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Konstantinos Skobridis[a]; Vassiliki Theodorou[a]; Dimitrios Alivertis[a]; Wilhelm Seichter[b]; Edwin Weber[b]; Ingeborg Csöregh[c]
[a] Department of Chemistry, University of Ioannina, Ioannina, Greece [b] Institut für Organische Chemie, Technische Universität Bergakademie Freiberg, Freiberg/Sachs, Germany [c] Arrhenius Laboratory, Department of Structural Chemistry, Stockholm University, Stockholm, Sweden

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Crystalline Complexes of 2,2′-Bis(9-hydroxy-9-fluorenyl) biphenyl Host with Oligofunctional and Conjugate Functional Group Guests

KONSTANTINOS SKOBRIDIS[a,*], VASSILIKI THEODOROU[a], DIMITRIOS ALIVERTIS[a], WILHELM SEICHTER[b], EDWIN WEBER[b] and INGEBORG CSÖREGH[c]

[a]*Department of Chemistry, University of Ioannina,GR-451 10 Ioannina Greece;* [b]*Institut für Organische Chemie, Technische Universität Bergakademie Freiberg, Leipziger Straße 29, D-09596, Freiberg/Sachs, Germany;* [c]*Arrhenius Laboratory, Department of Structural Chemistry, Stockholm University, S-10691 Stockholm, Sweden*

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Four crystalline inclusion compounds of the 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl host 1, containing diethylene glycol (1:1) (1a), bis(2-aminoethyl)amine (1:1) (1b), methacrylic acid (1:1) (1c) and 2-cyclopenten-1-one (1:2) (1d), have been studied by X-ray diffraction analysis from single crystals. Departure from the expectation, the multifunctional and conjugate functional guest molecules, potentially being able to offer multiple H donor-/acceptorships or other modes of polar interaction due to the conjugation, do not result in the formation of infinitely connected networks in the crystal structures. Instead of this, discrete 2:2 host–guest aggregates (1a, 1b), guest dimers (1c) and rather conventional host–guest units (1d) are found. Hence, inherent shielding effects of the host molecule owing to the fluorenyl moieties and the presence of a strong intramolecular hydrogen bond, impeding multiple intermolecular association, are not overcome by the merits of the guest molecules, showing that the host compound 1 is superior by structural constancy in its crystalline inclusions.

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

INTRODUCTION

Crystalline inclusion chemistry [1,2], rated as an important subfield of crystal-engineering [3–6], continues being of topical interest both from theoretical and practical points of view [7–9]. Host compounds, capable of forming crystalline inclusions (clathrates) with organic guest molecules, that may provide particular inclusion selectivities, have been designed in a great variety [10]. Among them are the scissor-type, the roof-shaped, the wheel-and-axle or the dumb-bell-shaped host molecules [11]. In many cases, they feature two bulky carbinol moieties being attached to a rigid central unit [12]. A well known exponent of this structure type is represented by the host compound 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl [13,14] given with formula **1** (Scheme 1).

This host compound has proven very efficient in the formation of crystalline inclusions with a broad variety of organic guest solvents, including protic, polar aprotic and apolar molecules of different chemical nature [12]. A great many of them have been studied by X-ray structure determination to show varied modes of supramolecular interactions [13–19]. However, as yet, in no such cases has an oligofunctional or a conjugate functional group containing guest molecule been involved which may give rise to high-level or more complex supramolecular networks using this wizard host compound. In contemplation of these facts, the present study has been performed.

We report on the preparation and X-ray crystal structures of four new inclusion compounds of the host molecule **1** with diethylene glycol (**1a**), bis(2-aminoethyl)amine (**1b**), methacrylic acid (**1c**) and 2-cyclopenten-1-one (**1d**), which are trifunctional and conjugate functional group containing organic guest molecules, respectively, not to mention that these compounds are a matter to organic synthesis.

*Corresponding author. Fax: + 30-2 65 10-9 86 82 E-mail: kskobrid@cc.uoi.gr

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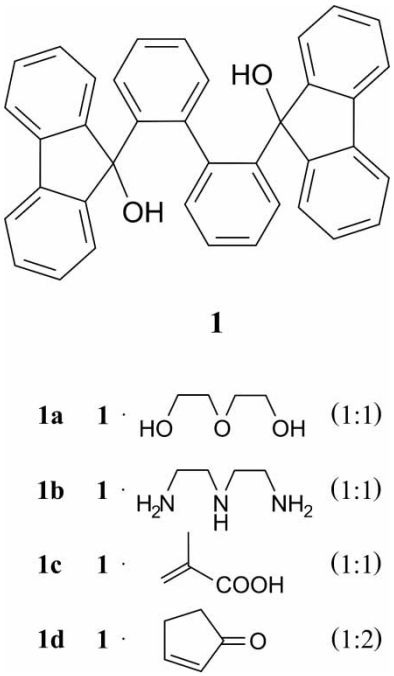

SCHEME 1 Compounds studied.

RESULTS AND DISCUSSION

All compounds involved in the discussion are specified in Scheme 1. The host compound **1** was prepared as described in the literature [13,14]. The crystalline inclusions **1a–d** were obtained by recrystallization of **1** from the respective guest solvent. These four inclusion compounds, **1**·diethylene glycol (1:1) (**1a**), **1**·bis(2-aminoethyl)amine (1:1) (**1b**), **1**·methacrylic acid (1:1) (**1c**) and **1**·2-cyclopenten-1-one (1:2) (**1d**), have been studied by X-ray diffraction on single crystals. Molecular illustrations and the packing diagrams are shown in Figs. 1–9. Crystallographic data, selected conformational parameters and information about hydrogen bond interactions are listed in Tables I–III.

