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Inclusion Compounds of Bulky Binaphthyl-type Bis-fluorenol Hosts

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Inclusion properties of a new family of clathrate hosts (1–4) containing two 9-hydroxy-9-fluorenyl units or chloro-, bromo- and *t*-butyl-substituted derivatives of this group attached in the 3,3′-position to a basic 2,2′-binaphthyl construction element are reported (115 examples of clathrates). The crystal structures of six selected clathrates, involving dimethylsulfoxide, cyclopentanol, diethylether, benzylamine, chloroform and acetone as the guest, have been determined by X-ray diffraction, showing varied modes of supramolecular interaction dependent on the host and guest constitutions, while the formation of an intramolecular hydrogen bond between the hydroxy groups of the fluorenol units is a common structural feature (except in 3a) controlling twisted conformation of the host molecules.

Keywords: Inclusion hosts; Organic guests; Crystalline inclusion compounds; Supramolecular interactions; X-ray crystal structure determinations

INTRODUCTION

Organic crystals with open network structures [1,2] are intriguing for a variety of fundamental and practical reasons [3,4]; essentially the potential accommodation of guest molecules to form crystalline host–guest inclusion [5,6], or clathrate compounds [7]. This has stimulated strategies for the design of clathrate hosts of which molecular rigidity and bulkiness paired with certain hydrogen-bonding functionality are important features [8,9]. Typical examples of hosts making use of these properties are the wheel-and-axle, scissor-type, roof-shaped or dumb-bell-shaped molecules [10,11]. Characteristic building blocks in the construction of these frameworks are central biaryl units with 9-hydroxy-9-fluorenyl moieties attached to them [12]. Such a combination of construction elements has proved to be highly efficient in many cases, including cocrystalline and adsorptive compound separation [13,14]. A sample compound of a respective host is specified by formula **1**, which is a parent of the substituted analogs **2**–**4** (Scheme 1). The host compound **1**, which forms a 1:3 (host:guest) clathrate with acetone, has been found to reveal promising supramolecular materials behavior in vapor sensing of this solvent [15]. Moreover, crystalline inclusion compounds of **2** and **3** with acetone have been studied by X-ray analysis and also by solid-state NMR, showing differently bound guest molecules [16].

Here we report the synthesis of the new host compound **4**, provide a detailed description of the clathrate formation of the whole compound series **1**–**4**, and present crystal structures of six clathrate compounds (**1a**–**1c**, **2a**, **3a**, **4a**) involving the hosts **1**–**4** and different guests.

RESULTS AND DISCUSSION

Synthesis

The host compounds **1**–**4** were synthesized from 3,3′-dibromo-2,2′-binaphthyl and 9-fluorenone, 2,7-dichloro-9-fluorenone, 2,7-dibromo-9-fluorenone or 2,7-di-*t*-butyl-9-fluorenone using a lithium organic reaction in accordance with a literature procedure [15,16]. The inclusion compounds were obtained by recrystallization of the host compound 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' [14].

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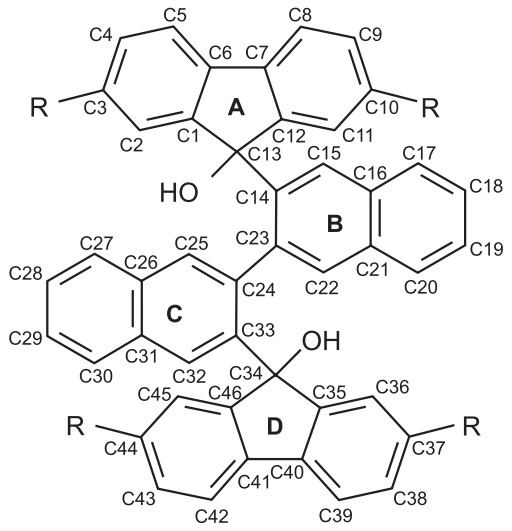

1 R = H
2 R = Cl
3 R = Br
4 R = $C(CH_3)_3$

1a = **1** · DMSO (2 : 5)
1b = **1** · cyclopentanol (1 : 2)
1c = **1** · diethylether (1 : 2)
2a = **2** · benzylamine (1 : 1)
3a = **3** · chloroform (1 : 2)
4a = **4** · acetone (1 : 1)

SCHEME 1 Compounds studied and the crystallographic numbering of the basic host skeleton.

Inclusion Properties

To study the inclusion capacity of this host family as completely as possible and to enable a good comparison between the members of the family, a broad variety of potential guest solvents, including alcohols, amines, ketones, nitriles and other aprotic dipolar solvents, heterocycles and aromatic hydrocarbons of different constitutions, were used for the recrystallization (clathration) experiments. This yieded no less than 115 individual crystalline inclusion compounds (Table I), showing the high efficiency of clathrate formation of this host family without notable differences in the total number of clathrates formed for each host compound. With very few exceptions (e.g. acetonitrile, nitromethane and chloroform), the range of solvents included are very similar. More perceptible differences are found for the stoichiometric host:guest ratios, showing in part considerable differences with the same solvent (e.g. as acetone, 1,4-dioxane, DMSO and morpholine). Nevertheless, the stoichiometric ratios most frequently used for all hosts were 1:1 (44 cases) and 1:2 (33 cases), followed by 1:3, 2:3 and 2:1 (6 or 7 species), although some rather uncommon host:guest ratios (2:5 and 1:4) were also present (Table I), indicating the variety of structures formed.

Structural Study

This study includes determination of the crystal structures of six exemplary inclusion compounds: **1a** [**1**·DMSO (2:5)], **1b** [**1**·cyclopentanol (1:2)], **1c** [**1**·diethyl ether (1:2)], **2a** [**2**·benzylamine (1:1)], **3a** [**3**·chloroform (1:2)] and **4a** [**4**·acetone (1:1)]. Basic crystallographic information for these structures is listed in Table II. A detailed numbering scheme of the framework carbon atoms of compounds **1**–**4** is included in Scheme 1. Perspective views of the molecules are depicted in Figures 1, 3, 4 and 6. Packing illustrations are presented in Figures 2, 5, 7, 8 and 9. Selected conformational features and geometric parameters of possible molecular interactions are listed in Tables III and IV, respectively.

