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ORIGINAL ARTICLE

# Crystalline inclusion compounds of new hydroxy hosts featuring a pentaaryl substituted cyclopentadienol framework

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**Abstract** The new host compounds **2** and **3** containing a biphenyl or terphenyl moiety attached to the 1-position of a bulky 2,3,4,5-tetraphenylcyclopentadiene-1-ol building unit have been synthesized. Crystal structures of corresponding inclusion complexes with *n*-hexane (**2a**), DMSO (**2b**) and THF (**3a**) are reported and comparatively discussed involving known inclusion structures of **1**, being the parent of this particular class of host molecules. The structural modification from **1** via **2**–**3** gives rise to distinct changes of the inclusion property concerning molecular assembly and stoichiometric ratio of the crystal components.

**Keywords** Hydroxy hosts · Organic guests · Crystalline inclusion compounds · X-ray crystal structures · Supramolecular interactions

## Introduction

Compounds featuring molecular shape awkwardness encounter difficulties with close-packing in the crystal lattice [1]. Owing to this, they frequently use a secondary molecule as a fill in to avoid the packing problem and hence give rise to the formation of crystalline host–guest inclusion compounds [2, 3]. The shape awkwardness of the host molecule is mostly caused by the concurrence of bulky residues attached to a rigid framework structure [4, 5]. In many cases, functional groups are also present rendering possible stronger binding of the guest molecule and increase of the complexation selectivity [6]. Very often these functional moieties are hydroxyl groups being established by the particular class of hydroxy hosts [7–10]. An individual example of such a host compound is given with formula **1** (Scheme 1) showing a bulky pentaphenyl substituted cyclopentadien-1-ol structure.

Remarkably, although the crystal structures of **1** and of its inclusion complexes with water, methanol, ethanol and DMSO are known for a long time [11, 12], there is no reference indicating further development of the topic. This prompted to synthesize related compounds of this structure type that are **2** [13, 14] and **3** (Scheme 1), i.e. the biphenyl and terphenyl analogous compounds of **1**, and study potential formation of crystalline inclusion complexes. In the present paper, we describe preparation of three inclusion complexes of **2** and **3**, namely **2a** [**2**·*n*-hexane (2:1)], **2b** [**2**·DMSO (1:2)] and **3a** [**3**·THF (1:2)], and report on their crystal structures, including a comparison with the existing structures of the parent compound **1** [11, 12].

## Results and discussion

### Synthesis

The host compounds **2** and **3** were prepared from 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone) and 4-biphenyllithium or 4-(*p*-terphenyl)lithium following a literature procedure [13]. Crystals of the inclusion compounds **2a**, **2b** and **3a** were obtained by slow evaporation of a solution of the respective host compound in the corresponding guest solvent. Details are specified in the "Experimental" section.

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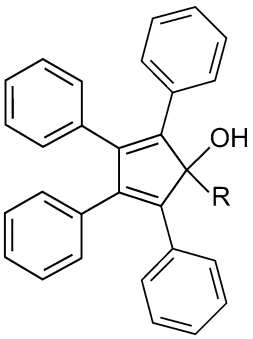


**1** R = Phenyl
**2** R = 4-Biphenylyl
**3** R = 4-*p*-Terphenylyl

**2a** = **2** · *n*-hexane (2:1)
**2b** = **2** · DMSO (1:2)
**3a** = **3** · THF (1:2)

**Scheme 1** Compounds studied in this paper

X-ray structural study

The solid phase structures of the inclusion compounds **2a** [**2**·*n*-hexane (2:1)], **2b** [**2**·DMSO (1:2)] and **3a** [**3**·THF (1:2)] have been determined by X-ray diffraction. Crystallographic data and selected refinement parameters are presented in Table 1. Perspective views of the molecular structures and illustrations of the crystal packings are displayed in Figs. 1, 2, 3, 4, 5, and 6. In order to simplify structural characterization, ring fragments of the host molecules are marked with capital letters in the illustrations of the molecular structures. The conformation can be described by a set of interplanar angles, which define the inclination of the aromatic rings with respect to the plane of the cyclopentadiene ring. These geometrical parameters together with relevant bond distanced are presented in Table 2. Information regarding hydrogen bonding in the crystals are listed in Table 3.

The aromatic rings B–E of the molecules **2** and **3** (Figs. 1, 3, 5) are arranged in a propeller-like fashion around the cyclopentadiene ring, which reduces intramolecular sterical strain. Consequently, restricted conformational freedom is found within these unit as follows from the geometric parameters listed in Table 2. The cyclopentadienyl and the aromatic rings hardly deviate from planarity. Taking into account experimental error, the bond lengths within the $C_5$ ring are similar for the hosts **2** and **3** and range between 1.344(2) and 1.355(2) Å for the double bonds and 1.529(2)–1.540(2) Å for the single bonds. The C(1)–C(30) bond is significantly longer [1.521(2)–1.539(2) Å] than the other bonds between the cyclopentadiene and the phenyl rings which range from 1.475(2) to 1.487(2) Å. These values agree with those found in the reported inclusion structures of the parent compound [11, 12].

Due to the steric crowding around the hydroxy substituent, crystals of this kind of compounds in general require the presence of a second molecular species capable to satisfy the hydrogen bond potential of the host [3, 6] or, in an occasionally successful solvent-free crystal, the molecules are associated only by weak hydrogen bonding [15] such as represented with the crystal structures involving the host compound **1** [11, 12]. Nevertheless, in the case of the solvent free **1**, the molecule can still use the hydroxyl group for weak conventional hydrogen bonding [11]. This, however, does not occur in the inclusion structure of **2** with hexane (2:1) (**2a**), in which the hydroxy hydrogen of the host is without an external strong hydrogen bond acceptor. Instead, a strong intramolecular hydrogen bond [C(7)–H(7)···O(1) 2.32 Å, 127.4°] dictates the position of the hydroxy hydrogen and thus favours formation of an intramolecular O–H···$\pi$ contact [16] with the phenyl ring E acting as an acceptor [O(1)–H(1)···C(29) 2.62 Å, 129.6°] (Fig. 1). Although the parameters of the O–H···$\pi$ interaction are not ideal, the IR analysis with $\tilde{\nu}$= 3,540 $cm^{-1}$ (KBr) for the hydroxyl stretching band provides further evidence of the O–H···$\pi$ contact in the crystal. This behaviour corresponds with the structural and spectroscopic data found for the intramolecular O–H···$\pi$ interactions of crystalline 2,6-diphenylphenol [17] and related 4-nitro-2,6-diarylphenols [18]. To achieve a reasonable hydrogen bond geometry of this interaction in **2a**, an individual carbon atom [C(29)] instead the centre of the aromatic ring was chosen as an acceptor site (cf. Fig. 1). The aromatic rings of the biphenyl part in **2a** are twisted at an angle of 41.2(1)°.

