

Anthracene Based Bulky Diol Hosts. Crystal Structures of a Free Host and of Inclusion Compounds with Dipolar Guests*

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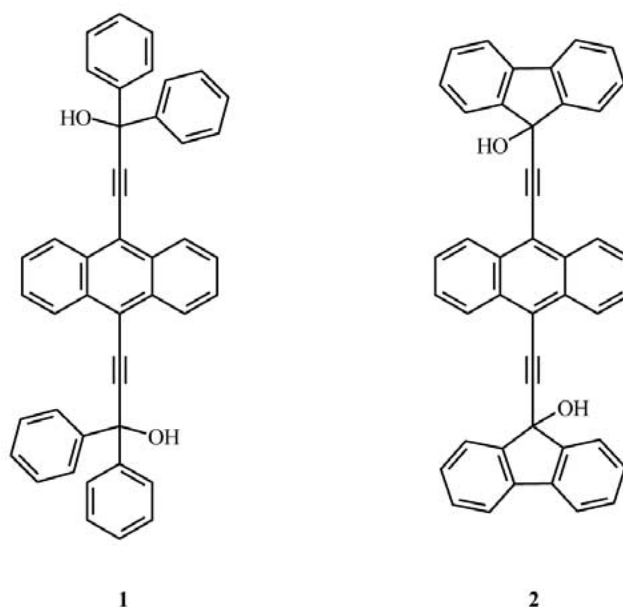
Abstract

X-ray crystal structures are reported of a free host compound **1**, comprising two diphenylmethanol terminal groups attached to a central 9,10-ethynyl substituted anthracene unit, and of three inclusion compounds of a fluoren-9-yl substituted analogous host **2** with acetone, dimethyl sulphoxide (DMSO) and dimethylformamide (DMF) as guest, respectively. Despite the presence of two hydroxyl groups in **1**, there is no O–H...O hydrogen bond between the molecules in the guest free crystal – only weaker C–H...O interactions and van der Waals' type connections. In the inclusion compounds of **2**, H-bonded 1:2 host–guest associates are formed, where each of the host hydroxyl groups binds to a guest oxygen atom. The orientations of the host–guest connections in these complexes vary, being **E** for acetone and **Z** for both DMSO and DMF guests, relative to the host anthracene unit. The DMSO and DMF inclusion compounds of **2** proved to be isostructural.

Introduction

Anthracene, ethylene and diaryl hydroxymethyl or 9-hydroxy-9-fluorenyl moieties have been used as versatile building blocks in the construction of crystalline inclusion hosts [1]. In most cases diphenylhydroxymethyl or 9-hydroxy-9-fluorenyl groups are attached *via* acetylene units as intermediate pieces at the 1,5-, 1,8- or 1,9-positions of the anthracene base in these host compounds, which show variable inclusion behaviour depending on the mode of substitution [2].

While structures of inclusion compounds involving anthracene hosts with 1,5- and 1,8-attachment of the bulky alcoholic groups have been studied rather extensively [3, 4], crystal structures of the 9,10-analogues have not yet been described. It is to be supposed that modification of the core molecular geometry of the host from bent or U-shaped to linear, corresponding to 1,5-, 1,8- and 9,10-attachment respectively, will have a bearing on the supramolecular structure and interaction mode of inclusion compounds [2]. This has prompted us to study the structure of hosts and crystalline inclusions formed of host compounds **1** and **2** (Scheme 1).



Scheme 1. Formulas of the compounds.

* **Supplementary Data** relating to this article have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K., as Supplementary Publication No. SUP 82306 (26 pages).