Inclusion Compounds of 1 (1a–1c)

The host **1** yields a 2:5 inclusion compound with dimethylsulfoxide (**1a**), which crystallizes in the monoclinic space group $P2_1/n$. The hydroxy groups

TABLE I Crystalline inclusion compounds (host:guest stoichiometric ratios)

	Host compound			
Guest solvent*	**1**	**2**	**3**	**4**
MeOH	1:1	1:1	1:1	†
EtOH	1:1	1:1	1:1	†
1-PrOH	1:1	1:1	1:1	2:1
1-BuOH	1:1	1:1	1:1	1:1
2-BuOH	1:2	1:2	1:2	1:2
iso-BuOH	1:2	1:1	2:3	2:3
t-BuOH	1:1	–	1:1	1:1
Cyclo-PentOH	1:2	1:2	1:2	1:2
1-$PrNH_2$	1:3	2:3	2:3	1:1
2-$BuNH_2$	1:2	1:2	1:1	1:1
$PhCH_2NH_2$	1:3	1:1	1:1	1:2
$(1\text{-}Pr)_3N$	1:2	1:2	1:1	1:1
Piperidine	1:2	1:2	1:2	1:4
Morpholine	1:4	1:3	1:2	1:2
Pyridine	1:1	1:1	1:2	1:2
Acetone	1:3	1:1	1:2	1:1
Cyclohexanone	1:2	1:1	1:2	1:3
Cycloheptanone	1:4	1:1	1:2	1:4
Acetonitrile	1:2	2:1	–	–
Propionitrile	1:4	2:1	1:1	2:1
Butyronitrile	1:1	1:1	1:1	1:1
Nitromethane	1:1	–	2:1	–
DMF	1:1	1:2	1:1	1:1
DMSO	2:5	1:1	1:3	1:1
Chloroform	–	–	1:2	–
Et_2O	1:2	1:2	1:2	–
THF	1:2	1:2	2:3	2:1
1,4-Dioxane	1:2	2:3	1:3	1:2
Toluene	–	1:1	1:1	1:1
Xylene	1:2	2:1	1:1	1:1

*Crystalline inclusion compounds were also obtained with **1** and iso-$BuNH_2$ (1:3), nitroethane (1:1); **2** and β-butyrolactone (1:3), γ-butyrolactone (1:3); **3** and β-butyrolactone (1:2), γ-butyrolactone (1:2); **4** and cyclopentanone (1:1). †Difficult to crystallize.

TABLE II Crystallographic and structure refinement data for the inclusion compounds of **1**–**4** (esds are in parentheses)

Compound	**1a**	**1b**	**1c**	**2a**	**3a**	**4a**
Empirical formula	$C_{46}H_{30}O_2{\cdot}2.5C_2H_6SO$	$C_{46}H_{30}O_2{\cdot}2C_5H_{10}O$	$C_{46}H_{30}O_2{\cdot}2C_4H_{10}O$	$C_{46}H_{26}O_2Cl_4{\cdot}C_7H_9N$	$C_{46}H_{26}O_2Br_4{\cdot}2CHCl_3$	$C_{62}H_{62}O_2{\cdot}C_3H_6O$
Formula weight	810.06	786.96	762.94	858.60	1169.04	897.19
Temperature (K)	155(2)	183(2)	133(2)	183(2)	143(2)	173(2)
Crystal system	monoclinic	triclinic	orthorhombic	triclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$	$C2/c$	$P2_1/c$
a (Å)	11.580(3)	11.597(3)	11.397(3)	11.903(3)	24.883(3)	23.833(2)
b (Å)	11.814(3)	13.578(3)	18.642(3)	14.064(3)	11.772(3)	17.461(1)
c (Å)	30.877(3)	15.406(3)	19.787(3)	14.480(3)	17.696(3)	26.423(2)
α (°)	90.0	108.18(3)	90.0	90.13(3)	90.0	90.0
β (°)	97.72(3)	95.87(3)	90.0	103.10(3)	117.25(3)	107.645(2)
γ (°)	90.0	112.21(3)	90.0	113.54(3)	90.0	90.0
V (Å^3)	4185.9(16)	2065.8(8)	4204.0(14)	2152.7(8)	4608.3(15)	10478.9(16)
Z	*4*	*2*	*4*	*2*	*4*	*8*
D_c (g cm^{-3})	1.285	1.265	1.205	1.325	1.685	1.137
μ (cm^{-1})	2.020	0.608	0.581	2.836	2.780	0.680
$F(000)$	1870	836	1624	886	2296	3856
Crystal size (mm)	0.15 × 0.12 × 0.1	0.2 × 0.2 × 0.2	0.2 × 0.15 × 0.15	0.25 × 0.2 × 0.2	0.3 × 0.2 × 0.2	0.5 × 0.2 × 0.2
No. of collected reflections	8231	9540	4768	8706	4737	27 618
θ-range (°)	2.89–74.7	3.12–75.00	3.26–74.85	3.15–75.00	4.00–74.87	0.90–31.29
No. of unique reflections	7195	8175	4252	8287	4533	27618
No. of refined parameters	551	566	556	494	273	1362
Final R indices						
R ($=\sum\|\Delta F\|/\sum\|F_o\|$)	0.0638	0.052	0.0609	0.0876	0.0504	0.0925
No. of values used [$I > 2\sigma(I)$]	5295	5897	4768	5884	3992	7960
wR on F^2	0.1557	0.1222	0.1171	0.2415	0.1132	0.1920
Goodness of fit on F^2	1.064	1.024	0.976	0.976	1.473	0.918

TABLE III Selected torsion angles (°) with their standard deviations

	1a	1b	1c	2a	3a	4a
C(1)—C(13)—C(14)—C(15)	79.5(3)	−71.1(2)	−75.8(3)	−86.1(3)	48.8(3)	31.3(5)
C(1)—C(13)—C(14)—C(23)	−96.9(3)	105.4(2)	101.6(3)	−93.6(3)	−131.9(3)	−150.5(4)
C(12)—C(13)—C(14)—C(15)	−33.7(3)	41.5(2)	37.1(3)	−27.8(4)	−63.7(3)	−82.5(4)
C(12)—C(13)—C(14)—C(23)	149.9(4)	−142.0(2)	−145.6(3)	152.5(3)	115.6(3)	95.7(4)
C(14)—C(23)—C(24)—C(25)	94.7(4)	−95.3(2)	−99.5(3)	98.4(3)		−97.2(5)
C(14)—C(23)—C(24)—C(33)	−88.0(4)	96.8(2)	93.5(3)	−88.0(4)		91.2(5)
C(22)—C(23)—C(24)—C(25)	−74.8(4)	76.9(2)	72.4(3)	−76.8(4)		80.0(5)
C(22)—C(23)—C(24)—C(33)	102.5(4)	−91.1(2)	−94.5(3)	96.8(3)		−91.6(5)
C(24)—C(33)—C(34)—C(35)	151.2(3)	81.4(2)	99.7(3)	−100.7(3)		105.3(4)
C(24)—C(33)—C(34)—C(46)	−97.4(4)	−149.5(2)	−145.5(4)	147.4(3)		−141.5(4)
C(32)—C(33)—C(34)—C(35)	−34.5(4)	−81.4(2)	−76.4(3)	77.8(3)		−73.7(5)
C(32)—C(33)—C(34)—C(46)	76.8(4)	31.7(2)	38.4(3)	−34.1(4)		39.5(5)
C(1°)—C(13A)—C(14A)—C(15A)						−35.7(5)
C(1°)—C(13A)—C(14A)—C(23A)						148.3(4)
C(12A)—C(13A)—C(14A)—C(15A)						78.1(5)
C(12A)—C(13A)—C(14A)—C(23A)						−97.9(4)
C(14A)—C(23A)—C(24A)—C(25A)						98.1(5)
C(14A)—C(23A)—C(24A)—C(33A)						−89.2(5)
C(22A)—C(23A)—C(24A)—C(25A)						−75.7(5)
C(22A)—C(23A)—C(24A)—C(33A)						
C(24A)—C(33A)—C(34A)—C(35A)						145.7(4)
C(24A)—C(33A)—C(34A)—C(46A)						−101.1(4)
C(32A)—C(33A)—C(34A)—C(35A)						−36.3(5)
C(32A)—C(33A)—C(34A)—C(46A)						76.8(4)
C(22)—C(23)—C(23′)—C(22′)					84.8(3)	
C(14)—C(23)—C(23′)—C(14′)					98.2(4)	
C(22)—C(23)—C(23′)—C(14′)					−88.5(4)	

