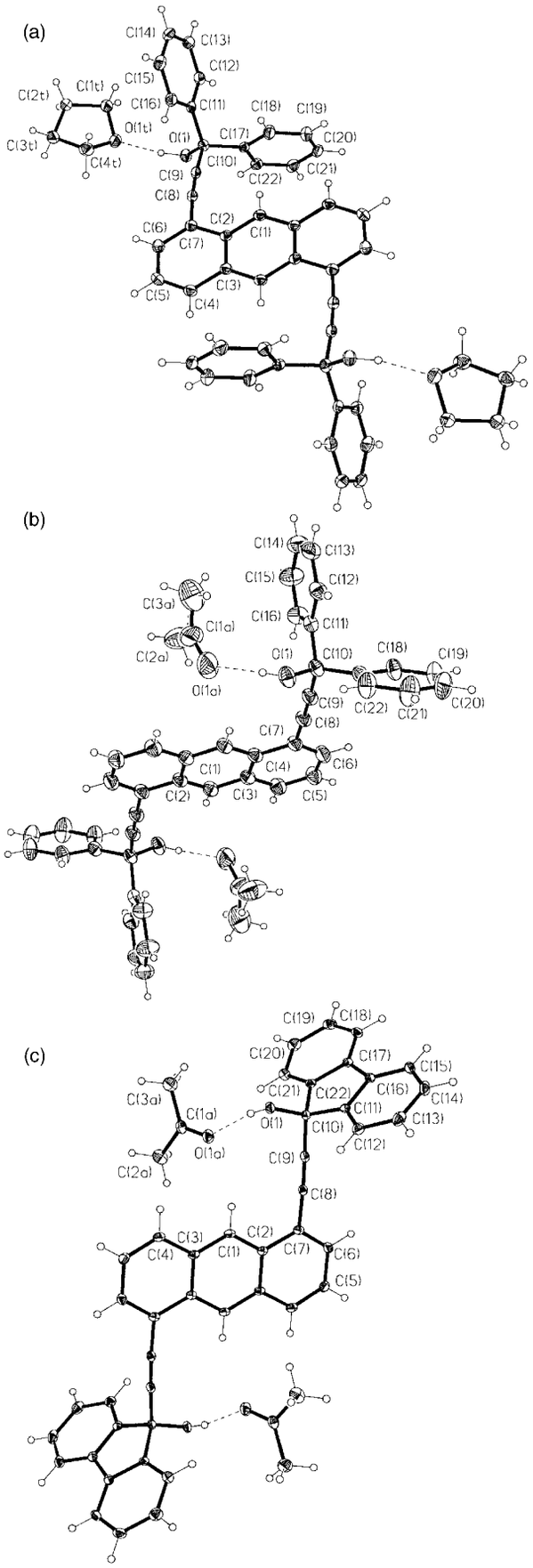


Fig. 1 Perspective views of the stoichiometric units of the inclusion compounds **1a**·THF (1 : 2) (a), **1a**·acetone (1 : 2) (b) and **1b**·acetone (1 : 2) (c), with the crystallographic labeling of the unique non-hydrogen atom positions. Solid and dashed lines mean covalent and hydrogen bonds, respectively. The ellipsoids of the C and O atoms are drawn at 50% [**1a**·THF (1 : 2) and **1b**·acetone (1 : 2)] or at 30% [**1a**·acetone (1 : 2)] probability level.

unbridged). A similar arrangement, involving *endo*-oriented binding of the acetone guest molecules, was found for a respective inclusion of the prototype host compound.[9] These previous studies also suggest that an extension of the bulk of the substituents by the addition of further substituents may change the orientation of binding guest molecules from *endo* to *exo*, giving rise to new crystalline networks. Moreover, a structural modification as defined by an extension of the linear acetylene connection would be a promising challenge in future clathrate design.[7]