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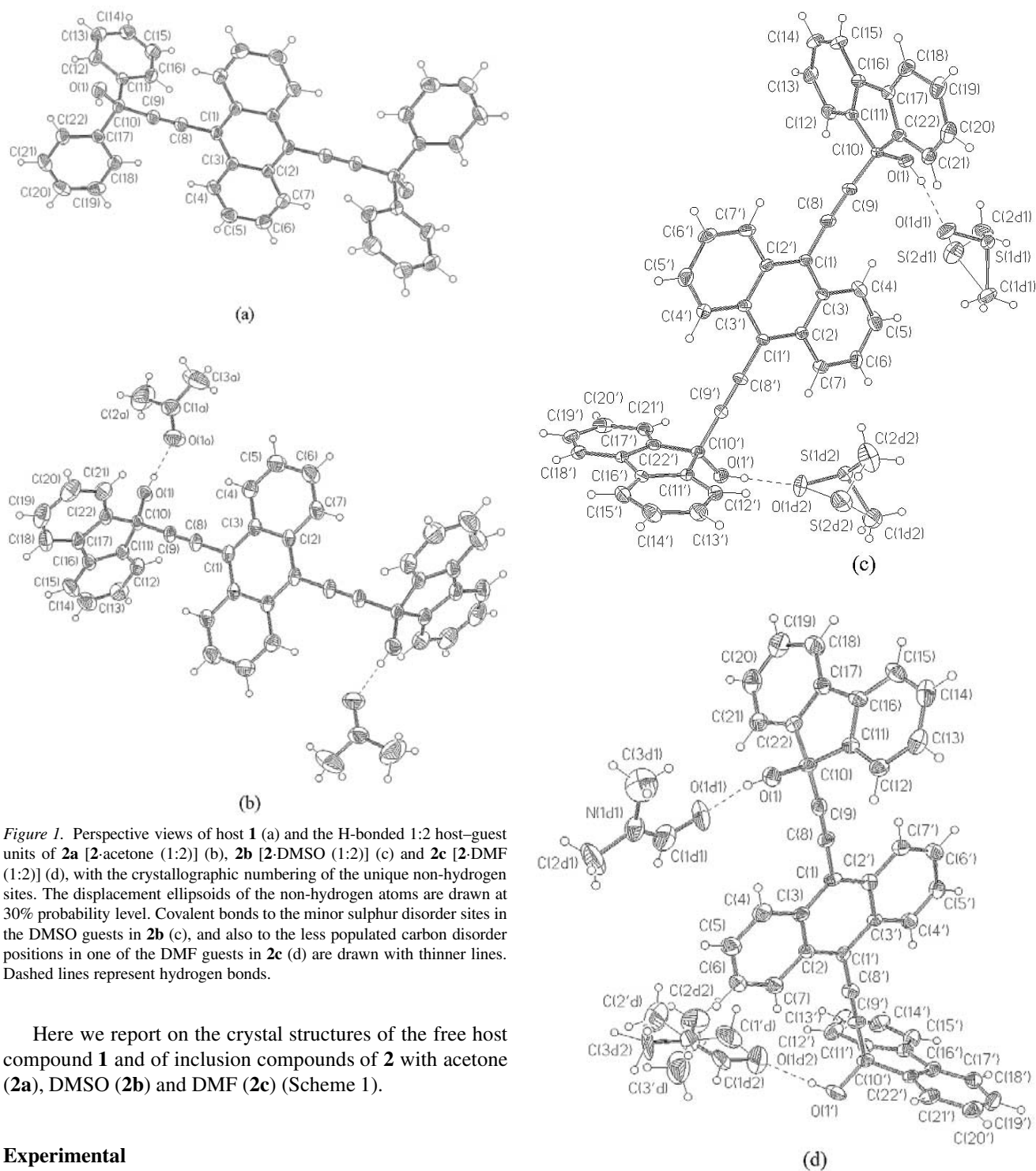


Figure 1. Perspective views of host **1** (a) and the H-bonded 1:2 host–guest units of **2a** [2-acetone (1:2)] (b), **2b** [2-DMSO (1:2)] (c) and **2c** [2-DMF (1:2)] (d), with the crystallographic numbering of the unique non-hydrogen sites. The displacement ellipsoids of the non-hydrogen atoms are drawn at 30% probability level. Covalent bonds to the minor sulphur disorder sites in the DMSO guests in **2b** (c), and also to the less populated carbon disorder positions in one of the DMF guests in **2c** (d) are drawn with thinner lines. Dashed lines represent hydrogen bonds.

Here we report on the crystal structures of the free host compound **1** and of inclusion compounds of **2** with acetone (**2a**), DMSO (**2b**) and DMF (**2c**) (Scheme 1).

Experimental

Preparation of the crystalline inclusion compounds

The host compounds **1** and **2** (Scheme 1) were synthesized as described earlier [4]. Single crystals of the inclusion compounds, containing acetone (**2a**), dimethyl sulphoxide (DMSO) (**2b**), and dimethylformamide (DMF) (**2c**) as guest component, were grown from the respective guest solvent, while the crystals of the free host compound **1** were obtained from a toluene solution on slow cooling. Crystals of the three inclusion compounds, when taken out of the mother liquor for X-ray studies, were immediately covered by epoxy glue in order to prevent solvent evaporation.

Figure 1. Continued.

X-ray data collection, structure determination and refinement

X-ray intensity data from the guest-free host **1** crystal were collected with a STOE IPDS (Imaging Plate Diffraction System) [5] instrument, using MoK α radiation, whereas different four-circle diffractometers [CAD4 (Enraf-Nonius) for **2a**, Phillips PW 1100 for **2b** and SEIFERTH for **2c**], CuK α radiation and $\omega/2\theta$ scan mode were used for the inclusion