of the host molecule are located in a cavity established by the bulky aromatic units, and form an intramolecular hydrogen bond [O(1)···O(2) 2.707 Å]. The structure determination revealed two alternative sites for the hydroxy hydrogens, which were included in the structure model in calculated positions based on reasonable hydrogen bond geometries. The oxygen atom of the guest molecule 2 occupies two sites, each

TABLE IV Distances (Å) and angles (°) of hydrogen bond-type interactions

		Distance		
Atoms involved D—H···A	Symmetry	D···A	H···A	Angle D—H···A
1a				
C(44)—H(44)···O(1G1)	$0.5-x, 0.5+y, 0.5-z$	3.259(5)	2.34	163
O(2)—H(2′)···O(1)	x, y, z	2.707(4)	1.95	148
O(1)—H(1′)···O(1G3)	x, y, z	2.550(4)	1.77	154
O(1)—H(1″···O(2)	x, y, z	2.707(4)	1.99	166
O(2)—H(″)···O(1G2)	x, y, z	2.741(5)	1.94	165
1b				
O(1G2)—H(2G′)···O(1)	$-x, 2-y, 2-z$	2.875(4)	2.00	160
O(2)—H(1O2)···O(1)	x, y, z	2.691(4)	1.82	162
O(2)—H(2O2)···O(1G1)	x, y, z	2.751(4)	1.83	171
O(1G1)—H(1G)···O(2)	x, y, z	2.751(5)	2.00	149
O(1)—H(2O1)···O(2)	x, y, z	2.691(4)	1.88	163
O(1)—H(1G′)···O(1G2)	$-x, 2-y, 2-z$	2.875(5)	2.06	176
1c				
O(2)—H(2′)···O(1)	x, y, z	2.688(4)	1.91	154
O(1)—H(1′)···O(1G2)	x, y, z	2.719(5)	1.89	171
C(19)—H(19)···O(1G1)	$0.5+x, 1.5+y, 1-z$	3.408(5)	2.50	159
2a				
O(1)—H(1′)···O(2)	x, y, z	2.698(5)	1.89	159
O(2)—H(2′)···N(1G1)	x, y, z	2.663(6)	1.85	160
N(1G1)—H(1B)···Cl(4)	$-x, -y, -z$	3.673(5)	2.67	178
3a				
O(1°)—H(1A)···centroid A*	x, y, z		2.77	138
C(1G)—H(1G)···centroid B*	x, y, z	3.356(7)	2.36	171
4a				
O(1)—H(1)···O(2)	x, y, z	2.758(4)	1.92	163
O(2)—H(2′)···O(1G1)	x, y, z	2.647(3)	1.81	163
O(1°)—H(1A)···O(2A)	x, y, z	2.691(3)	1.78	161
O(2°)—H(2″)···O(1G2)	x, y, z	2.664(3)	1.78	167

* Centroid means the center of the ring: ring A (C17—C22), ring B (C14—C17, C22—C23).

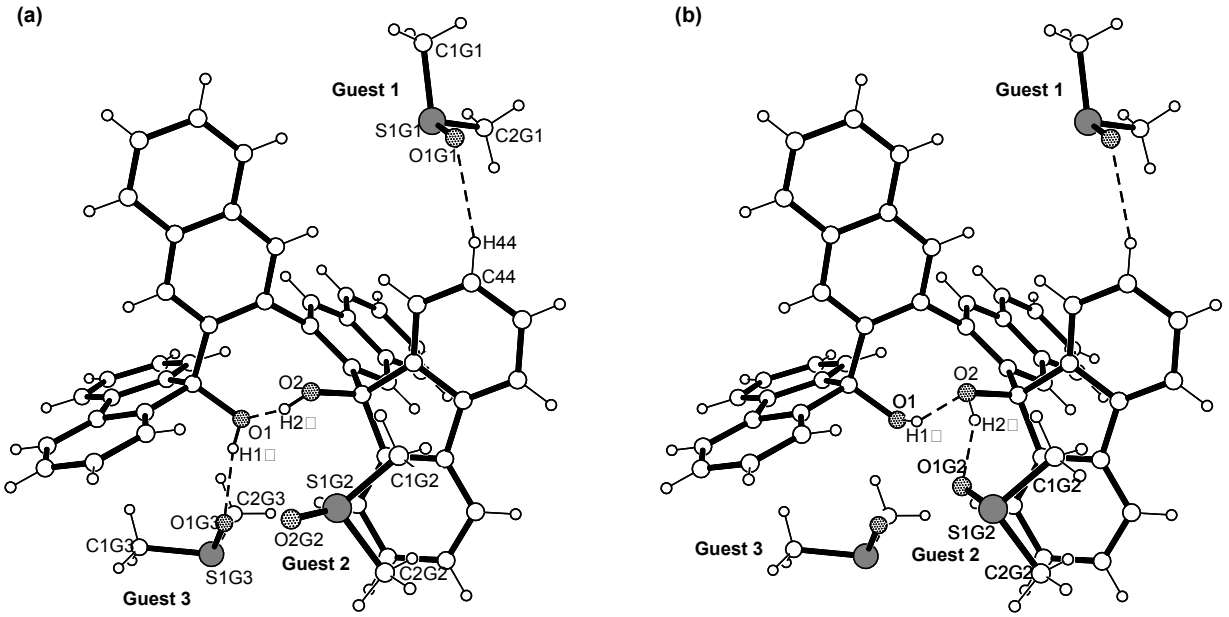

FIGURE 1 Perspective view of the 1:2.5 inclusion compound of **1** with dimethylsulfoxide (**1a**). H-bond contacts are shown by broken lines.

having an occupancy factor of 0.5. This is attributed to the fact that the formation of hydrogen bond systems between host and guest can, in principle, occur in two directions. The corresponding binding modes within the asymmetric unit of the cell are illustrated by two separate models in Fig. 1. The bond system that runs in direction O2 → O1 (Fig. 1a) includes a hydrogen bridge between H1′ of the host and O1G3 of the guest molecule 3. In this case, the oxygen atom of the non-coordinating guest molecule 2 occupies position O2G2. In the inversely orientated system of hydrogen bonds (Fig. 1b), the interaction with the guest molecule 3 is abolished. Instead, the oxygen atom of guest 2, which now occupies the alternative