In the crystal structure of **2a** the hexane molecule is located on a symmetry centre at ½, ½, ½. Being unable to form intermolecular contacts, the guest molecule is disordered over three positions with relative site occupancies in the ratio 2:2:1, which indicates a lack of spatial matching between the crystal components. Thus, the structural organization in the crystal of **2a** is mediated by a variety of weak CH···$\pi$ interactions [19] between the aromatic units of the host molecules. As displayed in Fig. 2, the guest molecules are accommodated in channel-like cavities extending in direction of the crystallographic *b*-axis.

Crystallization of **2** from DMSO yields an inclusion compound **2b** of the stoichiometric host:guest ratio 1:2, showing the monoclinic space group $P2_1/n$. The content of the asymmetric cell unit is displayed in Fig. 3. The twist angle between the rings of the biphenyl part is 23.0(1)°; the phenylene ring of this unit is oriented nearly orthogonal with respect to the cyclopentadiene moiety. The oxygen of the

**Table 1** Crystallographic and structure refinement data of the compounds studied

| Compound | **2a** | **2b** | **3a** |
|---|---|---|---|
| Empirical formula | $C_{41}H_{30}O^{\cdot}$ | $C_{41}H_{30}O^{\cdot}$ | $C_{47}H_{34}O^{\cdot}$ |
| | 0.5 $C_6H_{14}$ | 2 $C_2H_6SO$ | 2 $C_2H_8O$ |
| Formula weight | 581.74 | 694.91 | 758.95 |
| Crystal system | Triclinic | Monoclinic | Triclinic |
| Space group | $P-1$ | $P2_1/n$ | $P-1$ |
| $a$ (Å) | 9.9643(3) | 12.1417(7) | 10.2718(3) |
| $b$ (Å) | 10.1346(3) | 21.2276(12) | 10.5248(3) |
| $c$ (Å) | 18.1430(5) | 14.5344(8) | 20.0114(5) |
| α (°) | 79.029(1) | 90.0 | 76.615(1) |
| $\beta$ (°) | 75.200(1) | 97.877(3) | 85.409(1) |
| $\gamma$(°) | 65.864(2) | 90.0 | 81.098(1) |
| $V$ (Å$^3$) | 1,608.84(8) | 3,710.7(4) | 2,077.09(10) |
| $Z$ | 2 | 4 | 2 |
| $F$(000) | 618 | 1472 | 808 |
| $D_c$ (Mg m$^{-3}$) | 1.201 | 1.244 | 1.213 |
| $\mu$ (mm$^{-1}$) | 0.070 | 0.184 | 0.073 |
| Data collection | | | |
| Temperature (K) | 153(2) | 153(2) | 153(2) |
| No. of collected reflections | 35,456 | 45,601 | 51,896 |
| Within the $\theta$-limit (°) | 2.3–27.4 | 1.7–27.1 | 1.1–27.4 |
| Index ranges $\pm h$, $\pm k$, $\pm l$ | −12/12, −13/13, −23/22 | −15/15, −27/25, −18/18 | −13/13, −13/13, −25/25 |
| No. of unique reflections | 7,288 | 8,183 | 9,078 |
| $R_{int}$ | 0.0243 | 0.0659 | 0.0257 |
| Refinement calculations: full-matrix least- squares on all $F^2$ values | | | |
| Weighting expression $w$[a] | $[\sigma^2(F_o^2) + (0.0868P)^2 + 0.5278P)]^{-1}$ | $[\sigma^2(F_o^2) + (0.0688P)^2 + 0.8589P)]^{-1}$ | $[\sigma^2(F_o^2) + (0.0854P)^2 + 0.4874P)]^{-1}$ |
| No. of refined parameters | 429 | 455 | 528 |
| No. of $F$ values used [$I > 2\sigma(I)$] | 5,932 | 6,088 | 7,220 |
| Final $R$-Indices | | | |
| $wR$ on $F^2$ | 0.1505 | 0.1264 | 0.1449 |
| $S$ (=Goodness of fit on $F^2$) | 1.024 | 1.022 | 1.050 |
| Final $\Delta\rho\rho_{max}/\Delta\rho_{min}$ (e Å$^{-3}$) | 0.38/−0.33 | 0.72/−0.62 | 0.33/−0.31 |

[a] $P = (F_o^2 + 2F_c^2)/3$

disordered solvent molecule is associated to the hydroxy hydrogen of the host via O–H···O bonding [$d$(O···O) 2.685(2), 2.747(2) Å] and takes part in coordination to an arene hydrogen of a second host molecule [C(21)–H(21)···O(1H)/O(1HA) 2.65/2.38 Å, 168.9/169.8°]. In a similar fashion, the oxygen atom of the second DMSO molecule acts as bifurcated acceptor and is involved in host–guest interaction [C(15)–H(15)···O(1G) 2.58 Å, 176.2°] as well as in association to a symmetry related guest molecule [C(2G)–H(2G3)···O(1G) 2.61 Å, 145.9°] thus forming a centrosymmetric dimer.