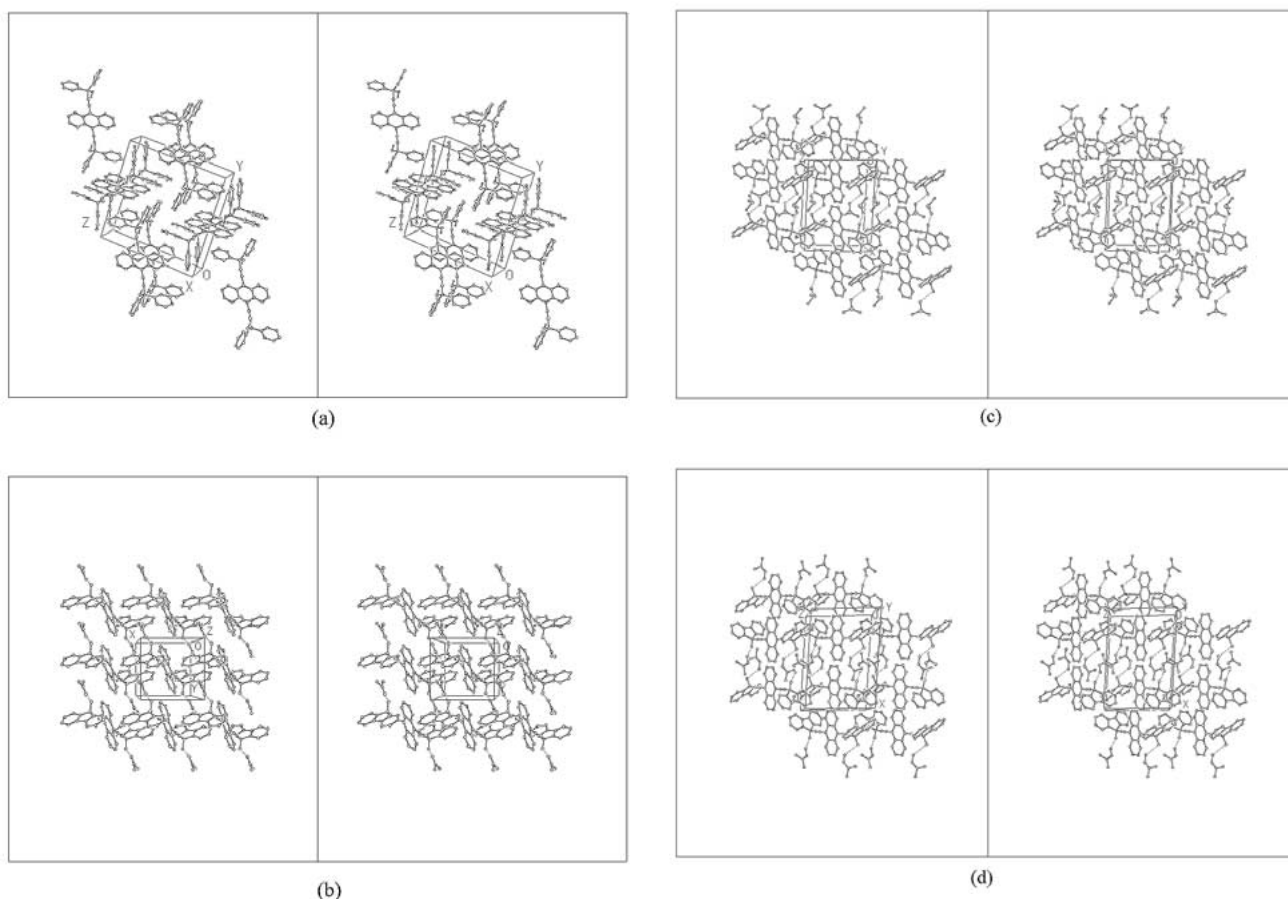


Figure 2. Stereo packing illustrations of compounds **1** (a), **2a** [2-acetone (1:2)] (b), **2b** [2-DMSO (1:2)] (c) and **2c** [2-DMF (1:2)] (d). The H atoms together with the minor guest disorder sites (in **2b** and **2c**) are omitted for clarity. Dashed lines represent hydrogen bonds.

Figure 2. Continued.

crystals. Data reduction calculations, in which the net intensities were corrected for Lorentz and polarization effects, yielded F^2 values for compounds **1**, **2a** and **2c**, and F for **2b**.

The preliminary model of each structure, derived by application of direct methods (SHELXS [6]) and usually comprising the host molecule and probable fragments of the guests, was completed and refined using the SHELXL [7] program. The alcoholic hydrogen positions were derived from difference electron density ($\Delta\rho$) maps, and were held riding on their parent O atoms during the subsequent calculations, whereas those of the carbon-bonded H atoms were obtained from geometric evidence [7] after each refinement cycle. The non-hydrogen atoms and disorder sites were refined together with their anisotropic displacement parameters, and isotropic vibrational parameters were refined for the hydrogens, except the H positions and H disorder sites of the DMF guests in **2c**, which have been included with fixed isotropic displacement parameters [$U_{\text{iso}}(\text{H}) = 1.5 \cdot U_{\text{eq}}$ (parent non-H)]. In the DMSO guests in **2b** the sulphur atoms were found to occupy two disorder sites each [Figure 1(c)]. Assuming that each pair of sites has full occupation, the site occupation factors (sof) converged to 0.807(3)/0.193(3) for S(1D1)/S(2D1), and 0.918(3)/0.082(3) for S(1D2)/S(2D2). Because of the limited probability of the minor sulphur positions, only the major methyl hydrogen sites of the guests

were included in the final structure model. One of the DMF guests in **2c**, namely molecule 2, was also found to exhibit partial disorder. In this latter case the three carbon atoms, together with the H atoms linked to them, can occur in either of two different positions [Figure 1(d)] with comparable probabilities. The sof values of the non-primed and primed guest positions were refined to 0.57(2) and 0.43(2), respectively. Crystal data and further details of the refinement calculations are given in Table 1.