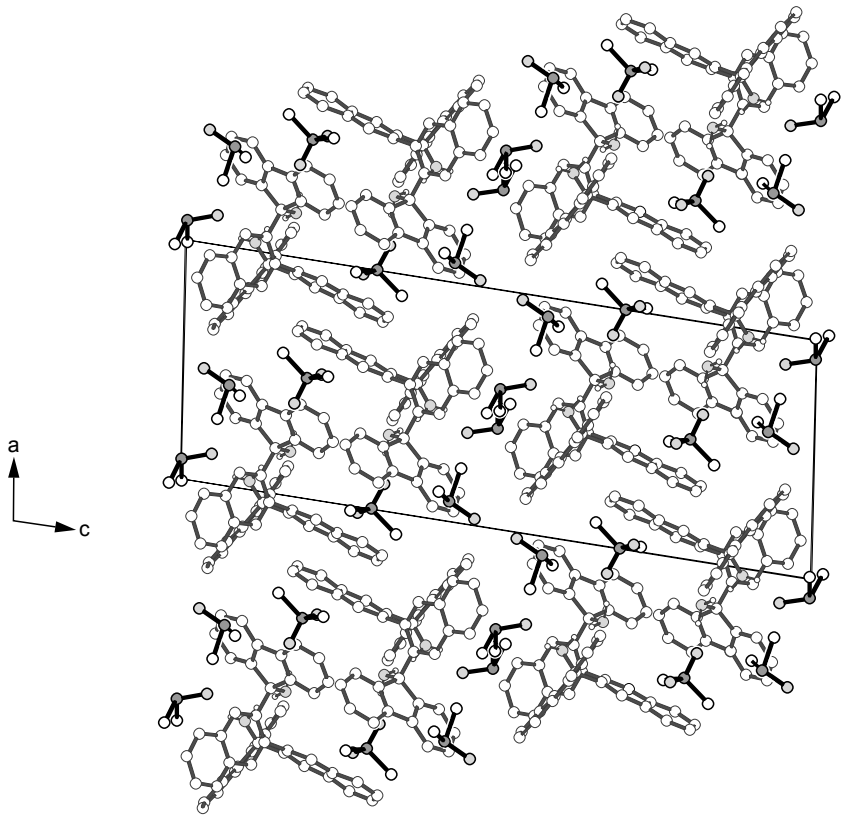

FIGURE 2 Packing illustration of the **1a** crystal. All non-relevant hydrogens and one position of each pair of disordered sites of hydroxy hydrogens are omitted for clarity. The O and S atoms are shaded in light and dark, respectively.

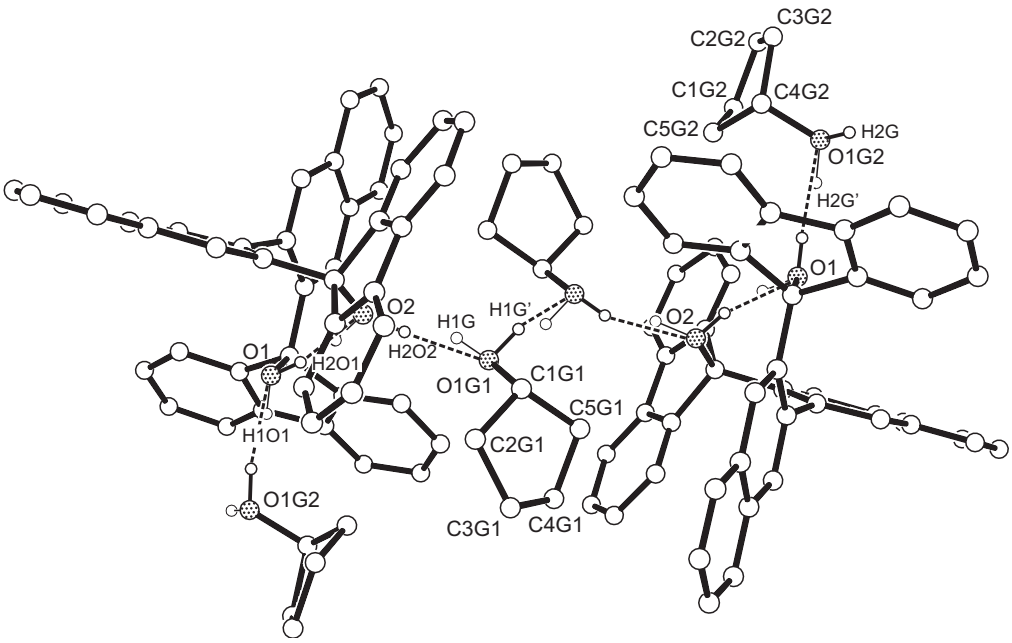

FIGURE 3 Structure motif of the **1**·cyclopentanol (1:2) clathrate (**1b**). For clarity, only one of the possible hydrogen bond systems (dotted lines) is depicted.

position O1G2, is included in the host–guest interaction. Thus, the formation of a hydrogen bond with H2″ of the host molecule is ensured.

As can be seen from the packing structure in Fig. 2, the guest molecules are incorporated in cavities confined by the aryl residues of the host molecules. The solvent molecule 3, which is disordered around the center of symmetry, is located between the fluorenyl groups of two host molecules. The partially disordered guest molecule 2 is enclathrated in a cage formed by four host molecules. It is fixed by one strong O—H···O bond and C—H···π contacts [17] to one of the naphthyl groups, whereas the guest molecule 1 involves an interaction of the C—H···O═C type [18]. According to the hydrophobic nature of the host backbone, the main contribution of host–host