According to the given pattern of hydrogen bonding, the crystal structure of **2b** (Fig. 4) can be regarded as being composed of molecular associates consisting of two O–H···O bonded (1:1) host–guest units which are linked to a cyclic dimer of guest molecules via C–H···O hydrogen bonding. The host lattice is dominated by aromatic edge-to-face interactions [20]. A comparative examination of the inclusion structure of **2b** with the corresponding DMSO complex of compound **1** [11], which crystallizes also in the space group $P2_1/n$, reveals different host:guest stoichiometries. The crystal structure of the latter complex is composed of discrete O–H···O bonded (1:1) host–guest pairs, i.e. the acidic hydrogens of the solvent molecule are excluded from coordination. The packing of the host in **1**·DMSO is characterized by stacking of aromatic building units along the $b$-axis.

Similar structural features are also found in the inclusion compound of **3** with THF (1:2), although it crystallizes in the triclinic space group $P-1$ with the cell unit containing one host molecule and two molecules of solvent. The

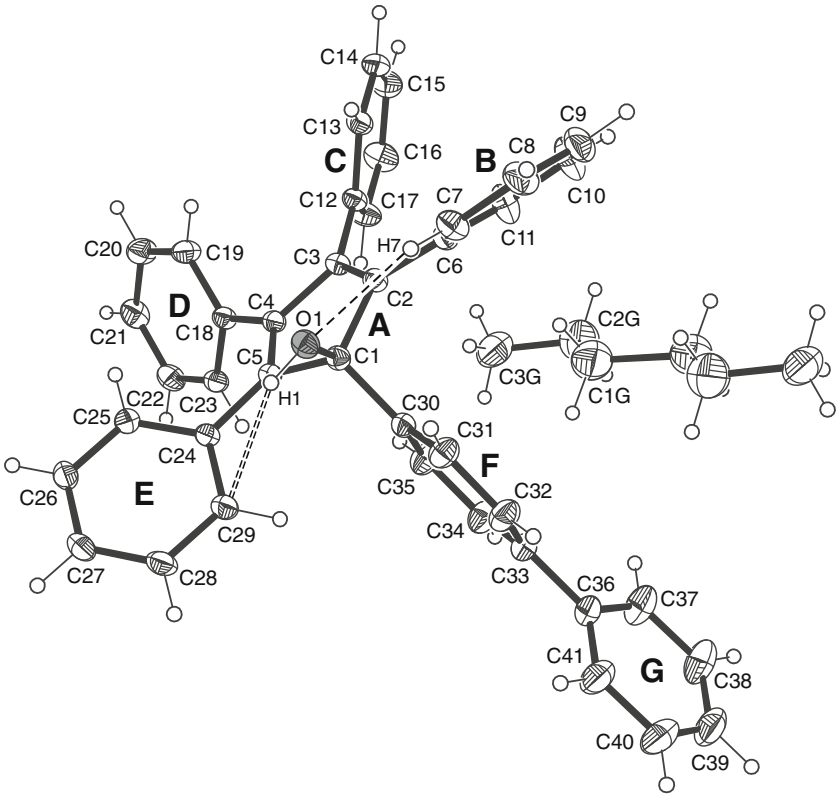


**Fig. 1** ORTEP plot of **2**·*n*-hexane (2:1) (**2a**), including the atom numbering scheme of non-hydrogen atoms. Thermal ellipsoids are drawn at 40% probability level. The hydrogen bond interaction is marked as *broken line* while the *broken double line* represents the intramolecular O–H···$\pi$ hydrogen bond

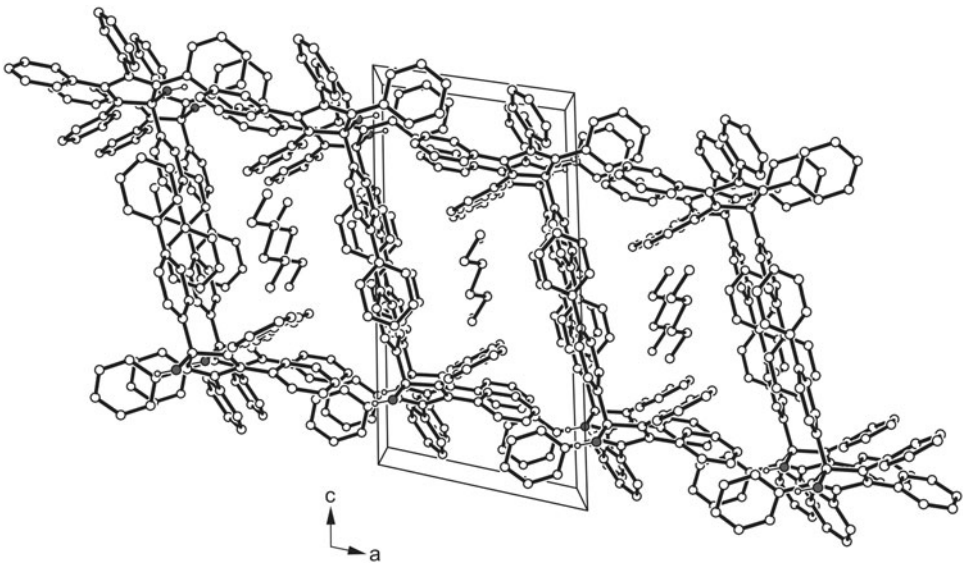


**Fig. 2** Packing diagram of **2a** viewed down the crystallographic *b*-axis. With exception of the hydroxy hydrogen all other hydrogen atoms are omitted for clarity. Oxygen atoms are *shaded*. Only one position of the disordered solvent molecule is displayed

stoichiometric unit of the complex is shown in Fig. 5. The aromatic rings of the terphenyl part of the host are twisted in the same direction at angles of 32.9(1) (rings F/G) and 43.4(1)° (rings G/H). Ring F of this unit is oriented nearly orthogonal with respect to the plane of the $C_5$ ring. One of the solvent molecules is coordinated by its disordered oxygen atom via O–H···O bonding with the hydroxy hydrogen of the host [O(1)–H(1)···O(1G)/O(1GA) 2.01, 1.98 Å, 174.2, 151.3°]. The oxygen atom of the second guest molecule is coordinated in an unsymmetric fashion by C–H···O bonding to two neighbouring host molecules [*d*(H···O) 2.53, 2.77 Å], while one of the acidic hydrogens of this guest is connected to the oxygen of a further host molecule [C(3H)–H(3H2)···O(1) 2.65 Å, 135.9°].