Results and discussion

Figure 1(a) shows a perspective view of host **1**, and Figures 1(b)–(d) illustrate the hydrogen bonded host–guest 1:2 units in compounds **2a–c**, respectively. Stereo packing diagrams of the four crystal structures **1** and **2a–c** are presented in Figures 2(a)–(d). Geometric features, such as selected torsion and dihedral angles, and characteristics of possible O–H \cdots O and C–H \cdots O hydrogen bonds, calculated with the program SHELXL [7], are listed in Tables 2 and 3, respectively.

Molecular structures

In principle, the present host molecules **1** and **2** are similar, both containing bulky alcoholic terminal groups attached via an acetylene connection element to opposite sides of

Table 1. Summary of crystal data, experimental parameters and selected details of the refinement calculations for compounds **1** (guest free), **2a** [2-acetone (1:2)], **2b** [2-DMSO (1:2)] and **2c** [2-DMF (1:2)]

Compound	1 [host 1 (guest free)]	2a [2-acetone (1:2)]
CCDC deposition number	199713	199714
Empirical formula (sum)	C ₄₄ H ₃₀ O ₂	C ₅₀ H ₃₈ O ₄
Empirical formula (moiety)	C ₄₄ H ₃₀ O ₂	C ₄₄ H ₂₆ O ₂ · 2(C ₃ H ₆ O)
Formula weight	590.68	702.80
Temperature/K	292(2)	298(2)
Wavelength/Å	MoKα/0.71073	Cu Kα/1.54180
Crystal system	Monoclinic	Monoclinic
Space group (No.)	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	<i>P</i> 2 ₁ / <i>c</i> (No. 14)
<i>a</i> /Å	5.991(1)	8.475(3)
<i>b</i> /Å	16.123(2)	8.237(3)
<i>c</i> /Å	16.312(2)	27.974(3)
α /deg	90.	90.
β /deg	97.51(2).	90.75(3)
γ /deg	90.	90.
<i>V</i> /Å ³	1562.1(4)	1952.7(10)
<i>Z</i>	2	2
<i>D_c</i> /g cm ⁻³	1.256	1.195
μ /mm ⁻¹	0.076	0.587
Crystal size/mm	0.08 × 0.11 × 0.34	0.50 × 0.40 × 0.25
Crystal colour	yellow	green
θ range for data collection/deg	2.52 to 26.11	3.16 to 74.78
No. of reflections collected	12444	4028
No. of unique reflections	2989	3748
<i>R</i> _{int}	0.067	0.011
No. of parameters refined	223	266
<i>wR</i> ₂ ^a /No. of <i>F</i> ² values ^b	0.078/2985	0.122/3746
<i>R</i> ₁ /No. of <i>F</i> with <i>F</i> > 4σ(<i>F</i>)	0.036/954	0.042/3106
<i>S</i> (Goodness-of-fit on <i>F</i> ²)	0.64	1.03
Extinction coefficient ^c	no extinction correction	0.007(1)
Final $\Delta\rho_{\max}$, $\Delta\rho_{\min}$ /e ⁻ Å ⁻³	+0.14, -0.15	+0.15, -0.13

a central anthracene construction unit (Scheme 1). However, whereas the fused rings of the fluorene group in **2** form a flat and rigid moiety, the phenyl rings in the diphenylmethanol functions of **1** have rotational freedom. The dihedral angle between the least-squares (LS) diphenylmethanol phenyl planes in **1** is 72.0(1)°, which is slightly less than the values, 99.35(5)° and 91.25(8)°, observed earlier for the same dihedral angle in two inclusion crystals of a closely related host molecule [4]. Also the dihedral angles formed by the LS planes of the central anthracene moiety, on the one hand, and each of the diphenylmethanol phenyl rings on the other (Table 2), are more widely scattered than those between the fluorene and anthracene LS planes, observed in **2** or in an earlier investigated related host [4]. Accordingly, the fluorene moieties were found to be roughly perpendicular to the anthracene ring system in the four fluorene-containing compounds cited above, with dihedral angles ranging between 78.1 and 99.5° (Table 2 and [4]), whereas in the three compounds with diphenylmethanol-containing host molecules, mentioned earlier, the observed dihedral angles, each formed by a phenyl ring plane and the anthracene plane, vary from 22 to 104°, thus indicat-

ing a more flexible terminal group in the latter molecule. Although both hosts, **1** and **2**, may have molecular inversion symmetry, and all four crystals in the present study [**1** and **2a–c**] have centrosymmetric space group symmetries (Table 1), only in compounds **1** [Figure 1(a)] and **2a** [Figure 1(b)] have the host molecules crystallographic (inversion) symmetry. As compounds **2a–c** have the same host and host-guest stoichiometry (Table 1), and the guest molecules (such as acetone in **2a**, DMSO in **2b** and DMF in **2c**) are H-bonded to the host OH functions and have comparable space requirements, the present three inclusion crystals have unit cells with similar volumes (Table 1), each containing two host and four guest molecules. If the crystallographic and molecular inversion symmetries coincide, as in **2a**, then the space group symmetry is monoclinic, whereas the dissymmetry of the host in **2b** and **2c** gives rise to the lower triclinic symmetry for the latter two compounds. The presence or absence of molecular inversion symmetry is crucial also for the solid-state conformation of the host molecules. Thus, in the centrosymmetric molecules, such as the guest-free host **1**, and also host **2** in its acetone inclusion compound, the hydroxy functions are exactly *trans*