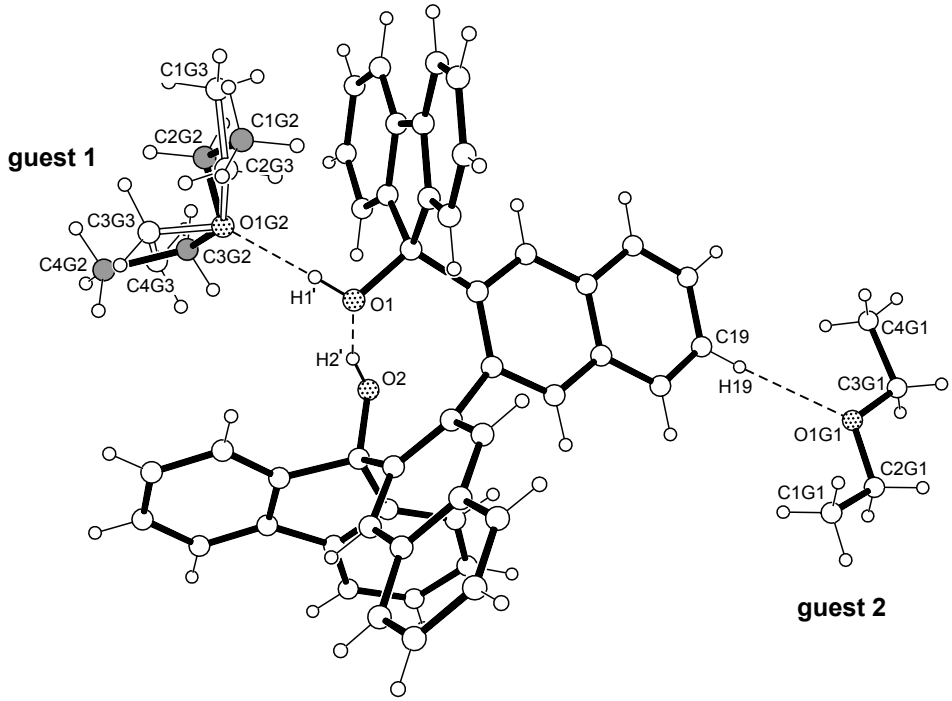

FIGURE 4 Perspective view of the **1**·diethyl ether (1:2) inclusion compound (**1c**). One position of the disordered guest molecule 1 is marked by shading of its carbon atoms.

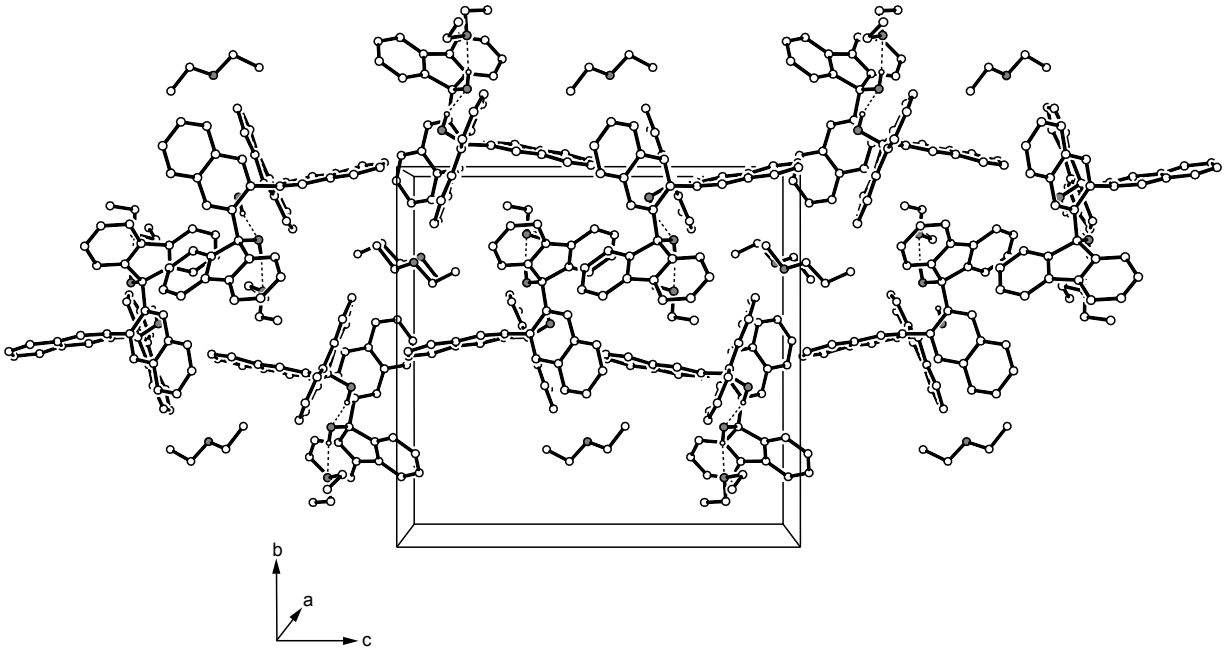

FIGURE 5 Packing diagram of the **1c** crystal. Non-relevant H atoms are omitted; broken lines represent H-bonds.

interaction arises from weak aromatic C—H···π contacts, which have a closest distance of 2.9 Å.

The 1:2 clathrate of **1** with cyclopentanol (**1b**) crystallizes in the triclinic space group $P\bar{1}$. In its crystal structure, the hydrogen atoms that are involved in hydrogen bond formation occupy two positions, each having an occupancy factor of 0.5. Because of the twofold donor character of the hydroxy groups, two identical open 14-membered hydrogen bonding schemes can be found, which run in opposite directions. Alternation of the running direction leads to donor and acceptor activity of the terminal functional groups. Although the intramolecular hydrogen bond length of the host molecule is similar to that found in the DMSO clathrate [O(1)···O(2) 2.691 Å], conformational differences, which become apparent by the interplanar angles between the aromatic building blocks, are caused by packing forces. As shown in Fig. 3, the smallest supramolecular motif of the crystal structure consists of a centrosymmetric dimer of host molecules bridged by two guest molecules with hydrogen bond lengths of 1.83 and 1.97 Å. These dimeric units are arranged in stacks along the crystallographic *a*-axis.

The **1**·diethyl ether (1:2) inclusion compound (**1c**) crystallizes in the orthorhombic space group $P2_12_12_1$.

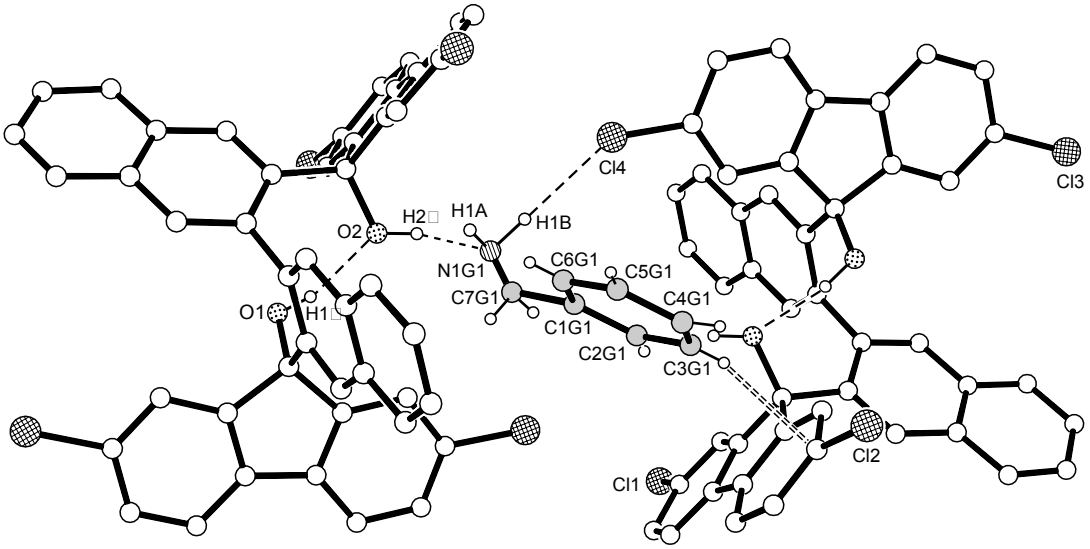

FIGURE 6 Structure motif of **2a**, showing the positioning of the guest molecule by intermolecular interactions (broken lines) with two host molecules. Only one position of the disordered arene moiety of the guest molecule is indicated.