Experimental

Synthesis

Mps were determined with a Reichert host-stage apparatus. IR spectra (cm^{-1}) were recorded with a Perkin-Elmer FT-IR 1600 spectrometer. ^1H and ^{13}C NMR spectra were measured for solutions (Me_4Si as internal standard, ppm) with Bruker AC-200 (^1H: 200 MHz; ^{13}C: 50.32 MHz), WM-250 (^1H: 250 MHz; ^{13}C: 62.89 MHz) and AMX-400 (^1H: 400 MHz; ^{13}C: 100.57 MHz) spectrometers, respectively. Mass spectra were obtained using an A.E.I. MS-50 instrument (EI) or a Kratos Concept 1H (FAB-MS). Microanalyses were carried out by the Microanalytical Laboratory of the Kekulé Institut für Organische Chemie und Biochemie, Universität Bonn. Solvents were dried by standard procedures. The starting compounds 1,5-dichloroanthraquinone, 1,8-dichloroanthraquinone, 9,10-dibromoanthracene, benzophenone, fluoren-9-one and lithium acetylide ethylenediamine complex were purchased from Janssen or Aldrich.

1,5-Dibromoanthracene[20] and 1,8-dibromoanthracene[21] were prepared from 1,5-dichloroanthraquinone and 1,8-dichloroanthraquinone, respectively, according to literature procedures.[22]

1,1-Diphenylprop-2-yn-1-ol (**4**) and 9-ethynylfluoren-9-ol (**5**) were obtained by ethynylation of benzophenone or fluoren-9-one as described elsewhere.[13,14]

Host compounds 1–3; general procedure[23,24]

To a stirred and boiling solution of 3.36 g (10 mmol) of the corresponding dibromoanthracene in triethylamine–toluene (2 : 1, v/v) 25 mmol of the respective alkynol (**4** or **5**) was added under argon. After cooling the solution to room temperature, Pd(II)–acetate (25 mg), triphenylphosphine (75 mg) and Cu(I) iodide (25 mg) were added. The mixture was heated to 90 °C for about 4 h until the reaction was complete (tested by thin-layer chromatography) and was then cooled to room temperature. The catalyst and the triethylammonium salts were filtered off and washed with diethyl ether (100 ml). The filtrate and washings were evaporated under reduced pressure, the residue was dissolved in diethyl ether and washed (diluted HCl, $NaHCO_3$, and H_2O, in this sequence). The organic layer was separated, dried (Na_2SO_4) and evaporated. Specific details for each compound are given below.

1,5-Bis[(diphenylhydroxymethyl)ethynyl]anthracene (1a). 1,5-Dibromoanthracene and **4** were used. Recrystallization from ethyl acetate yielded 4.9 g (83%) of pale yellow needles; mp 217–218 °C (Found: C, 88.05; H, 5.17. Calc. for $C_{92}H_{68}O_6$, 2 : 1 clathrate with ethyl acetate: C, 88.01; H, 5.45%); ν (KBr)/cm^{-1} 3534 (s, OH), 3047 (w, Ar–H), 2208 (w, C≡C), 1556, 1487, 1445 (s, Ar–H), 1023 (s, C–O); δ_H (200 MHz; [$^2H_6$]DMSO) 7.30–7.46 (14 H, m, Ar, OH), 7.72–7.92 (14 H, m, Ar), 8.78 (2 H, s, Ar); *m/z* (EI, 70 eV) 590.2241 (M^+).

1,5-Bis[(9-hydroxyfluoren-9-yl)ethynyl]anthracene (1b). 1,5-Dibromoanthracene and **5** were used. Recrystallization from ethyl acetate yielded 3.9 g (67%) of yellowish-orange crystals; mp 281–282 °C (Found: C, 88.32; H, 4.69. Calc. for $C_{44}H_{26}O_2$:

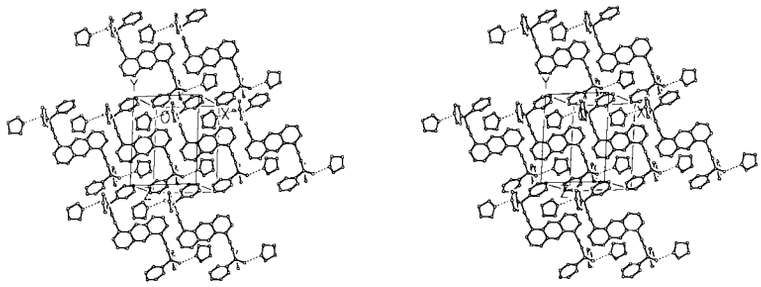


Fig. 2 Packing illustration of the crystal structure of **1a**·THF (1 : 2). The H atoms are excluded for clarity. Solid and dotted lines mean covalent bonds and O · · · O contacts in hydrogen bonds, respectively.