The conformation of the host molecules can be described by a set of three torsion angles. Those, which are given by the atomic sequences O(1)—C(13)—C(14)—C(19) and C(20)—C(21)—C(26)—O(2), denoted as τ_2 and τ_3 in Fig. 1, describe the orientation of the fluorenyl moieties with respect to the phenyl rings, to which they are attached, while τ_1 [C(14)—C(19)—C(20)—C(21)] defines the torsion angle between the aromatic rings of the central biphenyl unit. In the four inclusion compounds, the conformation of the host molecule is fixed by an intramolecular hydrogen bond between the hydroxy groups [O(2)—H(2′)...O1 2.700(2)–2.869(5)Å], which is also present in the previous structures involving this host compound [13–19]. Although the phenyl rings are arranged nearly orthogonal to each other ($\tau_1 = 90.0–93.9°$), the torsion angles τ_2 and τ_3 range between $-16.5°$ and 29.5°, and $-15.3°$ and 28.1°, respectively, indicating conformational freedom of the fluorenyl moieties with regard to their adjacent phenyl rings. The distortion of the host molecule along its biphenyl axis, which can be expressed by the dihedral angle between atoms C(16)—C(19)—C(20)—C(23), should be attributed to packing affects rather than intramolecular strain.

In the 1:1 crystalline inclusion of **1** with diethylene glycol (**1a**) (space group: *P*-1), the asymmetric unit of the cell contains one host and one guest molecule

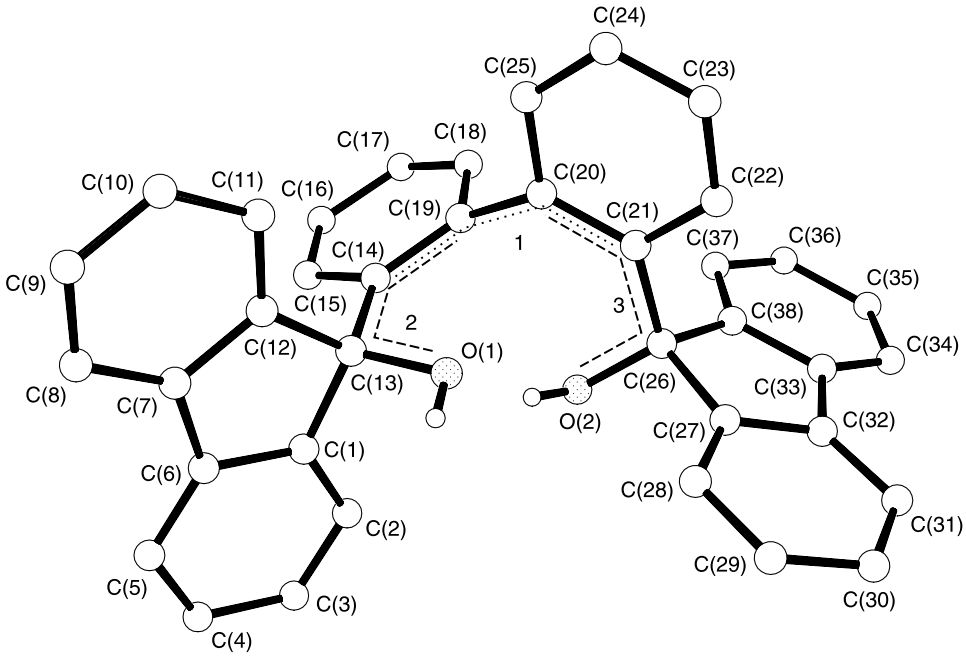

FIGURE 1 Conformation and numbering scheme of the host molecule **1** in the inclusion structures **1a–d**. The torsion angles τ_2 and τ_3 are depicted as dashed lines, and τ_1 as dotted line.

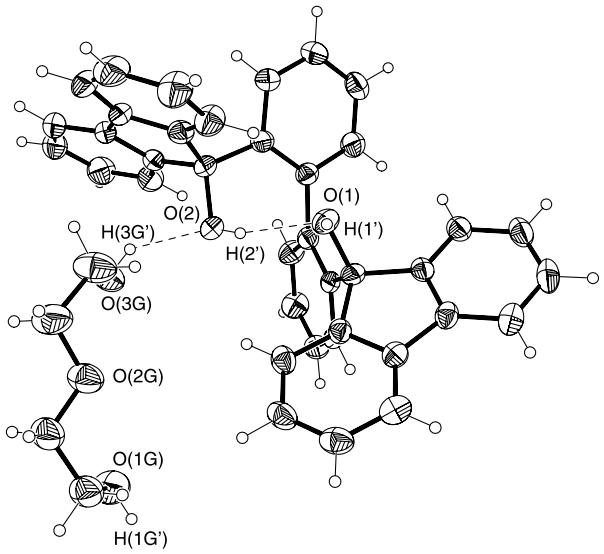

FIGURE 2 Perspective view of the asymmetric unit of the 1:1 inclusion compound of **1** with diethylene glycol (**1a**). Thermal ellipsoids of the non-hydrogen atoms are of 50% probability level. H-bond contacts are shown by broken lines.

(Fig. 2). Host–guest interaction in the crystal is accomplished by a conventional hydrogen bond [O(3G)—H(3G′)...O(2) = 2.732(6)Å] [20] while the second hydroxy hydrogen H(1G′) of the guest is associated to a symmetry related guest molecule [O(1G)—H(1G′)...O(3G) = 2.696(5)Å]. The conformation of the diethylene glycol deviates only slightly from mirror symmetry. The O—C—C—O torsion angles are *gauche* [−59.6(7)°, 64.2(7)°], whereas the C—O—C—C sequences exhibit an *anti* conformation [175.9(5)°, −169.1(5)°]. According to the given mode of intermolecular hydrogen bonding, the crystal of **1a** is composed of discrete 2:2 host–guest aggregates in which the host molecules are coordinated to a cyclic dimer of guest molecules (Fig. 3). Weak intermolecular interactions involving aromatic molecule parts contribute significantly to the stabilization of the crystal packing. The closest distances between aromatic rings being arranged in a face-to-face manner or exhibiting an edge-to-face relationship [21,22] are 3.55 Å and 2.84 Å, respectively. In order to realize a close packing structure, host–guest aggregates are aligned such that their extended fluorenyl moieties fit into the voids left by the narrow guest dimers (Fig. 3).