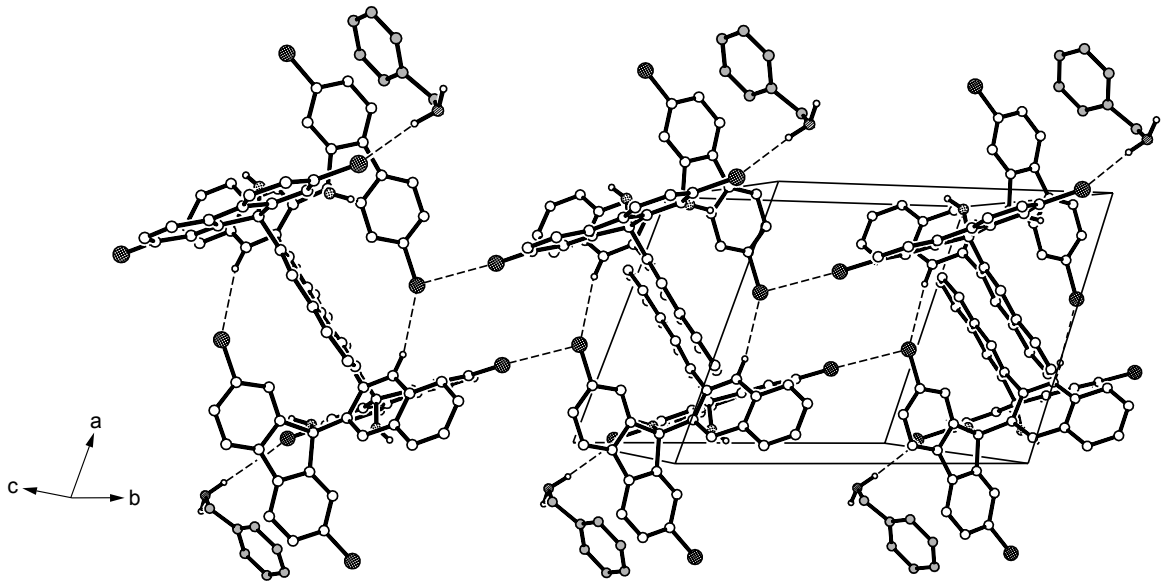

FIGURE 7 Packing diagram of the **2a** crystal. Intermolecular contacts are represented by broken lines.

The non-centrosymmetry of the crystal implies that the inclusion compound crystallizes as a conglomerate, that is the host molecules of a given crystal exhibit the same chirality. Another interesting structural feature consists in different binding modes of the guest molecules and thus in the differences regarding their molecular environment. Because of the presence of the intramolecular hydrogen bond (1.91 Å), the host molecule can form a conventional hydrogen bond (1.89 Å) to only one of the guest molecules.

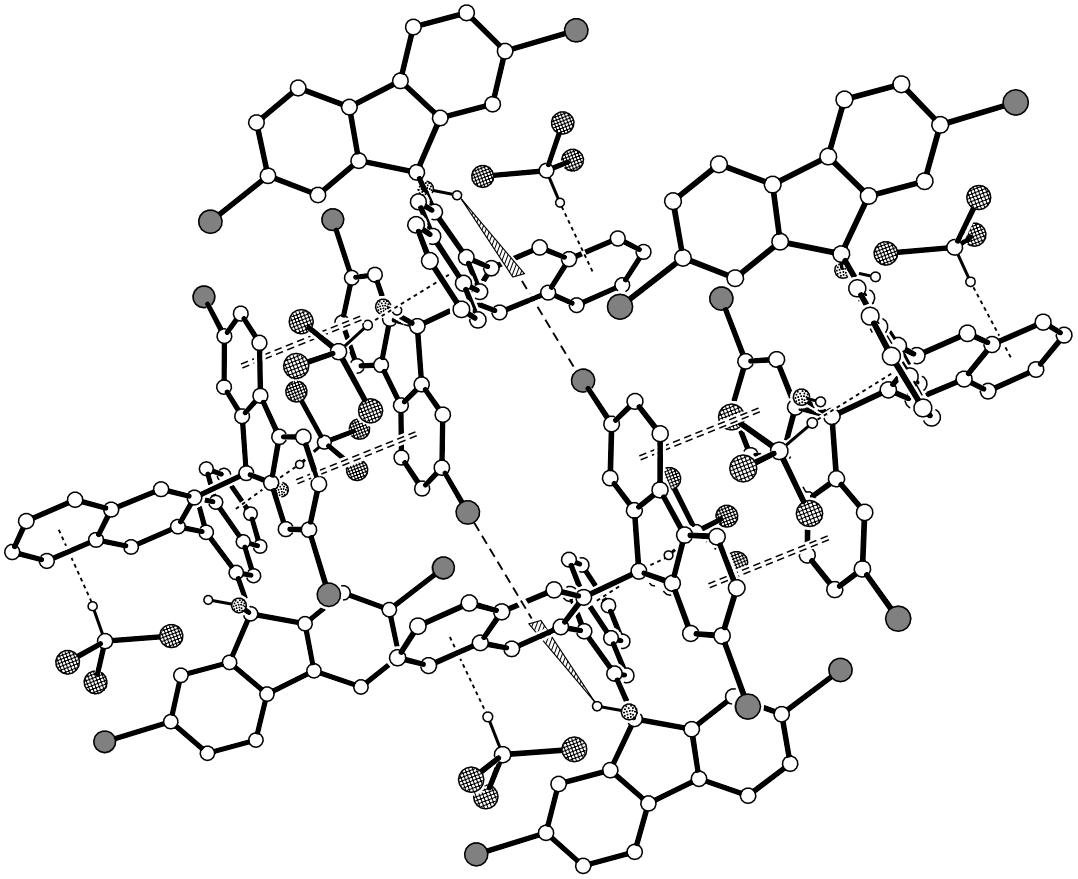

FIGURE 8 Packing diagram of the **3a** crystal. Dashed lines are used for Br···π, hatched triangles represent C—H···π and dashed double lines aromatic π···π interactions.