The crystal structure of **3a** is characterized by a stacking-like arrangement of host molecules in direction of the *b*-axis. As depicted in Fig. 6, the host lattice contains cavities each occupied with a pair of guest molecules. The environment of the first solvent component which is firmly bound within the crystal lattice is given by the bulky parts

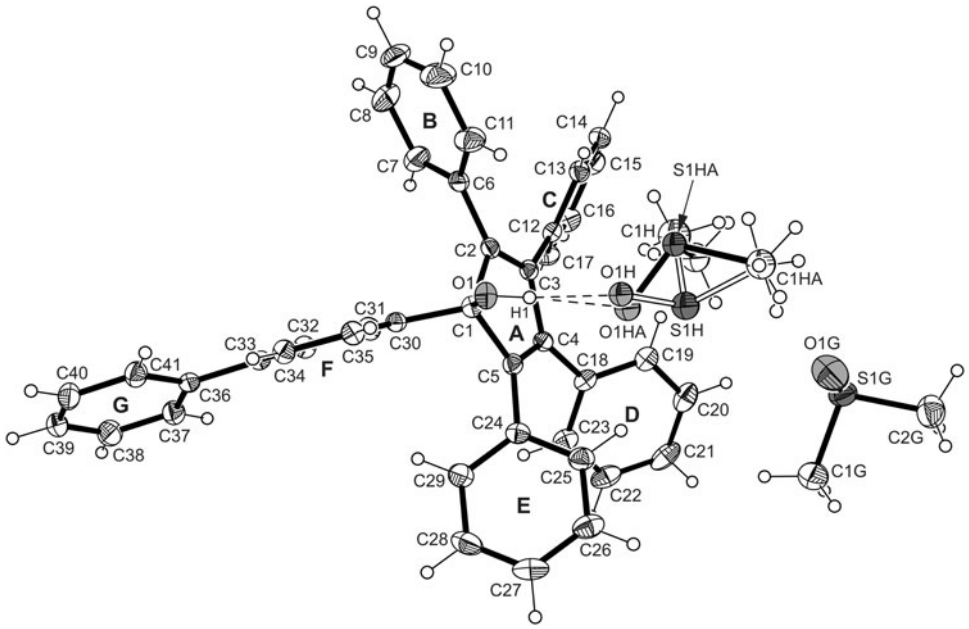


**Fig. 3** ORTEP plot of the stoichiometric unit of **2**·DMSO (1:2) (**2b**), including the atom numbering scheme of non-hydrogen atoms. Broken lines represent hydrogen bond type interactions. The two disordered positions of the coordinated solvent molecule are marked by *different bond types*. Thermal ellipsoids are drawn at 40% probability level

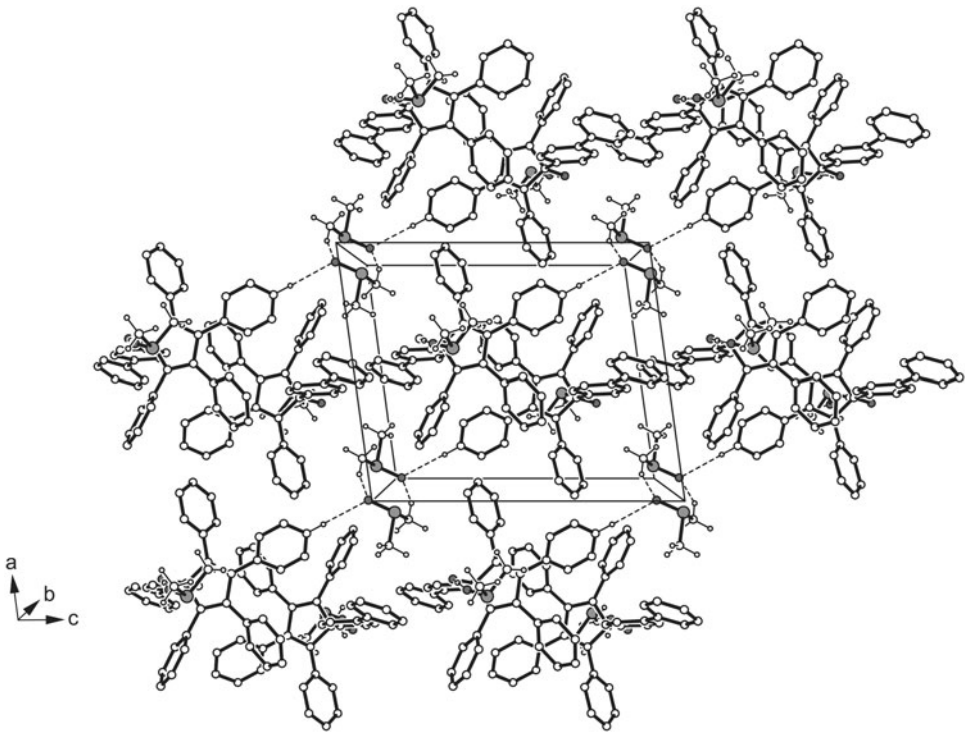


**Fig. 4** Packing structure of **2b** viewed down the *b*-axis. Only the host hydrogens involved in H bonding are depicted for clarity. Heteroatoms are *shaded*. *Broken lines* represent hydrogen bond type interactions

of four host molecules, while pairs of the second solvent component are included in cavities defined by the terphenyl fragments of six host molecules.