Similar structural features are found in the 1:1 inclusion structure of the diol host **1** with bis(2-aminoethyl)amine (**1b**) (Fig. 4) which, however, crystallizes in the monoclinic space group $P2_1/n$. The secondary amino nitrogen of the guest is hydrogen bonded to the host molecule [O(1)—H(1O)...N(2) = 2.695(2)Å], whereas the primary amino groups of the guest are used to form a cyclic dimer [N(3)—H(31N)...N(1) = 3.431(2)Å] thus giving 2:2 host–guest aggregates of structure resembling the above case (Fig. 5). Hence, only one of the five amino hydrogens of the guest molecule takes part in intermolecular hydrogen bond formation.

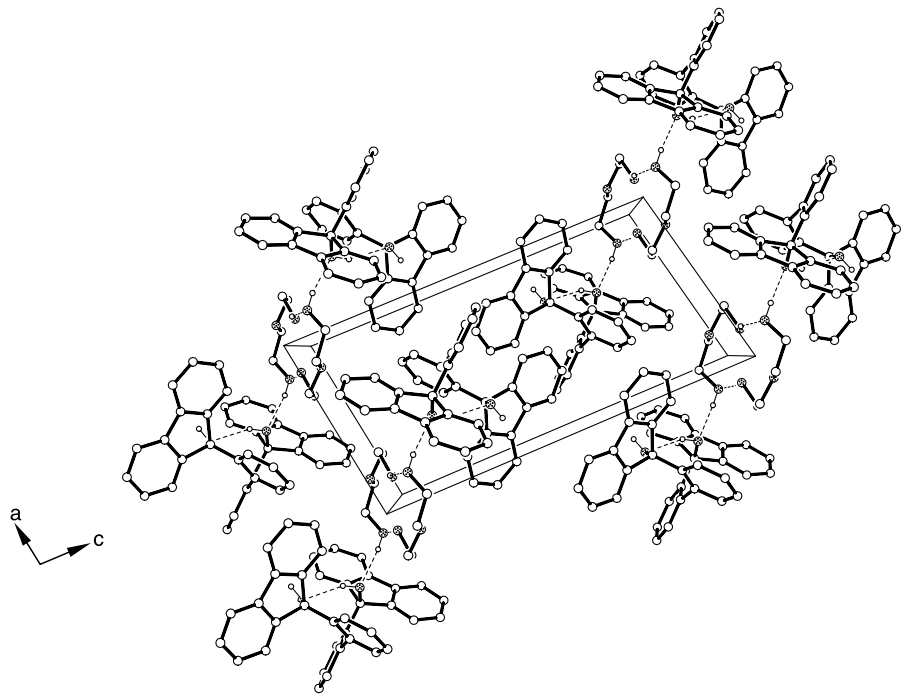

FIGURE 3 Packing illustration of the **1a** crystal viewed down the *b*-axis. With the exception of hydroxy hydrogens, all other hydrogens are omitted for clarity; broken lines represent H-bonds.

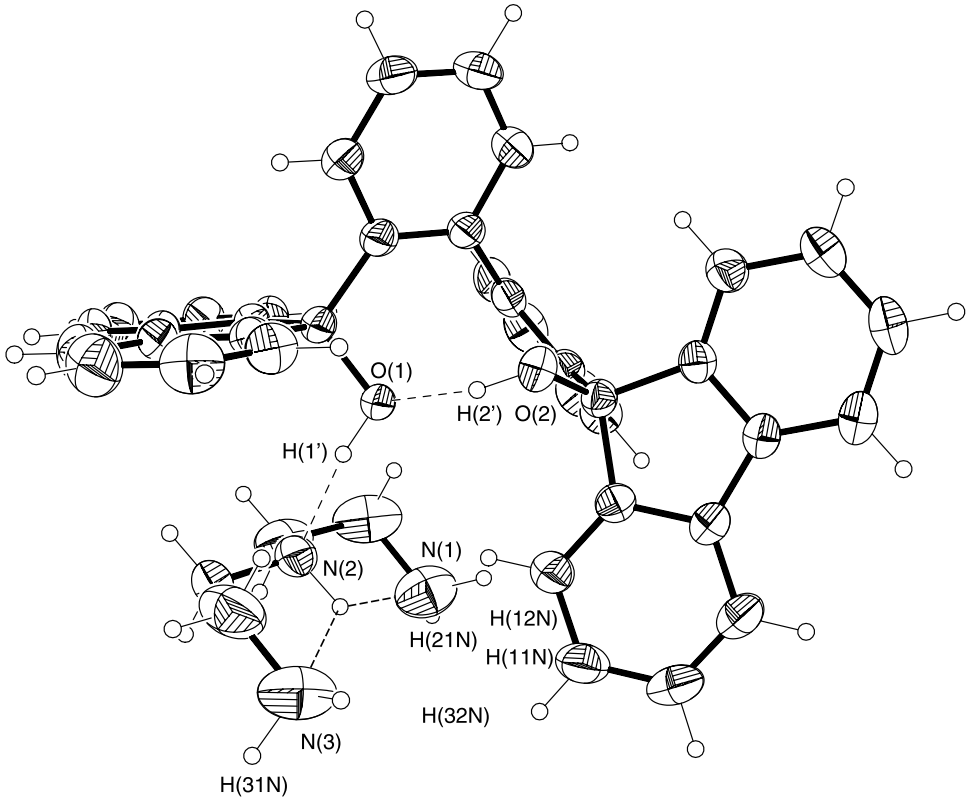

FIGURE 4 Perspective view of the asymmetric unit of the 1:1 inclusion compound of **1** with bis(2-aminoethyl)amine (**1b**). Thermal ellipsoids of the non-hydrogen atoms are of 50% probability level. H-bonds are shown by broken lines.