Table 1. Continued

Compound	2b [2-DMSO (1:2)]	2c [2-DMF (1:2)]
CCDC deposition number	199715	199716
Empirical formula (sum)	C ₄₈ H ₃₈ O ₄ S ₂	C ₅₀ H ₄₀ N ₂ O ₄
Empirical formula (moiety)	C ₄₄ H ₂₆ O ₂ · 2(C ₂ H ₆ O S)	C ₄₄ H ₂₆ O ₂ · 2(C ₃ H ₇ N O)
Formula weight	742.90	732.84
Temperature/K	225(2)	293(2)
Wavelength/Å	CuK _α /1.54180	CuK _α /1.54180
Crystal system	Triclinic	Triclinic
Space group (No.)	<i>P</i> – 1 (No. 2)	<i>P</i> – 1 (No. 2)
<i>a</i> /Å	15.4476(9)	15.9748(2)
<i>b</i> /Å	11.6576(6)	11.5648(3)
<i>c</i> /Å	11.2357(2)	11.1881(2)
<i>α</i> /deg	105.702(2)	105.67(2)
<i>β</i> /deg	85.360(3)	85.04(3)
<i>γ</i> /deg	98.378(4)	97.00(4)
<i>V</i> /Å ³	1925.2(2)	1972.2(1)
<i>Z</i>	2	2
<i>D_c</i> /g cm ⁻³	1.282	1.234
<i>μ</i> /mm ⁻¹	1.610	0.617
Crystal size/mm	0.40 × 0.26 × 0.30	0.30 × 0.20 × 0.30
Crystal colour	yellow	yellow
<i>θ</i> Range for data collection/deg	2.89 to 67.62	2.79 to 65.00
No. of reflections collected	6517	6404
No. of unique reflections	6517	6404
<i>R</i> _{int}	–	–
No. of parameters refined	545	562
<i>wR</i> ₂ ^a /No. of <i>F</i> ² values ^b	0.099/6509	0.075/6400
<i>R</i> ₁ /No. of <i>F</i> with <i>F</i> > 4σ(<i>F</i>)	0.038/1880	0.049/1427
<i>S</i> (Goodness-of-fit on <i>F</i> ²)	0.36	0.68
Extinction coefficient ^c	no extinction correction	0.003(0)
Final Δρ _{max} , Δρ _{min} /e ⁻ Å ⁻³	0.15, -0.24	+0.19, -0.17

^aIn the refinement calculations (using SHELXL) *F*² values have been used as input for compounds **1**, **2a** and **2c**, but *F* for **2b**. The weights of the *F*² values were calculated as $w = [\sigma^2(F^2) + (c_1 \cdot P)^2 + c_2 \cdot P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$, and the constants, *c*₁ and *c*₂ had the values 0.0164 and 0.0 for **1**, 0.062 and 0.0 for **2a**, 0.08 and 0.0 for **2b**, and 0.010 and 0.0 for **2c**.

^bA few reflections (4 for **1**, 2 for **2a**, 8 for **2b**, and 4 for **2c**) were excluded from the final least-squares calculations due to extinction effects or potential systematic errors.

^cIn case of extinction correction, *F_c* is multiplied by $k[1 + 0.001x F_c^2 \lambda^2 / \sin(2\theta)]^{-1/4}$, where *x* is an extinction coefficient, refined by least-squares calculation, and *k* is the overall scale factor.

oriented {τ₁[O(1)–C(10)–···–C(10')–O(1')] = 180°}, whereas the low values, 6.6° and 6.3° (Table 2), for the same angle (τ₁) indicate *cis* orientation for the OH groups of host **2** in its inclusion compounds with DMSO and DMF guests, respectively. Furthermore, the corresponding phenyl rings in **1** [rings C₁₁–···–C₁₆ and C_{11'}–···–C_{16'} on the one hand, and rings C₁₇–···–C₂₂ and C_{17'}–···–C_{22'} on the other; Figure 1(a)], and the two fluorene moieties of **2** in **2a** [Figure 1(b)], are parallel with each other due to the symmetry requirement. On the contrary, the two fluorene moieties in each dissymmetric host molecule (i.e. **2** in **2b** and **2c**) tend to be perpendicular to each other (Table 2). At the same time, the unit cells in the triclinic crystals (**2b** and **2c**) have not only similar volumes but also similar cell parameters (Table 1), hence indicating possible isostructurality for these two compounds. The suggested relationship has been proved by calculating the three descriptors of isostructurality [i.e. Π,

I(*s*) and *I*(*m*)] for these two crystal structures, following Kálmán *et al.* [8, 9]. Accordingly, the unit cell similarity index is Π = 0.0230, the isostructurality index, *I*(*s*), has the value 0.72, and the molecular isometricity index, *I*(*m*), which may be seen as the direct measure of isomorphism, is 94.41%. These results suggest that the inclusion crystals **2b** and **2c** are a homeostructural crystal pair [8]. In the calculation of the isostructurality and isometricity indices, only the 46 unique non-hydrogen positions of the host molecules were used.