## Conclusion

Compounds featuring a 'wheel-and-axle' geometry [10, 21, 22] have proven efficient hosts for crystalline inclusion formation. In a sense, the pentaaryl substituted cylcopentadiene derivatives **1**–**3** are related to this type of host structure as they comprise a variable narrow element attached to a bulky pentacyclic fragment corresponding to one half a of 'wheel-and-axle' molecule. According to this structural relationship, compounds of this particular type are expected to form crystalline inclusions, which has previously been shown with compound **1** as the parent of this substance class [11, 12]. Modification of the phenyl group in the 1-position of the compound **1** to give the biphenyl and terphenyl analogous compounds **2** and **3**, respectively,

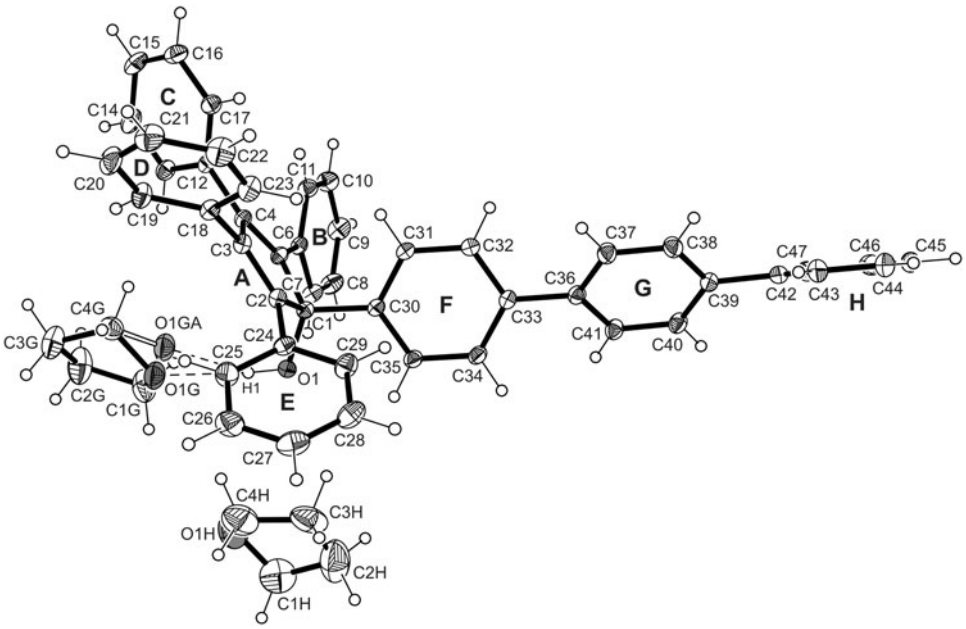


**Fig. 5** ORTEP plot of the stoichiometric unit of **3**·THF (1:2) **3a**, including the atom numbering scheme of non-hydrogen atoms. *Broken lines* represent hydrogen bond type interactions. The two disordered oxygen positions of the coordinated solvent molecule are marked by *different bond types*. Thermal ellipsoids are drawn at 40% probability level

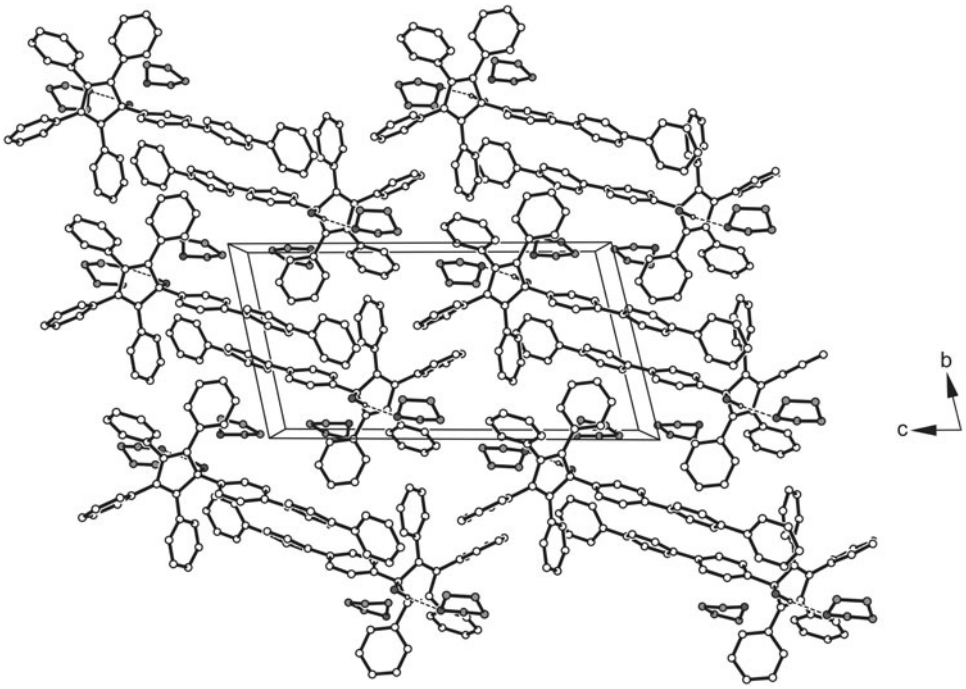


**Fig. 6** Packing structure of **3a** viewed down the *a*-axis. Only the host hydrogens involved in H bonding are depicted for clarity. Heteroatoms are *shaded*. *Broken lines* represent hydrogen bond type interactions

causes an increase of the bulk in the molecule and thus gives rise to distinct changes of the inclusion behaviour, involving both the molecular assembly in the crystal and the stoichiometric ratio of the crystal components.

The reported inclusion structures of **1** exclusively contain polar solvents, namely $H_2O$, DMSO, MeOH and EtOH [11, 12]. Their crystals are composed of discrete O–H···O bonded 1:1 host–guest units, showing poor association among one another. Introduction of the more extended biphenyl and terphenyl units attached to C1 of the five-membered ring creates an enlarged number of weak donor- and acceptor sites which promote formation of multiple intermolecular CH···$\pi$ contacts and/or arene stacking. Interactions of this type as well as the irregular molecular geometry favour a packing structure with an antiparallel arrangement of neighbouring host molecules. This is realized in the present inclusion structures of **2** and **3**, most perceptible with the **2**·*n*-hexane (2:1) inclusion compound **2a**. Due to the hydrophobic nature of the solvent molecule, the hydroxy hydrogen of the alcoholic host is used for intramolecular