The hydrogen H(21N) of the guest forms a bifurcated intramolecular N—H...N hydrogen bond [20] to the flanking nitrogens N(1) and N(2) [N(2)...N(1) = 2.940(3)Å, N(2)...N(3) = 2.867(3)Å; N—H...N 97.4°, 110.1°]. Due to the presence of translational symmetry elements, the assembly of host–guest units in the crystal structure of **1b** (Fig. 5) must be different from that of structure **1a**. Nevertheless, also in the present case the crystal structure is dominated by arene–arene interactions of the face-to-face and edge-to-face type [21,22] in which the aromatic rings have distances of 3.20 Å and 2.63 Å, respectively.

Crystallization of **1** from methacrylic acid yields thin colorless needles that proved to be a 1:1 inclusion compound (**1c**) (space group *P*-1) with two crystallographically independent host molecules and two guests in the asymmetric unit (Fig. 6). A remarkable feature of the structure is the irregular geometry of the carboxylic acid dimer, in which the COOH groups are inclined in an angle of 28.6(2)°. Moreover, the methacrylic acid molecules themselves deviate significantly from planarity, which is reflected by torsion angles of 164.2(6)° and 175.5(6)° of their C = C—C = O sequences. In the ideal case, this torsion angle is expected to be 180°. The distortion of the individual guest molecules together with the inclination between them results in a strongly twisted overall conformation of the dimer. The O—H...O hydrogen bonds within the dimer have nearly the same length [O...O = 2.608(5)Å, 2.617(6)Å]. Consideration of the packing structure of **1c** in direction of the crystallographic *a*-axis (Fig. 7) reveals that the guest molecules reside in parallel channels created by the host molecules. It also shows that the unusual geometry of the dimeric guest species follows the shape of these channels, in which each carboxylic acid dimer is surrounded by four host molecules in an unsymmetric manner. Because there is no mentionable host–guest association, T-shaped and π-stacked arrangements of aromatic building blocks, the latter showing a zipper-like mode between the interacting fluorenyl residues, play an important role for the stabilization of the crystal structure.

The inclusion compound formed between **1** and 2-cyclopenten-1-one (**1d**) shows host–guest ratio 1:2. The intensity statistics, obtained from direct methods, indicate that the inclusion compound crystallizes in the non-centrosymmetric space group Cc with two crystallographically independent host molecules and four guest molecules in the asymmetric unit of the cell. Both host molecules are of the same chirality and exhibit similar conformational parameters. Hydrogen bonded 1:2 host–guest units can be regarded as the smallest supramolecular entities of this structure. The molecular structure, displayed in Fig. 8, reveals different modes of intermolecular interactions within each 1:2 host–guest unit. The oxygen of guest **1** forms a bifurcated hydrogen bond [20] to the hydroxy

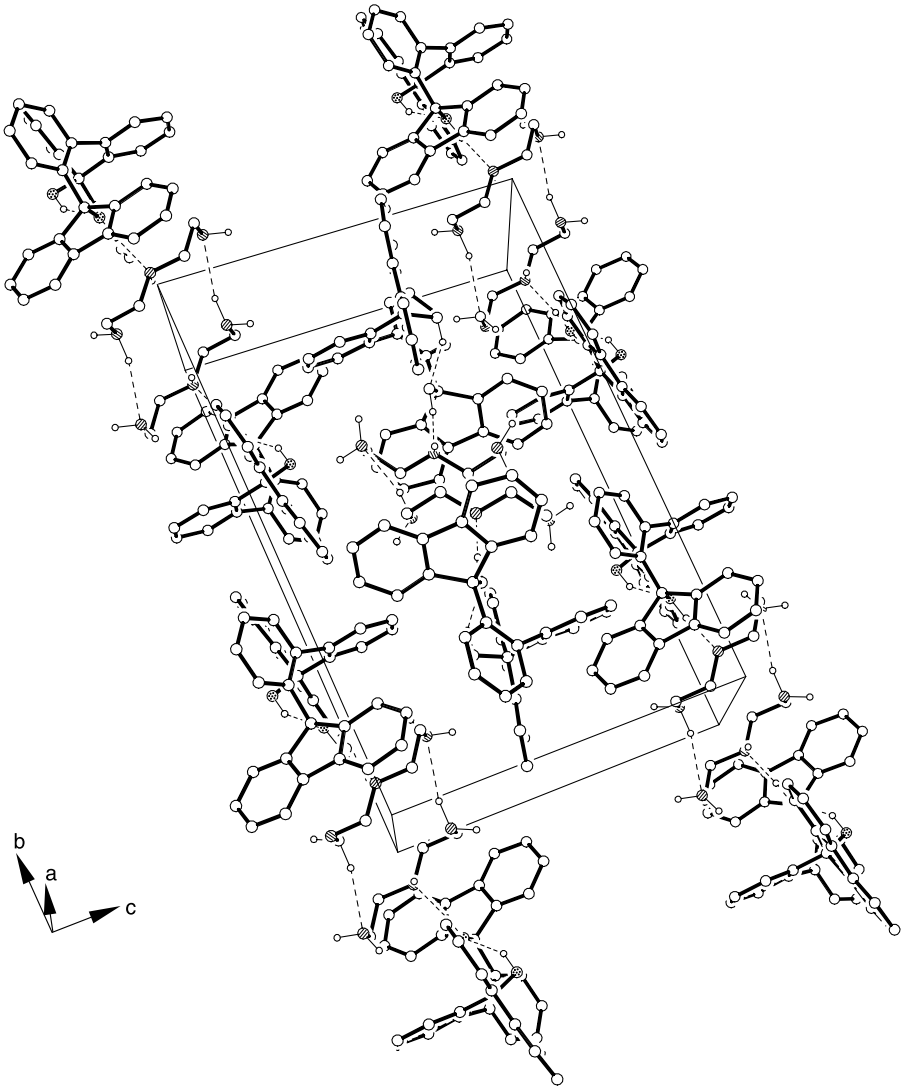

FIGURE 5 Packing diagram of the **1b** crystal. All non-relevant H atoms are omitted; broken lines represent H-bonds.