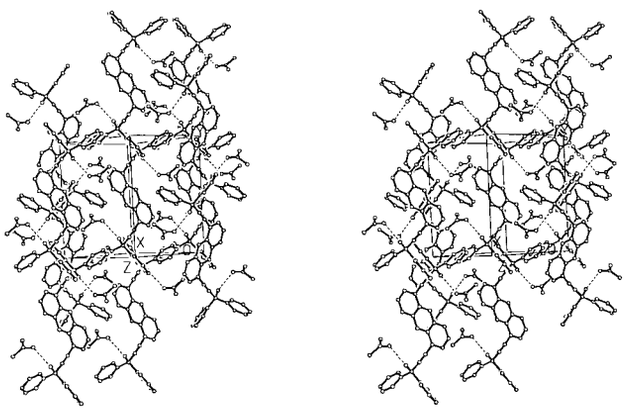


Fig. 3 Packing diagram of compound **1a**·acetone (1 : 2). H atoms are omitted for clarity. The O · · · O contact in hydrogen bonds is drawn as a dotted line.

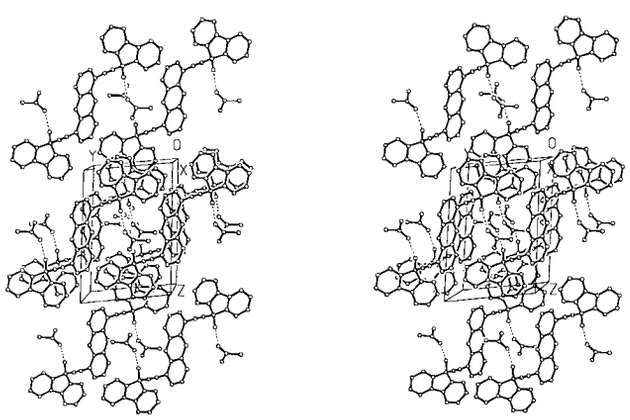


Fig. 4 Packing illustration of compound **1b**·acetone (1 : 2). H atoms are omitted for clarity. The O · · · O contact in hydrogen bonds is drawn as a dotted line.

C, 88.57; H, 4.84%); ν (KBr)/cm^{-1} 3557 (s, OH), 3030 (w, Ar–H), 2210 (w, C≡C), 1602, 1448 (s, Ar–H), 1012 (s, C–O); δ_H (250 MHz; [$^2H_6$]DMSO) 7.03 (2 H, s, OH), 7.43–7.58 (10 H, m, Ar), 7.69 (2 H, d, $^3J_{(H,H)}$ = 6.4 Hz, Ar), 7.85 (4 H, dd, $^3J_{(H,H)}$ = 5.4, 3.3 Hz, fluorenyl-H), 7.94 (4 H, dd, $^3J_{(H,H)}$ = 5.4, 3.3 Hz, fluorenyl-H), 8.01 (2 H, d, $^3J_{(H,H)}$ = 8.6 Hz, Ar), 8.74 (2 H, s, Ar); *m*/*z* (EI, 70 eV) 586.1924 (M$^+$).