**Table 2** Selected structural parameters of the host molecules **2** and **3** in their inclusion structures

| Compound | **2a** | **2b** | **3a** |
|---|---|---|---|
| Interplanar angles (°)[a] | | | |
| A/B | 37.9(1) | 63.0(1) | 33.7(1) |
| A/C | 52.1(1) | 47.7(1) | 54.9(1) |
| A/D | 51.8(1) | 48.6(1) | 59.8(1) |
| A/E | 36.3(1) | 62.7(1) | 58.0(1) |
| A/F | 83.3(1) | 89.7(1) | 89.2(1) |
| F/G | 41.2(1) | 23.0(1) | 32.9(1) |
| G/H | | | 43.4(1) |
| Bond lengths (Å) | | | |
| C(1)–C(2) | 1.531(2) | 1.534(2) | 1.540(2) |
| C(1)–C(5) | 1.529(2) | 1.533(2) | 1.532(2) |
| C(1)–C(30) | 1.539(2) | 1.525(2) | 1.521(2) |
| C(2)–C(3) | 1.355(2) | 1.349(2) | 1.353(2) |
| C(2)–C(6) | 1.482(2) | 1.483(2) | 1.472(2) |
| C(3)–C(4) | 1.492(2) | 1.501(2) | 1.495(2) |
| C(3)–C(12) | 1.481(2) | 1.478(2) | 1.480(2) |
| C(4)–C(5) | 1.350(2) | 1.344(2) | 1.347(2) |
| C(4)–C(18) | 1.481(2) | 1.484(2) | 1.483(2) |
| C(5)–C(24) | 1.475(2) | 1.487(2) | 1.478(2) |
| C(33)–C(36) | 1.493(2) | 1.488(2) | 1.484(2) |
| C(39)–C(42) | | | 1.484(2) |
| Bond angles (°) | | | |
| C(1)–C(2)–C(3) | 108.5(1) | 109.8(1) | 109.1(1) |
| C(2)–C(3)–C(4) | 109.8(1) | 108.8(1) | 109.4(1) |
| C(3)–C(4)–C(5) | 109.2(1) | 109.6(1) | 109.6(1) |
| C(4)–C(5)–C(1) | 109.1(1) | 109.6(1) | 109.4(1) |
| C(5)–C(1)–C(2) | 103.1(1) | 102.2(1) | 102.5(1) |

[a] Means angle between the best plane through atoms of the rings. Ring A: C(1)…C(5), ring B: C(6)…C(11), ring C: C(12)…C(17), ring D: C(18)…C(23), ring E: C(24)…C(29), ring F: C(30)…C(35), ring G: C(36)…C(41), and ring H: C(42)…C(47)

O–H···π(arene) bonding, while the oxygen is involved in a strong intramolecular C–H···O hydrogen bond. This may explain the high degree of dynamic disorder of the solvent within the channel-like cavity structure of the host lattice. The elongated geometry of **2** and **3** involves also a higher ratio of crystal solvent, which is reflected by the 1:2 host–guest stoichiometry of **2b** and **3a**. As expected, in each of the structures one of the solvent molecules is tightly connected to the host via O–H···O bonding, whereas the second, weakly bonded solvent component occupies the lattice voids left by the 1:1 host–guest entities.

On general inspection of the new inclusion structures, one may gain the impression that the host molecules assemble to pairs via specific interaction of the modifying aromatic moiety imitating a 'wheel-and-axle' host geometry similar to the transition metal [23] and carboxylic dimer [24] mediated mimicries of wheel-and-axle hosts. Hence, it is shown that modification of **1** along the lines of **2** and **3**, or potentially otherwise, is a promising approach to open a new versatile class of inclusion hosts being easily to vary in structure and producible at low cost.

## Experimental

### General

Melting points (uncorrected) were determined using a microscope heating stage PHMK Rapido (Wägetechnik Dresden). IR spectra were measured on a Nicolet FT-IR 510 as KBr pellets. $^{1}$H and $^{13}$C NMR spectra were recorded on a Bruker Avance DPX 400 at 400 and 100 MHz, respectively, using TMS as reference. MS spectra were obtained from Hewlett Packard 5890II/MS 5989A (GC MS) and Micromass Zabspec (FAB MS) instruments. Elemental analyses were performed on a Heraeus CHN rapid analyzer. All solvents were purified by standard procedures [25].

4-Bromobiphenyl was purchased from Fluka, 4-bromo-*p*-terphenyl was prepared as described in the literature [26].

### Synthesis of host compounds **2** and **3**: general procedure

Tetracyclone (2.88 g, 7.50 mmol) was added (at the beginning as a solid and after that as a solution in dry toluene) to a stirred solution of the corresponding organyllithium compound (8.65 mmol), prepared from the respective aryl bromide (8.65 mmol) and *n*-BuLi (1.6 M in hexane 6.25 mL, 10 mmol) in dry diethylether (10 mL), at room temperature under argon. Stirring of the mixture was continued until completeness of the reaction, which is indicated by bleaching of the black–violet colour of the tetracyclone, then quenched with water and acidified (diluted hydrochloric acid). The organic layer was separated, filtered and dried ($Na_2SO_4$). The layer was concentrated on evaporation of solvent to about 10% of its volume. Petroleum ether (90–100 °C) was added to precipitate the crude product, which was collected and recrystallized from petroleum ether. Details for the individual compounds are given below.