The small guest molecules, on the other hand, generally conform to expected geometries, although the calculated parameters for the guests are often somewhat more uncertain than those of the hosts due to possible static and/or dynamic disorder of the guest entities. The non-hydrogen atoms of the acetone guest in **2a** [Figure 1(b)] are co-planar to within 0.010 Å. In the pyramidally shaped and partially disordered

Table 2. Selected conformational features of compounds **1** and **2a–c**

Compounds	1 (guest free)	2a [2-acetone (1:2)]	2b [2-DMSO (1:2)]	2c [2-DMF (1:2)]
<i>Selected torsional angles/deg</i>				
C(8)–C(9)–C(10)–O(1)	–25(3)	104(2)	–4(3)	12(16)
C(8)–C(9)–C(10)–C(11)	91(3)	–135(2)	115(3)	132(15)
C(8)–C(9)–C(10)–C(17)	–146(3)			
C(8)–C(9)–C(10)–C(22)		–23(3)	–133(3)	–112(15)
O(1)–C(10)–C(11)–C(12)	–40.4(3)	56.3(2)	57.8(2)	61.3(7)
O(1)–C(10)–C(17)–C(18)	–153.3(2)			
O(1)–C(10)–C(22)–C(21)		–62.5(2)	–63.5(3)	–64.0(7)
C(8')–C(9')–C(10')–O(1')	25(3)	–104(2)	–118(9)	–160(24)
C(8')–C(9')–C(10')–C(11')	–91(3)	135(2)	10(9)	–34(25)
C(8')–C(9')–C(10')–C(22')	146(3)	23(3)	120(9)	77(24)
O(1')–C(10')–C(11')–C(12')	40.4(3)	–56.3(2)	57.3(3)	56.9(8)
O(1')–C(10')–C(22')–C(21')	153.3(2)	62.5(2)	–50.8(2)	–54.2(8)
<i>Selected conformation angles/deg</i>				
O(1)–C(10)–...–C(10')–O(1')	180	180	6.7(1)	6.3(5)
C(9)–C(10)–O(1)–...–O(guest 1)		–55.0(1)	–52.7(2)	–53.3(5)
C(9')–C(10')–O(1')–...–O(guest 2)		55.0(1)	55.0(2)	50.4(6)
C(11)–C(10)–O(1)–...–O(guest 1)		–178.6(1)	–175.1(1)	–176.4(3)
C(11')–C(10')–O(1')–...–O(guest 2)		178.6(1)	–68.6(2)	–71.8(5)
C(22)–C(10)–O(1)–...–O(guest 1)		68.7(1)	74.5(2)	71.8(4)
C(22')–C(10')–O(1')–...–O(guest 2)		–68.7(1)	178.2(1)	174.3(4)
<i>Dihedral angle between the LS planes^a/deg</i>				
– Anthracene and fluorene 1 (C ₁₀ –...–C ₂₂)		78.15(4)	87.20(3)	83.28(7)
– Anthracene and fluorene 2 (C _{10'} –...–C _{22'})		78.15(4)	86.48(3)	83.97(7)
– Fluorene 1 and fluorene 2		0	76.92(3)	75.08(8)
– Anthracene and phenyl 1 (C ₁₁ –...–C ₁₆)	82.0(1)			
– Anthracene and phenyl 2 (C ₁₇ –...–C ₂₂)	22.0(1)			
– Phenyl 1 and phenyl 2	72.0(1)			
– Anthracene and guest 1		9.3(2)	42.9(1)	10.0(5)
– Anthracene and guest 2		9.3(2)	44.8(1)	89.1(4)
– Anthracene and guest 2'				80.4(5)
– Fluorene 1 and guest 1		83.4(1)	58.7(1)	88.2(2)
– Fluorene 2 and guest 2		83.4(1)	69.7(1)	9.1(8)
– Fluorene 2 and guest 2'				19.8(1.1)
– Guest 1 and guest 2		0	86.8(1)	82.9(4)
– Guest 1 and guest 2'				89.1(6)
– Guest 2 and guest 2'				10.7(1.4)

^aThe LS planes were calculated through the non-hydrogen positions forming the anthracene and fluorene moieties, and the guest molecules, respectively. In case of the pyramidally shaped DMSO guests in **2b**, the plane defined by the oxygen and the two methyl carbon atoms in each guest was used. Because guest 2 in **2c** is disordered [Figure 1(d)], the LS plane was calculated involving either the major (non-primed) or minor (primed) carbon disorder sites, yielding the plane for guest 2 and 2', respectively.

DMSO guests in **2b**, the sulphur disorder sites in molecule **1**, S(1D1)/S(2D1) [Figure 1(c)], deviate by 0.67/–0.63 Å from the plane defined by the O and C atoms (used as 'guest LS plane' in Table 2), and the corresponding deviations for S(1D2)/S(2D2) in guest 2 have been found to be –0.70/0.59 Å, respectively. In compound **2c** only guest 2 exhibits static disorder [Figure 1(d)] by occurring in two orientations, related to each other by a rotation through about 60° around the central N position, accompanied by a moderate tilt of the molecular plane (through approximately 11°, Table 2). The skeleton of DMF guest 1 (comprising the non-hydrogen atoms only) is flat to within 0.046 Å, and the O, N and C positions in guest 2 and 2', involving either the non-primed

(guest 2) or primed (guest 2') C disorder sites, are co-planar to within 0.042 and 0.108 Å, respectively.