1,8-Bis[(diphenylhydroxymethyl)ethynyl]anthracene (2a). 1,8-Dibromoanthracene and **4** were used. The oily residue was digested with methanol to give a yellowish solid. Recrystallization from acetone yielded 4.3 g (73%) of pale yellow crystals; mp 203–205 °C (Found: C, 89.37; H, 5.20. Calc. for $C_{44}H_{30}O_2$: C, 89.46; H, 5.12%); ν (KBr)/cm^{-1} 3500–3300 (br s, OH), 3050 (w, Ar–H), 2270 (w, C≡C), 1488, 1447 (s, Ar–H), 1004 (s, C–O); δ_H (400 MHz; [$^2H_6$]DMSO) 6.90 (2 H, s, OH), 7.23 (4 H, t, $^3J_{(H,H)}$ = 8.1 Hz, Ph), 7.33 (8 H, t, $^3J_{(H,H)}$ = 8.1 Hz, Ph), 7.61 (2 H, dd, $^3J_{(H,H)}$ = 8.2, 7.0 Hz, anthracene), 7.74 (8 H, d, $^3J_{(H,H)}$ = 8.1 Hz, Ph), 7.99 (2 H, d, $^3J_{(H,H)}$ = 7.0 Hz, anthracene), 8.19 (2 H, d, $^3J_{(H,H)}$ = 8.2 Hz, anthracene), 9.32 (1 H, s, anthracene); δ_C (100.58 MHz; [$^2H_6$]DMSO) 73.73 (C≡C), 83.78 (C–OH), 99.02 (C≡C), 119.98 (C_q), 122.31, 125.57, 125.75, 125.80, 127.14, 128.16, 128.22, 128.43, 129.40 (9 CH), 130.33, 131.08 (2 C_q), 132.12 (CH), 146.08 (C_q); *m*/*z* (EI, 70 eV) 590.2243 (M$^+$).

1,8-Bis[(9-hydroxyfluoren-9-yl)ethynyl]anthracene (2b). 1,8-Dibromoanthracene and **5** were used. Recrystallization from DMF yielded 4.2 g (72%) of a pale yellow powder; mp 217–218 °C (Found: C, 88.27; H, 4.63. Calc. for $C_{44}H_{26}O_2$: C, 88.57; H, 4.84%); ν (KBr)/cm^{-1} 3528 (s, OH), 3036 (w, Ar–H), 2212 (w, C≡C), 1567, 1452 (s, Ar–H), 1018 (s, C–O); δ_H (250 MHz; [$^2H_6$]DMSO) 6.87 (2 H, s, OH), 7.33–7.62 (12 H, m, fluorenyl), 7.68 (2 H, d, anthracene), 7.82 (4 H, m, fluorenyl), 8.02 (2 H, d, anthracene), 8.27 (2 H, d, anthracene), 8.82 (1 H, s, anthracene), 9.45 (1 H, s, anthracene); δ_C (62.89 MHz; [$^2H_6$]DMSO) 74.21 (C≡C), 81.59 (C–OH), 101.05 (C≡C), 118.38, 120.77, 123.25, 123.92, 124.15, 126.13, 126.44, 127.14, 128.23, 128.70, 130.32, 131.25, 135.39, 146.83 (14 CH, C_q); *m*/*z* (EI, 70 eV) 586.1923 (M$^+$).

9,10-Bis[(diphenylhydroxymethyl)ethynyl]anthracene (3a). 9,10-Dibromoanthracene and **4** were used. The crude product was washed with cold methanol and recrystallized from toluene to yield 4.7 g (80%) of yellow needles; mp 260–261 °C (Found: C, 89.05; H, 5.06. Calc. for $C_{44}H_{30}O_2$: C, 89.46; H, 5.12%); ν (KBr)/cm^{-1} 3520 (ss, OH), 3050 (w, Ar–H), 2360 (s, C≡C), 1487, 1451 (s, Ar–H), 1013 (m, C–O); δ_H (200 MHz; [$^2H_6$]DMSO) 3.32 (2 H, s, OH), 7.24–7.51 (12 H, m, Ar), 7.66–7.85 (12 H, m, Ar), 8.52–8.68 (4 H, m, Ar); δ_C (50.32 MHz; [$^2H_6$]DMSO) 74.06 (C≡C), 81.91 (C–OH), 106.82 (C≡C), 117.47, 125,82, 126.76, 127.44, 127.74, 128.34, 131.67 (7 CH, C_q); *m*/*z* (FAB, mNBA) 590.3 (M$^+$).