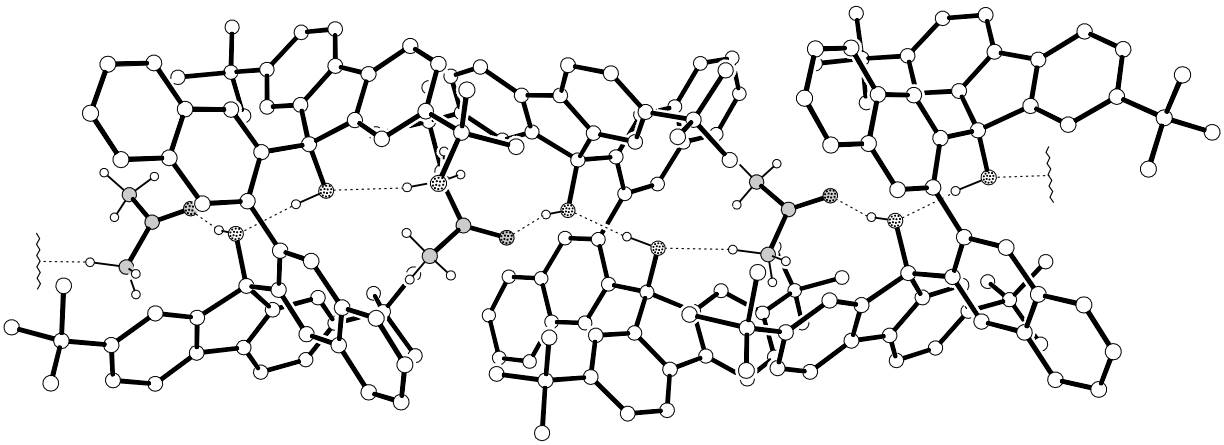

FIGURE 9 Structure motif illustrating H-bonding (dotted lines) in **4a**.

As shown in Fig. 4, the guest molecule 1 moves freely around its O—H···O bond axis so that the other molecular components occupy two positions (occupancy factors 0.5). The way this guest molecule is organized in the crystal may be explained by the lack of adaptation between the rigid host lattice and the extension of the guest. Moreover, its conformation deviates significantly from a planar arrangement of the non-hydrogen atoms. This becomes evident by the torsion angles C2G1—O1G1—C3G1—C4G1 and C1G1—C2G1—O1G1—C3G1, which are −76.5 and 175.2°, respectively. The second diethyl ether molecule forms only a weak C—H···O bond [18] to the naphthyl hydrogen H19 (2.50 Å). It is located in channel-like cavities extending in the direction of the crystallographic *a*-axis (Fig. 5).

Inclusion Compounds of 2–4 (2a, 3a and 4a)

The introduction of rigid substituents in 2- and 7-positions of the fluorenyl residues is interesting for two reasons. Halogen-substituted host systems potentially give rise to a wide variety of intermolecular interactions in the solid phase [19,20]. In addition, the size of the substituents exerts influence on the structure of the host lattice and should therefore affect the binding behavior of the inclusion components.

The chloro-substituted compound **2** yields a 1:1 clathrate with benzylamine (**2a**), which crystallizes in the space group $P\bar{1}$. According to the host/guest stoichiometry, only one coordination site of the host molecule is used for guest binding, whereas the acceptor atom of the second hydroxy group remains free. For the aromatic part of the benzylamine, two nearly overlapping disorder models with equal probability could be found. As in previous cases, the host molecule forms an intramolecular hydrogen bond [H(1′)···O(2) 1.89 Å]. The structure motif, depicted in Fig. 6, shows a strong O—H···N hydrogen bond (1.85 Å). The amine hydrogen H(7B) is connected with the chlorine Cl(4) [2.676 Å] of the symmetry-related host molecule. The aromatic ring of the guest molecule is in a nearly ideal edge-to-face orientation to one of the fluorenyl moieties [21,22], of which the closest intermolecular distance (2.76 Å) indicates a weak binding affinity between them.

The packing diagram, illustrated in Fig. 7, is characterized by cross-linking of host molecules induced by their chlorine atoms. A well-known binding behavior observed in many aromatic chloro-containing compounds includes direct interaction between chlorine atoms [19,20,23]. In the inclusion compound **2a**, two chlorine atoms of each host molecule are involved in contacts of this type, the C—Cl···Cl—C moiety with a Cl···Cl distance of 3.43 Å and C—Cl···Cl angles of 88.5 and 167.7°, respectively [24]. Additionally, one chlorine atom is associated with a C—H···Cl contact [20,25], with the hydrogen atom of the α-position of one naphthyl group. In the crystal packing of the inclusion compound, host molecules are arranged in infinite double strands extending in the direction of the crystallographic *b*-axis (Fig. 7).

The bromo-substituted compound **3** forms a 1:2 inclusion compound with chloroform (**3a**), which crystallizes in the monoclinic space group $C2/c$ with one half of the host molecule in the asymmetric unit of the cell. Remarkably, the guest molecule is not involved in a conventional hydrogen bond [26]. Instead, the weakly acidic hydrogen atom of the chloroform molecule lies almost directly above the center of the outer aromatic ring of the naphthyl moiety, giving rise to a C—H···π(aryl) contact [18] with a distance of 2.30 Å (Fig. 8). Because the host molecule exhibits molecular symmetry, the formation of an intramolecular hydrogen bridge is excluded here. This is also reflected in the oxygen–oxygen distance of 3.4 Å, which is much larger than those found in the inclusion compounds mentioned above. The close intramolecular contact of the hydroxy

hydrogens to the inner rings of the naphthyl residues, with a distance of 2.76 Å to the ring center, suggests weak attractive O—H···π interactions [18].

The mode of halogen interactions is different from that observed in the inclusion compound of the chloro-substituted host analog **2**. In the present case, the hydrogen atom H(1′) of the hydroxy group and the bromine atom Br(2A) of the symmetry-related host molecule ($-x$, $-y$, $1-z$) interact with the inner aromatic ring of the naphthyl group [18,27]. In this O—H···π(aryl)···Br—C pattern, the bromine atom is almost directly below the center of the aromatic ring, showing a Br···π(centroid) distance of 3.39 Å (Fig. 8). A possible explanation for this recognition mode can be seen in the different electronic characters of the groups involved. The interaction with the acidic hydroxy hydrogen atom reduces the electron density of the aromatic ring, whereas the bromine atom on the opposite side of the ring acts as a nucleophilic electron donor.

The sum of all polar host–host interactions, together with the rigidity of the molecular skeleton, induces a packing structure with the guest molecules occupying open inter-host channels aligned parallel to the *b*-axis. The chlorine atoms of the guest do not participate in any significant interaction with the host (Fig. 8).

The 1:1 inclusion compound of the *tert*-butyl-substituted host **4** with acetone (**4a**) adopts the monoclinic space group $P2_1/c$ with two crystallographic independent molecules in the asymmetric unit of the cell. As expected, the acetones are linked to the host molecules by strong O—H···O hydrogen bonds (1.78, 1.81 Å) [23] that are superposed by weak C—H···π(aryl) contacts [17] (Fig. 9). This linkage of host and guest molecules results in infinite helical strands running along the crystallographic *b*-axis. In this connection, acetone molecules have acceptor and donor characteristics, the latter being established by one of their methyl hydrogens. The others are located above the aromatic residues of the host molecules.