Intermolecular interactions and packing relations

Although the diol host molecule **1** was found to form crystalline inclusion compounds with a variety of small guests (such as various amines, piperidine, DMF, DMSO, cyclopentanone, cyclohexanone, 1,4-dioxane, etc. [4]), it proved to be capable of forming a stable crystal also on its own. Despite the presence of two OH functional groups per molecule, there is no O–H...O hydrogen bond to be found in the guest-free crystal of **1** [Figure 2(a)]. This is in line with our earlier observations in solvent-free crystals of related

Table 3. Distances (Å) and angles (deg) in possible hydrogen-bond connections,^a observed in **1** and in the inclusion crystals **2a–c**

Atoms involved	Symmetry	Distance D...A/Å	Distance D–H/Å	Distance H...A/Å	Angle <D–H...A/deg
1 (guest free)					
C(20)–H(20)···O(1)	$x - 0.5, -y + 1.5, z - 0.5$	3.546(3)	0.93	2.66	158
C(16)–H(16)···O(1)	$x - 1, y, z$	3.557(3)	0.93	2.74	147
2a [2:acetone (1:2)]					
O(1)–H(1O)···O(1A)	x, y, z	2.809(2)	0.88	1.93	178
C(4)–H(4)···O(1A)	x, y, z	3.623(2)	0.93	2.74	160
C(21)–H(21)···O(1A)	x, y, z	3.502(2)	0.93	2.74	140
2b [2:DMSO (1:2)]					
O(1)–H(1O1)···O(1D1)	x, y, z	2.650(2)	0.84	1.82	170
O(2)–H(1O2)···O(1D2)	x, y, z	2.693(2)	0.79	1.91	176
C(4)–H(4)···O(1D1)	x, y, z	3.404(3)	0.94	2.67	136
C(12')–H(12')···O(1D2)	x, y, z	3.522(3)	0.94	2.74	141
C(21)–H(21)···O(1D1)	x, y, z	3.585(3)	0.94	2.87	134
C(1D2)–H(22D)···O(1D2)	$-x + 1, -y, -z + 2$	3.342(5)	0.97	2.79	117
C(2D2)–H(26D)···O(1)	$x, y, z + 1$	3.502(4)	0.97	2.78	132
C(1D1)–H(12D)···O(1D1)	$-x + 1, -y + 1, -z + 1$	3.707(4)	0.97	2.79	158
C(2D1)–H(16D)···O(1)	$-x + 1, -y + 1, -z$	3.565(3)	0.97	2.66	156
2c [2:DMF (1:2)]					
O(1)–H(1O1)···O(1D1)	x, y, z	2.723(6)	0.81	1.92	167
O(2)–H(1O2)···O(1D2)	x, y, z	2.707(2)	0.82	1.89	178
C(4)–H(4)···O(1D1)	x, y, z	3.453(8)	0.93	2.68	141
C(7)–H(7)···O(1D2)	x, y, z	3.826(9)	0.93	2.96	156
C(21)–H(21)···O(1D1)	x, y, z	3.454(8)	0.93	2.74	135
C(12')–H(12')···O(1D2)	x, y, z	3.527(11)	0.93	2.76	141
C(3D1)–H(32D)···O(1)	x, y, z	3.665(8)	0.96	2.89	138
C(3D1)–H(33D)···O(1)	$-x + 1, -y + 1, -z$	3.460(7)	0.96	2.66	141
C(1D1)–H(1D1)···O(1D1)	$-x + 1, -y + 1, -z + 1$	3.653(7)	0.93	2.87	143

^aEsd's, where given, are in parentheses. The (O)–H atoms, located from difference electron density maps, were held riding on their parent O atoms during the subsequent refinement calculations, whereas the (C)–H atom positions were calculated using geometric evidence [7]. The listed distances/angles have been calculated without correction or normalisation of the H positions.

host molecules, including different 9-substituted fluorene-9-ols [10] and a bis(9-hydroxy-9-fluorenyl) host that contains a linear triphenyl spacer unit between the alcoholic functions [11]. We have previously concluded that increasing size of the 9-substituent, or of the whole molecule, increases the difficulties for these compounds to form aggregates, *via* O(H)···O bonds, which can pack with acceptable crystal density. As a consequence, the mono-fluorenols with biphenyl or naphthyl substituents, or the bis-fluorene molecule, cited above, proved to form close-packed crystals held together by weaker and more flexible intermolecular interactions instead of conventional O(H)···O bonds. Thus, beside the common van der Waals' forces, the alcoholic O(9) atom of 9-(1-naphthyl)fluorene-9-ol has been found to participate in some shorter intermolecular O···C approaches, indicating an electrostatically favourable packing for that compound [10], whereas O–H··· π (aryl) interactions have been observed between the molecules in the 9-(2-biphenyl)fluorene-9-ol [10] and the 9,9'-(terphenyldiyl)bis(fluorene-9-ol) [11] compounds. Inspection of the packing illustration of host **1** [Figure 2(a)] may give a hint