9,10-Bis[(9-hydroxyfluoren-9-yl)ethynyl]anthracene (3b). 9,10-Dibromoanthracene and **5** were used. The oily residue was digested with methanol to give a yellow solid. Recrystallization from toluene yielded 4.9 g (84%) of yellowish-orange needles; mp 268–270 °C (Found: C, 88.48; H, 4.75. Calc. for $C_{44}H_{26}O_2$: C, 88.57; H, 4.84%); ν (KBr)/cm^{-1} 3316 (s, OH), 3050 (w, Ar–H), 2204 (w, C≡C), 1448, 1394 (s, Ar–H), 1025 (s, C–O); δ_H (200 MHz; [$^2H_6$]DMSO) 7.10 (2 H, s, OH), 7.43–7.52 (8 H, m, fluorenyl), 7.62–7.73 (4 H, m, anthracene), 7.82–7.98 (8 H, m, fluorenyl), 8.32–8.42 (4 H, m, anthracene); δ_C (62.89 MHz; [$^2H_6$]DMSO) 74.34 (C≡C), 77.59 (C–OH), 105.05 (C≡C), 117.18, 120.57, 121.20, 123.92, 123.95, 124.53, 126.44, 127.74, 128.63, 129.50, 131.53, 133.25, 135.39, 138.62, 147.85 (15 CH, C_q); *m*/*z* (EI, 70 eV) 586.1922 (M$^+$).

Crystalline inclusion compounds

The appropriate host compound was dissolved by heating in a minimum amount of the respective guest solvent. After storage for 12 h at room temperature, the crystals which formed were collected and dried (1 h, 15 Torr, room temperature). The

host : guest stoichiometric ratios were determined by ^{1}H NMR integration. Data for each compound are given in Table 1.

Crystallography

Sample preparation. Crystals of the inclusion compounds suitable for X-ray diffraction studies were invariably obtained through dissolution of the respective hosts in the guest solvent and subsequent slow solvent evaporation. In order to prevent crystal deterioration during the X-ray data collection, the single crystal of **1a**·acetone (1 : 2) was sealed in a glass capillary, whereas the selected crystals of **1a**·THF (1 : 2) and **1b**·acetone (1 : 2), when taken out of the mother liquor, were immediately covered by epoxy glue. Intensity data for **1a**·THF (1 : 2) and **1b**·acetone (1 : 2) were collected at low temperature with an Imaging Plate Diffraction System,[25] while the reflection intensities for **1a**·acetone (1 : 2) were measured at room temperature using a SEIFERT four-circle diffractometer. The derived F^2 values were corrected for background, Lorentz and polarization effects.

Structure solution and refinement. Preliminary structure models were derived by application of direct methods (SHELXS),[26] and were refined by full-matrix least-squares (LS) calculations based on F^2 for all reflections (SHELXL-93).[27] The (C–)H positions were recalculated before each refinement cycle, using geometric evidence,[27] whereas the (O–)H atoms were located from difference electron density ($\Delta\rho$) maps and were held riding on their parent oxygens during the subsequent calculations. In the final LS calculations the non-hydrogen atoms were refined together with their anisotropic displacement parameters, and isotropic vibrational parameters were refined for the hydrogen positions. Crystal data and further details of the refinement calculations together with the final crystallographic R values are shown in Table 2.

Supplementary data. Lists of fractional atomic coordinates with isotropic (for H atoms) or equivalent isotropic displacement parameters (for C and O atoms), and of covalent bond distances and bond angles (Tables 5–8) have been deposited as supplementary data at the Cambridge Crystallographic Data Centre.† Further experimental details as well as lists of the anisotropic displacement parameters (Tables 9–10) and of the F_{obs}–F_{calc} values are available directly from one of the authors (I. C.)

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† CCDC reference number 188/204. See http://www.rsc.org/suppdata/p2/a9/a908151h for crystallographic files in .cif format.

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