The overall structure of the molecular strand can be regarded as consisting of a polar core region established by the functional groups that is surrounded by the non-polar parts of the host molecules (Fig. 9). A structural comparison between **4a** and the previously reported **1**·acetone (1:3) clathrate [15] clearly documents the influence of bulky substituents on host–guest interaction. In the former case, the three acetone molecules show different binding modes. The introduction of *tert*-butyl groups in **4**, however, yields more extended lattice voids, which results in the observed supramolecular binding pattern. In the packing structure of **4a**, linear host–guest aggregates are arranged in molecular layers that are aligned parallel to the crystallographic *A*-plane.

CONCLUSION

The attachment of two 9-hydroxy-9-fluorenyl units or chloro-, bromo- and *t*-butyl-substituted derivatives of this group to 3,3′-positions of a basic 2,2′-binaphthyl construction element has produced a new family of highly efficient crystalline inclusion hosts (115 isolated clathrates). However, with regard to the variety and number of inclusion compounds, they are little influenced by individual substitutions, although these do provide an indication of the effectiveness of the basic host framework. This particular behavior is probably due to the twisted conformation of the basic host skeleton being stabilized by a strong intramolecular hydrogen bond between the fluorenyl hydroxy groups, as is found in all the previous [15,16] and currently solved structures of respective inclusion compounds, except for **3a**, which seems to be a very specific case. Nevertheless, the type of substitution shows differences in the stoichiometric host:guest ratios for the same guests and also in the modes of supramolecular interaction of the inclusion structures, including, aside from conventional hydrogen bonding [23], specific C—H···π(aryl) [18], C—H···halogen [20,25] and halogen···halogen contacts [19,20,23].

Thus, the constitution of the present host family fits into the class of 'versatile inclusion hosts' [28], which may give rise to further structural modifications and future studies with regard to vapor sorption/desorption [15,29,30] and polymorphism [31,32].

EXPERIMENTAL

Measurements and Materials

Melting points were determined with a hot-stage microscope (VEB Dresden Analytik) and are uncorrected. The IR spectrum was measured as KBr pellets with a Perkin-Elmer FT-IR 1600 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker DPX 400 instrument. The chemical shifts (δ) are reported as ppm relative to $SiMe_4$. The MS spectrum was obtained with a HP 59987 A (EI) instrument. Elemental analyses were performed with a Heraeus CHN rapid analyzer.

Starting compounds 3,3′-dibromo-2,2′-binaphthyl [15], 2,7-dichloro-9-fluorenone [33], 2,7-dibromo-9-fluorenone [34] and 2,7-di-*t*-butyl-9-fluorenone [35] were prepared following the literature descriptions. 9-Fluorenone was purchased from Acros. Solvents were dried and purified according to standard procedures [36].

General Procedure for Synthesis of Host Compounds 1–4

To a stirred suspension of 3,3′-dibromo-2,2′-binaphthyl (1.50 g, 2.91 mmol) in dry diethyl ether

(15 mL), a solution of *n*-BuLi (1.6 M in *n*-hexane, 6.8 mL, 72 mmol) was added at 0°C during 30 min. Stirring was continued for 2 h at the same temperature and the corresponding fluorenone (7.28 mmol) suspended in diethyl ether was added in small amounts. The solution was allowed to warm up to room temperature, stirred for 2 h at this temperature, and then refluxed for 40 h. After cooling, the solid was collected, washed with diethyl ether and recrystallized from dioxane. Decomposition of the clathrates yielded the pure compounds. Specific details are given for each compound.

3,3′-Bis(9-hydroxy-9-fluorenyl)-2,2′-binaphthyl (1)

9-Fluorenone was used. Yield 70%, colorless crystals, mp $>$ 300°C (lit. [15] mp $>$ 300°C).

3,3′-Bis(2,7-dichloro-9-hydroxy-9-fluorenyl)-2,2′-binaphthyl (2)

2,7-Dichloro-9-fluorenone was used. Yield 55%, yellow crystals, mp $>$ 300°C (lit. [16] mp $>$ 300°C).

3,3′-Bis(2,7-dibromo-9-hydroxy-9-fluorenyl)-2,2′-binaphthyl (3)

2,7-Dibromo-9-fluorenone was used. Yield 45%, orange crystals, mp $>$ 300°C. (lit. [16] mp $>$ 300°C).

3,3′-Bis(2,7-di-t-butyl-9-hydroxy-9-fluorenyl)-2,2′-binaphthyl (4)

2,7-Di-*t*-butyl-9-fluorenone was used. Yield 48%, colorless crystals, mp $>$ 300°C. IR (KBr, cm^{-1}) υ 3436 (OH), 3053 (CH, Ar), 2960, 2909, 2872 (CH, Alkyl), 1625 (C═C, Ar), 1477 (CH), 1364 (C—Me), 1254 (OH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (s, 18 H, *t*-Bu), 1.31 (s, 18 H, *t*-Bu), 3.82 (s, 2 H, OH). 7.21-8.11 (m, 24 H, Ar-H); ^{13}C NMR (100.61 MHz, $CDCl_3$) δ 31.5, 35.0, 87.6, 118.9, 119.6, 121.4, 121.7, 125.68, 125.74, 126.06, 126.17, 126.6, 127.1, 127.9, 131.1, 131.4, 132.3, 136.2, 137.6, 141.3, 141.7, 150.9, 151.5, 152.0, 152.8. MS *m/z* 820.32 (M^+). Anal. calcd. for $C_{60}H_{62}O_2$(%): C, 88.73; H, 6.62. Found: C, 88.60; H, 6.89.

General Procedure for Formation of the Crystalline Inclusion Compounds

The corresponding host compound was dissolved under heating in a minimum amount of the respective guest solvent. After leaving the mixture for 12 h at room temperature, the crystals formed were collected, washed with diethyl ether, and dried (1 h, 15 Torr, room temperature). Host–guest stoichiometric ratios were determined by ^{1}H NMR integration. Data for each compound are given in Table I.

X-ray Crystallography

Crystals suitable for X-ray investigations were obtained by slow evaporation of solutions of the host compounds in the respective guest solvent.

The intensity data of the inclusion compounds **1a**–**1c**, **2a** and **3a**, collected on a CAD-4 diffractometer (graphite-monochromated Cu Kα radiation), were measured in the $\omega - 2\theta$ scan mode. Cell constants and orientation matrices were refined by least-squares fits of 25 reflections. Three standard reflections were measured after every hour, showing no decay of the crystal during the data collection. The intensity data for the inclusion compound **4a** were collected on a Bruker Smart CCD diffractometer using ω-scans. Reflections were corrected for background Lorentz and polarization effects. Preliminary structure models were derived by application of direct methods [37] and were refined by full-matrix least-squares calculations based on F^2 for all reflections [38]. Absorption corrections for structures **1c** and **2b** were performed by using semiempirical methods (psi-scans) [39], and for **4a** the SADABS [40] program was used. All non-hydrogen atoms were refined anisotropically. The hydroxy hydrogen atoms of structures **1b** and **2a** were extracted from the electron density map whereas all other hydrogen atoms were included in the models in calculated positions and were refined as constrained to bonding atoms. The crystal data and experimental parameters are summarized in Table II. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 257777 to CCDC 257782. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: . E-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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