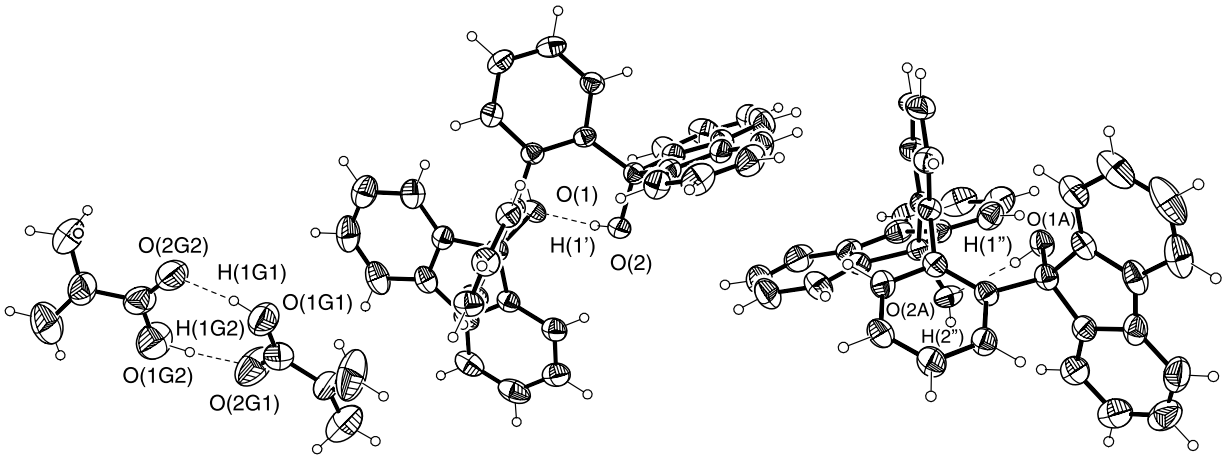

FIGURE 6 Perspective view of the asymmetric unit of the 1:1 inclusion compound of **1** with methacrylic acid (**1c**). Thermal ellipsoids of the non-hydrogen atoms are of 30% probability level. H-bond contacts are shown by broken lines.

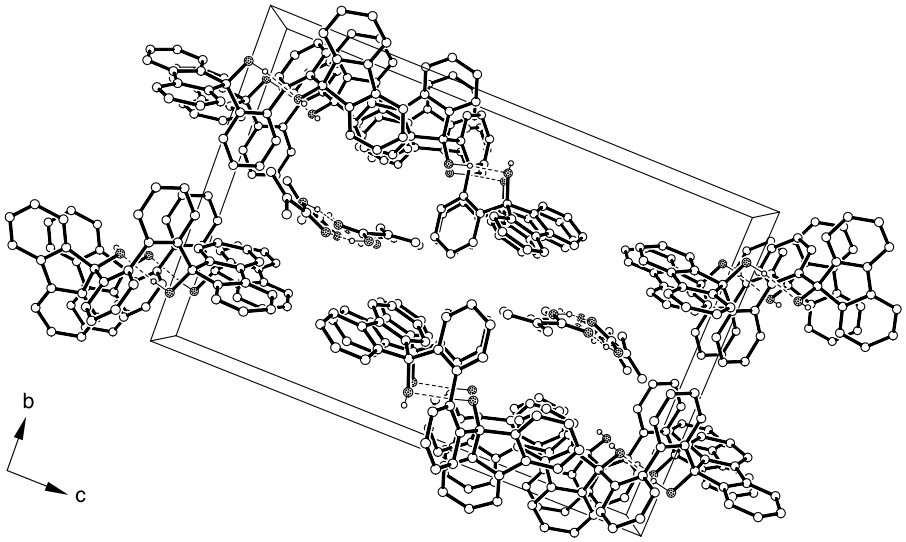

FIGURE 7 Packing diagram of the **1c** crystal. All non-relevant H atoms are omitted. H-bonds are shown by broken lines.

hydrogen H(1′) and the hydrogen H(28) of the host 1, while the guest molecule 2 of this unit is associated by a weak C—H…O bond [23,24] to the hydrogen atom H(25) of the phenyl ring. In the second host–guest unit one of the cyclopentenone molecules (guest 3) is connected by a conventional O—H…O bond to host 2 and by a C—H…O contact to the other cyclopentenone molecule (guest 4). The pentagons of the cyclopentenone molecules exhibit a regular nearly planar geometry. The crystal structure of **1d** viewed along the *b*-axis is shown in Fig. 9. In contrast to the methacrylic acid guests, the cyclopentenone molecules are located in elongated cavities which extend along the *a*-axis. Each cavity contains four guest molecules which adopt coplanar and tilted arrangements. The distances between ring centriods of consecutive guest molecules range between 3.99 Å and 5.95 Å.