### 1-Biphenylyl-2,3,4,5-tetraphenylcyclopentadiene-1-ol (**2**)

4-Bromobiphenyl (2.02 g, 8.65 mmol) was used to yield 2.4 g (52%) of a colourless powder. Mp: 212–215 °C (lit. [13] mp: 214–216 °C). IR (KBr) $\tilde{\nu}$, cm$^{-1}$: 3,550 (O–H), 3,084, 3,053, 3,028 (Ar–H), 1,629, 1,600 (C=C), 1,486, 1,440, 1,078 (C–O), 809 (Ar, 1,4-disubst.), 757, 700 (Ar, monosubst.). $^{1}$H NMR ([D$_6$] DMSO) $\delta$, ppm: 6.41 (s, 1 H, O*H*), 6.97–7.18 (m, 20 H, Ar–*H*), 7.29–7.65 (m, 9 H,

**Table 3** Parameters of possible hydrogen-bond type interactions in **2a**, **2b** and **3a**

| Atoms involved | Symmetry | Distances (Å) | | Angles (°) |
|---|---|---|---|---|
| | | D···A | H···A | D–H···A |
| **2a** | | | | |
| O(1)–H(1)···C(29)[a] | *x*, *y*, *z* | 3.223(3) | 2.58 | 132.1 |
| C(7)–H(7)···O(1) | *x*, *y*, *z* | 2.997(3) | 2.32 | 127.5 |
| C(7)–H(7)···C(22)[a] | *x*, $-1 + y$, *z* | 3.620(3) | 2.86 | 138.1 |
| C(13)–H(13)···C(27)[a] | $-1 + x$, *y*, *z* | 3.703(3) | 2.89 | 144.3 |
| C(19)–H(19)···C(27)[a] | $2 - x$, $1 - y$, $-z$ | 3.699(3) | 2.82 | 154.0 |
| **2b** | | | | |
| O(1)–H(1)···O(1H) | *x*, *y*, *z* | 2.747(2) | 1.91 | 171.8 |
| O(1)–H(1)···O(1HA) | *x*, *y*, *z* | 2.685(2) | 1.86 | 166.6 |
| C(1G)–H(1G2)···O(1) | $0.5 + x$, $0.5 - y$, $-0.5 + z$ | 3.622(3) | 2.64 | 176.0 |
| C(14)–H(14)···O(1H) | $-0.5 + x$, $0.5 - y$, $-0.5 + z$ | 3.525(3) | 2.60 | 170.7 |
| C(21)–H(21)···O(1H) | $0.5 + x$, $0.5 - y$, $-0.5 + z$ | 3.589(3) | 2.65 | 169.8 |
| C(21)–H(21)···O(1HA) | $0.5 + x$, $0.5 - y$, $-0.5 + z$ | 3.321(3) | 2.38 | 168.9 |
| C(15)–H(15)···O(1G) | $-0.5 + x$, $0.5 - y$, $-0.5 + z$ | 3.523(3) | 2.58 | 176.2 |
| C(2G)–H(2G3)···O(1G) | $2 - x$, $1 - y$, $-z$ | 3.470(3) | 2.61 | 145.9 |
| C(10)–H(10)···C(27)[a] | $-1 + x$, *y*, *z* | 3.731(3) | 2.80 | 165.9 |
| C(13)–H(13)···C(39)[a] | $1.5 - x$, $0.5 + y$, $0.5 - z$ | 3.693(3) | 2.87 | 144.9 |
| C(32)–H(32)···C(20)[a] | $2 - x$, $-y$, $-z$ | 3.760(3) | 2.86 | 159.1 |
| C(34)–H(34)···C(34)[a] | $2 - x$, $-y$, $1 - z$ | 3.398(3) | 2.77 | 124.3 |
| **3a** | | | | |
| O(1)–H(1)···O(1G) | *x*, *y*, *z* | 2.846(2) | 2.01 | 174.2 |
| O(1)–H(1)···O(1GA) | *x*, *y*, *z* | 2.751(2) | 1.98 | 151.3 |
| C(3H)–H(3H2)···O(1) | *x*, $-1 + y$, *z* | 3.433(3) | 2.65 | 135.9 |
| C(23)–H(23)···O(1H) | $-1 + x$, $1 + y$, *z* | 3.267(3) | 2.53 | 134.9 |
| C(46)–H(46)···O(1H) | $1 - x$, $-y$, $-z$ | 3.540(3) | 2.77 | 138.8 |
| C(7)–H(7)···C(47)[a] | $1 - x$, $1 - y$, $-z$ | 3.545(3) | 2.79 | 137.0 |
| C(21)–H(21)···C(15)[a] | $1 - x$, $2 - y$, $1 - z$ | 3.630(3) | 2.86 | 138.9 |
| C(27)–H(27)···C(41)[a] | *x*, $1 + y$, *z* | 3.810(3) | 2.89 | 162.5 |
| C(14)–H(14)···*centroid* ring(B)[b] | $1 - x$, $1 - y$, $1 - z$ | 3.561(3) | 2.74 | 144.7 |
| C(32)–H(32)···*centroid* ring(H)[b] | $-x$, $1 - y$, $-z$ | 3.505(3) | 2.72 | 140.2 |

[a] In order to achieve reasonable hydrogen bond geometries, individual carbon atoms instead of ring entries were chosen as acceptors

[b] Means centre of the aromatic ring. Ring A: C(1)…C(5), ring B: C(6)…C(11), ring C: (12)…C(17), ring D: C(18)…C(23), ring E: C(24)…C(29), ring F: C(30)…C(35), ring G: C(36)…C(41), and ring H: C(42)…C(47)

Ar–*H*). $^{13}$C NMR ([$D_6$] DMSO) $\delta$, ppm: 89.4 (*C*–O), 125.6–184.5 (*C*=*C*, Ar–*C*). MS (GC) *m/z*: 538 ($M^+$). Anal, calcd for $C_{41}H_{30}O$: C 91.42, H 5.61; found C 91.20, H 5.73.

### 1-Terphenylyl-2,3,4,5-tetraphenylcyclopentadiene-1-ol (**3**)

4-Bromoterphenyl (2.67 g, 8.65 mmol) was used to yield 1.5 g (28%) of a colourless powder. Mp: 228–231 °C. IR (KBr) $\tilde{\nu}$, $cm^{-1}$: 3,550 (O–H), 3,084, 3,053, 3,033 (Ar–H), 1,631, 1,605 (C=C), 1,498, 1,484, 1,440, 1,078 (C–O), 832, 803 (Ar, 1,4-disubst.), 762, 747, 700 (Ar, monosubst.). $^1$H NMR ([$D_6$] DMSO) $\delta$, ppm: 6.41 (s, 1 H, O*H*), 6.98–7.18 (m, 20 H, Ar–*H*), 7.35–7.77 (m, 13 H, Ar–*H*). $^{13}$C NMR ([$D_6$] DMSO) $\delta$, ppm: 89.7 (*C*–O), 126.0–148.8 (*C*=*C*, Ar–*C*). MS (FAB) *m/z*: 615 ($M^+$). Anal calcd for $C_{47}H_{34}O$: C 91.82, H 5.57; found C 91.68, H 5.45.