that the OH groups point in the direction of the π electron cloud of the nearest ethynyl C \equiv C triple bond. Nevertheless, the calculated distances [O(1)··· $\pi_{x+1,y,z} = 3.824(3)$, H(1O)··· $\pi_{x+1,y,z} = 3.36$ Å, where π means the centre of the C(8)–C(9) bond] seem to be too long for such an interaction [12]. Instead, crystals of the diol host **1** are held together mainly by common van der Waals' forces, although the two shortest intermolecular approaches to the hydroxy oxygen [i.e. O(1)···C(20) _{$x+0.5, -y+1.5, x+0.5$} = 3.546(3); and O(1)···C(16) _{$x+1,y,z$} = 3.557(3); Table 3] suggest weak C–H···O interactions between the molecules [12]. The packing coefficient [13], i.e. the ratio of the volume occupied by the molecules to the total unit cell volume, has been calculated [14]. The value yielded for **1** (67.7%) is normal for close-packed organic crystals [13], and the calculations indicate no voids accessible to solvent between the molecules.

The presently studied inclusion compounds **2a–c** are built up by discrete hydrogen-bonded 1:2 host–guest associates, where each of the host hydroxy groups binds to a guest oxygen atom [Figure 1(b)–(d)], similarly also to our earlier observations in three inclusion compounds of closely related

host molecules [4]. However, the host–guest arrangements within the H-bonded units may vary, depending among other things on the presence or absence of crystallographic symmetry in the host molecules. Thus, the location of the host on the crystallographic inversion centre in the acetone inclusion crystal **2a** [Figure 1(b)] gives rise to **E**(=entgegen)-positioned guest molecules. Furthermore, the flat acetone guests in the H-bonded 1:2 associate are parallel with each other, nearly parallel with the anthracene plane, and each one is approximately perpendicular to the nearest fluorene LS plane (Table 2). In the 1:2 host–guest units of **2b** and **2c** [Figures 1(c) and (d)] without crystallographic centrosymmetry, each pair of guests is connected by *cis*-oriented host OH functions (i.e. in *syn*-positions), and may have different locations with respect to each other and/or to the host they are linked to. Thus, although the best planes of the guests in **2b** (defined by the O and C atoms of the DMSO molecules 1 and 2, respectively) are nearly perpendicular to each other, they form similar dihedral angles with the anthracene moiety, and also with the nearest fluorene plane (Table 2). On the other hand, the molecular LS planes of the DMF guests 1 and 2 (or 2') in **2c** are also approximately perpendicular to each other, but the two guests form considerably different dihedral angles with the central anthracene moiety, and also with the nearest fluorene plane (Table 2). In the crystals of **2b** and **2c** [Figures 2(c) and (d)], the H-bonded 1:2 host–guest associates seem to be held together by weak van der Waals' forces, supported by several host–guest and guest–guest C–H...O interactions (Table 3). Calculation of the packing density [14] in the three inclusion compounds of **2** yielded 68.0 and 67.9% filled space in **2b** and **2c**, respectively, and no voids in the unit cells. In contrast, in compound **2a** the calculation indicated about 37 Å³ potential residual solvent-accessible volume per unit cell, and the packing coefficient received the relatively low value 64.4%. Normal close-packed organic crystal structures are expected to have a packing coefficient in the range 65–77% [13]. Comparison of packing densities in the three closely related compounds **2a–c** leads to the conclusion that higher symmetry (**2a** is monoclinic *P*2₁/*c*; **2b** and **2c** are both triclinic *P* – 1) gives rise to lower packing density and density (see *D_c* in Table 1) as well. Interestingly enough, we made the same observation previously when comparing three solid inclusion compounds that belong to the same family as the present ones [4].

Conclusions

The presently studied guest-free crystal (**1**) and inclusion compounds (**2a–c**) afford further insight into the structural features of the significant family of bis(diphenylmethanol)- and bis(fluorene-9-ol)-substituted diethynylanthracenes [4] and related host compounds [2, 3, 11]. A comparison shows that in all structures, including the previous cases with 1,5- and 1,8-substitution of the anthracene moiety [4], and irrespective of the aryl part of the alcoholic terminal groups, the compounds are bifunctional hydrogen-bond donor hosts to polar guests. This similarity in the behaviour of the hosts

towards their guest molecules may lead to homeostructurality, as shown in the present study (**2b** and **2c**). Another remarkable finding in our investigations of series of related compounds is that higher symmetry of the inclusion crystals give rise to lower packing density and density (*D_c*) as well, which is an important point in inclusion design [1, 2, 15]. On the other hand, the packing coefficient yielded by host **1** on its own indicates dense packing for the guest-free crystal, which would explain the lower efficiency of inclusion formation by **1**, as compared with that of **2** [4]. A further challenge would be to prove potential polymorphism [16] and sensor properties [17] of this compound class [18].

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