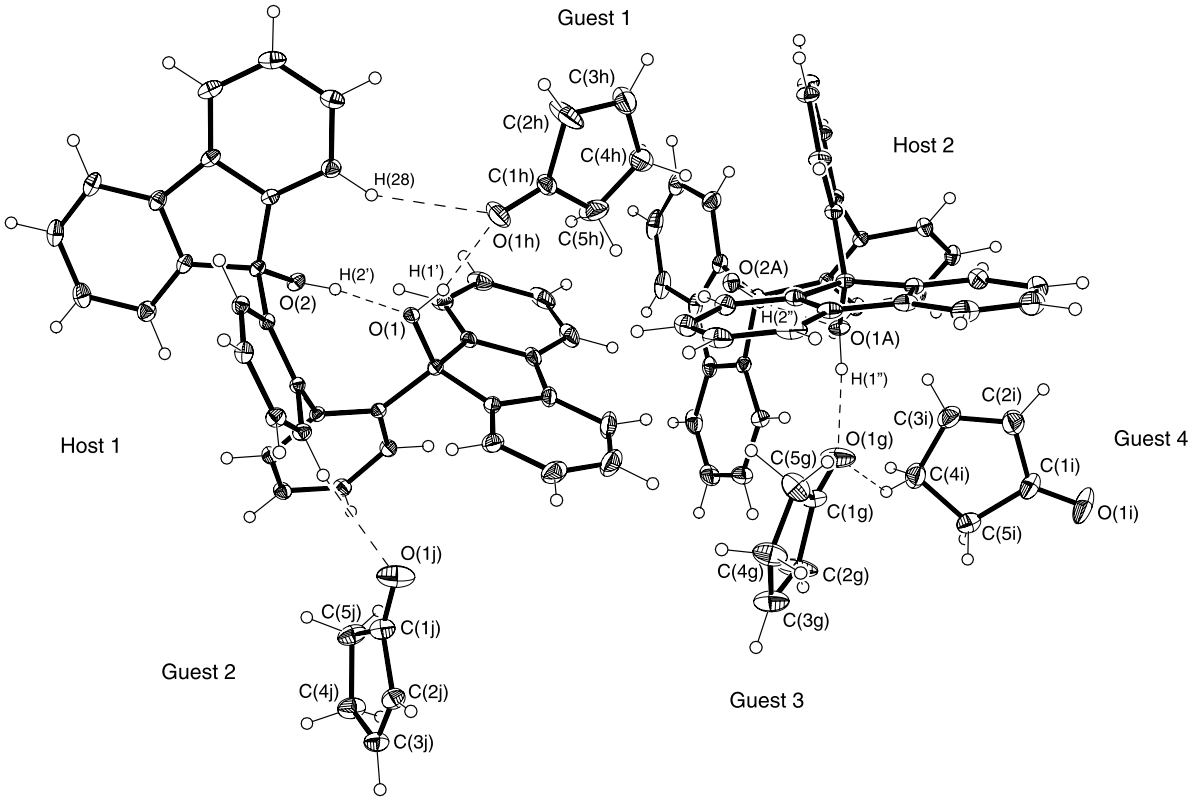

FIGURE 8 Perspective view of the asymmetric unit of the 1:2 inclusion compound of **1** with 2-cyclopenten-1-one (**1d**). Thermal ellipsoids of the non-hydrogen atoms are of 30% probability level. H-bonds are shown by broken lines.

TABLE I Crystallographic and structure refinement data for the inclusion compounds studied (esds are in parentheses)

Compound	**1a**	**1b**	**1c**	**1d**
Empirical formula	$C_{38}H_{26}O_2 \cdot C_4H_{10}O_3$	$C_{38}H_{26}O_2 \cdot C_4H_{13}N_3$	$C_{38}H_{26}O_2 \cdot C_4H_6O_2$	$2\ C_{38}H_{26}O_2 \cdot 4\ C_4H_6O$
Formula weight	620.71	617.76	600.68	1357.56
Crystal system	Triclinic	Monoclinic	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/n$	*P*-1	*Cc*
a (Å)	8.966(2)	11.901(1)	8.487(1)	29.8244(5)
b (Å)	11.655(2)	20.369(3)	16.139(2)	13.2030(2)
c (Å)	17.229(3)	14.694(2)	23.900(3)	18.9782(3)
α(°)	97.60(3)	90.0	88.941(17)	90.0
β(°)	97.37(3)	111.014(7)	87.441(17)	110.959(1)
γ(°)	109.19(3)	90.0	76.628(16)	90.0
V (Å^3)	1656.8(5)	3325.1(7)	3181.6(7)	6978.63(19)
Z	2	4	4	8
F(000)	656	1312	1264	2864
D_c (Mg m^{-3})	1.244	1.234	1.254	1.292
M (mm^{-1})	0.642	0.076	0.080	0.081
Data collection				
Temperature (K)	298(2)	293(2)	293(2)	93(2)
No. of collected reflections	5732	28375	22647	97860
within the θ-limit (°)	2.63–64.97	2.09–25.96	2.13–26.16	1.46–39.06
Index ranges $\pm h, \pm k, \pm l$	0/10, −13/12, −20/20	−14/14, −24/24, −18/18	−10/9, −19/18, −29/29	−51/52, −23/23, −33/30
No. of unique reflections	5356	6278	11626	36676
Refinement calculations: full-matrix least-squares on all F^2 values				
Weighting expression *w*†	$[\sigma^2(F_o^2) + (0.1218P)^2 + 0.000P)]^{-1}$	$[\sigma^2(F_o^2) + (0.0555P)^2 + 0.000P)]^{-1}$	$[\sigma^2(F_o^2) + (0.0225P)^2 + 0.000P)]^{-1}$	$[\sigma^2(F_o^2) + (0.1000P)^2 + 0.0185P)]^{-1}$
No. of refined parameters	424	463	882	947
No. of F values used [$I > 2\sigma(I)$]	2759	4295	3631	28136
Final *R*-Indices				
$R(=\Sigma\lvert\Delta F\rvert/\Sigma\lvert F_o\rvert)$	0.0739	0.0389	0.0568	0.0507
wR on F^2	0.2248	0.0991	0.1071	0.1473
S (= Goodness of fit on F^2)	0.995	0.992	0.820	0.927
Final $\Delta\rho_{max}/\Delta\rho_{min}$ (eÅ^{-3})	0.40/−0.34	0.15/−0.15	0.18/−0.15	0.49/−0.47

† $P = (F_o^2 + 2F_c^2)/3$

TABLE II Selected conformational parameters of the molecule **1** in the inclusion compounds **1a–d**

Compound	**1a**	**1b**	**1c**	**1d**
Torsion angles (°)				
τ_1 [C(14)—C(19)—C(20)—C(21)]	−90.0(5)	−94.4(2)	−92.0(5)	93.6(1)
			93.7(5)	−93.9(1)
τ_2 [O(1)—C(13)—C(14)—C(19)]	23.8(5)	29.5(2)	21.0(5)	−19.1(1)
			−22.7(5)	−16.5(1)
τ_3 [C(20)—C(21)—C(26)—O(2)]	19.4(6)	21.4(2)	28.1(4)	−15.5(1)
			−25.3(5)	18.1(1)
O(1G)—C(1G)—C(2G)—O(2G)	−59.6(7)			
O(2G)—C(3G)—C(4G)—O(3G)	64.2(7)			
C(1G)—C(2G)—O(2G)—C(3G)	175.9(5)			
C(2G)—O(2G)—C(3G)—C(4G)	−169.1(5)			
N(1)—C(1G)—C(2G)—N(2)		66.0(2)		
N(2)—C(3G)—C(4G)—N(3)		−61.4(2)		
C(1G)—C(2G)—N(2)—C(3G)		−177.7(1)		
C(2G)-N(2)-C(3G)-C(4G)		173.0(1)		
O(2G1)—C(1G1)—C(2G1)—C(3G1)			−175.5(6)	
O(2G2)—C(1G2)—C(2G2)—C(3G2)			−164.2(6)	
Dihedral angles (°)				
C(16)—C(19)—C(20)—C(23)	−13.2(3)	−18.0(1)	−9.7(0)	−12.8(3)
C(16A)—C(19A)—C(20A)—C(23A)			5.9(0)	16.9(3)

CONCLUSION

Four inclusion compounds of 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl (**1**) containing diethylene glycol (1:1) (**1a**), bis(2-aminoethyl)amine (1:1) (**1b**), methacrylic acid (1:1) (**1c**) and 2-cyclopenten-1-one (1:2) (**1d**) as guest components were characterized crystallographically. The shielding effect of the extended fluorenyl moieties within the host molecule as well as the presence of an intramolecular hydrogen bond and thus the availabilty of only one strong hydrogen bond donor/acceptor comprise restrictions for intermolecular association. Moreover, imbalances regarding hydrogen bonding abilities of the inclusion components, which are especially evident in the cases of the oligofunctional guest species, may explain why formation of discrete host–guest aggregates are favoured over three dimensional association via hydrogen bonding. In the inclusion structures **1a** and **1b**, compact discrete 2:2 host–guest entities are formed. Regardless of structural similarities of these aggregates,

TABLE III Distances (Å) and angles (°) of hydrogen bond-type interactions of **1a–d**

Atoms involved D—H…A	Symmetry	Distance D…H	Distance D…A	Angle H…A	Angle D—H…A
1a					
O(2)—H(2′)…O(1)	*X, y, z*	0.82	2.755(6)	1.99	155
O(3G)—H(3G′)…O(2)	*1 + x, y, z*	0.82	2.732(6)	2.02	145
O(1G)—H(1G′)…O(3G)	*2 − x, 1 − y, z*	0.82	2.696(5)	1.96	150
C(4)—H(4)…C(33)	*-1 + y, 1 + y, z*	0.93	3.772(6)	2.84	175
1b					
O(2)—H(2′)…O(1)	*X, y, z*	0.92	2.700(2)	1.86	150
O(1)—H(1′)…N(2)	*X, y, z*	0.94	2.695(2)	1.76	170
N(3)—H(31N)…N(1)	*1 − x, y, z*	1.07	3.431(2)	2.38	167
N(2)—H(21N)…N1	*X, y, z*	1.00	2.940(3)	2.64	97
N(2)—H(21N)…N3	*X, y, z*	1.00	2.867(2)	2.36	110
C(35)—H(35)…$\pi_{(1)}$†	*1 + x, y, z*	0.93	3.536(2)	2.63	163
1c					
O(2)—H(2′)…O(1)	*X, y, z*	0.99	2.842(5)	1.90	160
O(1A)—H(1″)…O(2A)	*X, y, z*	0.95	2.869(5)	1.95	165
O(1G1)—H(1G1)…O(2G2)	*X, y, z*	0.93	2.608(5)	1.70	164
O(1G2)—H(1G2)…O(2G1)	*X, y, z*	0.95	2.617(6)	1.67	172
1d					
O(2)—H(2′)…O(1)	*X, y, z*	0.84	2.760(2)	1.96	159
O(2A)—H(2″)…O(2A)	*X, y, z*	0.90	2.803(2)	1.92	167
O(1)—H(1′)…O(1J)	*X, y, z*	0.84	2.731(2)	1.91	161
C(37)—H(37)…O(1J)	*X, y, z*	0.95	3.443(2)	2.58	155
O(1A)—H(1″)…O(1G)	*X, y, z*	0.90	2.693(1)	1.81	166
C(21)—H(21)…O(1H)	*0.5 + x, 0.5 − y, 0.5 + z*	0.95	3.476(2)	2.54	170
C(31)—H(31)…O(1I)	*0.5 + x, −0.5 + y, z*	0.95	3.197(2)	2.50	130
C(31)—H(3I1)…O(1 g)	*0.5 + x, −0.5 + y, z*	0.99	3.314(2)	2.49	140

† Means the center of ring 1 (C1…C6).

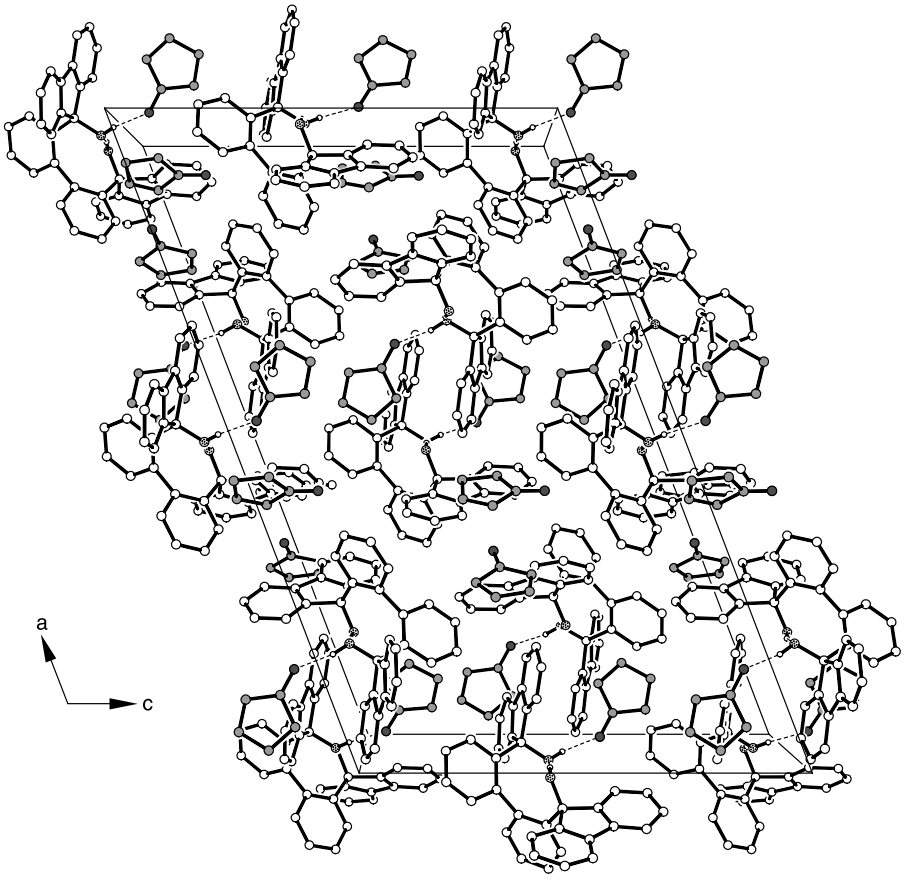

FIGURE 9 Packing diagram of the **1d** crystal. H atoms not involved in H-bonding are omitted for clarity.

their three-dimensional arrangement in the crystal deviate significantly from each other. A different situation is found in the inclusion structure of **1c**. Because of the self-complementarity of binding sites, carboxylic acids tend to form molecular dimers which prevents effective host–guest interaction. The inclusion behaviour of **1** with 2-cyclopenten-1-one seems unexpected because of its 1:2 host–guest stoichiometry. A common feature of the inclusion compounds examined is that their packing structures are controlled by a complex interplay of weak intermolecular interactions between the aromatic building blocks of the host molecules. The distance between arene planes exhibiting an offset parallel arrangement is in the same order of magnitude (3.2–3.6 Å) and therefore can be taken as a criterion for suggesting attractive forces between them.

Thus, even in the presence of oligofunctional and conjugate functional group guest molecules, offering multiple H donor/acceptor ability or other modes of polar interaction due to the conjugation, the host compound **1** basically remains in the well known binding behaviour, previously documented with a great many of monofunctional and apolar guest inclusions [13–19]. Relating to this, only a few exceptions have been found for some of the inclusions of tetrasubstituted analogues of **1** [16]. In these cases, the lack of intramolecular hydrogen bonding between the hydroxyl groups leads to uncoiling of the spiral-like conformation of the host molecule resulting in a bifunctional binding mode for guest molecules, as contrasted with compound **1**. From this particular behaviour of the host compound **1**, one may deduce a helpful parameter for supramolecular inclusion design in future, which may also provide good examples for topochemical photoreactions of guest molecules in inclusion complexes that take place with considerable reorganization of the molecules [25].

EXPERIMENTAL

Synthesis and Sample Preparation

The host compound **1** was synthesized according to the literature procedure [13,14]. Crystals of the inclusion compounds **1a–d** suitable for X-ray investigations were obtained by slow evaporation of solutions of **1** in the respective guest solvent. The selected crystals, although showing mosaicity for **1b** and **1c**, proved to be relatively stable during the period of data collection.

Crystal Structure Determination

The X-ray diffraction data of **1**·diethylene glycol (1:1) (**1a**) were collected on a CAD-4 diffractometer in the $\omega-2\theta$ scan mode ($\lambda_{CuK\alpha} = 1.5418$ Å, graphite monochromator). X-ray intensity data of the inclusion compounds **1**·bis(2-aminoethyl)amine (1:1) (**1b**) and **1**·methacrylic acid (1:1) (**1c**) were collected on a STOE Imaging Plate Diffraction System (IPDS), equipped with a rotating anode, using area detector scans [26]. X-ray diffraction studies of **1**·2-cyclopenten-1-one (1:2) (**1d**) were carried out on a Bruker-AXS APEX II diffractomerter with a CCD area detector ($\lambda_{MoK\alpha} = 0.71073$ Å, graphite monochromator): Frames were collected at $T = 93$ K with ω and ϕ rotation at 10 s per frame. The net intensities were corrected for Lorentz and polarization effects [26–28]. Preliminary structure models were derived by application of direct methods [29] and were refined by full-matrix least squares calculation based on F^2 values for all unique reflections [29]. The non-hydrogen atom positions were refined anisotropically. The carbon-bonded H atoms and the hydroxy hydrogens in **1a** and **1d** were included in the models in calculated positions, whereas the hydroxy, amino and carboxy hydrogen positions in **1b** and **1c** were extracted from difference electron density maps and were held riding on their parent oxygen and nitrogen atoms during subsequent calculations. The crystal data and experimental parameters are summarized in Tables I–III. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 610123 to 610126 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: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.uk).

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