### Preparation of inclusion compounds

Single crystals of the inclusion compounds **2a**, **2b** and **3a** were obtained from solutions of the corresponding host compounds (**2** and **3**) in the respective guest solvents (*n*-hexane, DMSO, THF) and subsequent slow evaporation at room temperature.

X-ray crystallography

Intensity data were collected on a Bruker Kappa APEX II diffractometer with $MoK_\alpha$ radiation ($\lambda = 0.71073$ Å) using $\omega$ and $\varphi$ scans. Reflections were corrected for Lorentz and polarization effects. Preliminary structure models were derived by application of direct methods [27] and were refined by full-matrix least squares calculation based on $F^2$ for all reflections [27]. All hydrogens were included in the models in calculated positions and were refined as constrained to the bonding atoms. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Centre as supplementary publication numbers CCDC 777314–CCDC 777316 copies of data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

## References


1. Kitaigorodsky, A.I.: Molecular Crystals and Molecules. Academic Press, New York (1973)
2. Nangia, A.: Organic host–guest structures in the solid state. In: Lu, G.Q., Zhao, X.S. (eds.) Nanoporous Materials, pp. 165–187. Imperial College Press, London (2004)
3. Desiraju, G.R.: Review of general principles. In: MacNicol, D.D., Toda, F., Bishop, R. (eds.) Comprehensive Supramolecular Chemistry. Solid-state Supramolecular Chemistry: Crystal Engineering, vol. 6, pp. 1–22. Pergamon (Elsevier), Oxford (1996)
4. Weber, E.: Scissor-type hosts: molecular design and inclusion behaviour. In: Atwood, J.L., Davies, J.E.D., MacNicol, D.D. (eds.) Inclusion Compounds. Key Organic Host Systems, vol. 4, pp. 188–262. Oxford University Press, Oxford (1991)
5. Weber, E.: Shape and symmetry in the design of new hosts. In: MacNicol, D.D., Toda, F., Bishop, R. (eds.) Comprehensive Supramolecular Chemistry. Solid-state Supramolecular Chemistry: Crystal Engineering, vol. 6, pp. 535–592. Pergamon (Elsevier), Oxford (1996)
6. Weber, E., Czugler, M.: Functional group assisted clathrate formation-scissor-like and roof-shaped host molecules. In: Weber, E. (ed.) Molecular Inclusion and Molecular Recognition-Clathrates II. Topics in Current Chemistry, vol. 149, pp. 45–135. Springer-Verlag, Berlin (1988)
7. Toda, F.: Diol, bisphenol, and diamide host compounds. In: MacNicol, D.D., Toda, F., Bishop, R. (eds.) Comprehensive Supramolecular Chemistry: Crystal Engineering, pp. 465–516. Pergamon (Elsevier), Oxford (1996)
8. Bishop, R.: Designing new lattice inclusion hosts. Chem. Soc. Rev. **25**, 311–319 (1996)
9. Jacobs, A., Masuku, N.L.Z., Nassimbeni, L.R., Taljaard, J.H.: Inclusion of pyridine and acetone by a diol host: structure, thermal stability and kinetics of desolvation. CrystEngComm **10**, 322–326 (2008)
10. De Vries, E.J.C., Nassimbeni, L.R., Weber, E.: Inclusion of amides by a fluorenyl diol host. J. Incl. Phenom. Macrocycl. Chem. **63**, 203–210 (2009)
11. Bourne, S.A., Nassimbeni, L.R., Niven, M.L., Modro, A.M.: Complexation with hydroxy host compounds, part 5. Structures and thermal analyses of 1,2,3,4,5-pentaphenylcyclopenta-2,4-dien-1-ol and its inclusion compounds with water and dimethylsulphoxide. J. Incl. Phenom. Mol. Recogn. Chem. **13**, 301–310 (1992)
12. Bourne, S.A., Nassimbeni, L.R., Niven, M.L.: Inclusion compounds of hydroxy hosts. 6. Structures and thermal analysis of 1,2,3,4,5-pentaphenylcyclopenta-2,4-dien-1-ol with methanol and ethanol. J. Phys. Org. Chem. **5**, 769–775 (1992)
13. Broser, W., Siegle, P., Kurreck, H.: Unsymmetrisch *p*-methyl- und *p*-phenyl-substituierte Pentaphenylcyclopentadienyl-Kationen und-Radikale. Chem. Ber. **101**, 69–83 (1968)
14. Oldaker III, G.B., Perfetti, T.A., Ogliaruso, M.A.: Reactions of polyarylated carbinols, 6. Kinetics of the thermal [1,5] sigmatropic phenyl and para-substituted-phenyl rearrangements in 3,4-bis[*p*-substituted-phenyl]-1,2,5-triphenyl-2,4-cyclopentadien-1-ols and 1-[*p*-substituted-phenyl]-2,3,4,5-tetraphenyl-2,4-cyclopentadien-1-ols. J. Org. Chem. **45**, 3910–3912 (1980)
15. Skobridis, K., Theodorou, V., Seichter, W., Weber, E.: Conflicting behavior of a versatile host compound: X-ray crystal structures arising from solvent-free and solvent-containing crystal formation. Cryst. Growth Des. **10**, 862–869 (2010)
16. Desiraju, G.R., Steiner, T.: The Weak Hydrogen Bond. Oxford University Press, New York (1999)
17. Nakatsu, K., Yoshioka, H., Kunimoto, K.: 2,6-Diphenylphenol: a structure containing an intramolecular O-H···$\pi$ hydrogen bond. Acta Crystallogr. **B34**, 2357–2359 (1978)
18. Kurjatschij, S., Seichter, W., Weber, E.: Synthesis and structures of crystalline solvates formed of pyridium *N*-phenoxide (Reichardt's-type) betaine dyes and alcohols. New J. Chem. **34**, 1465–1477 (2010)
19. Nishio, M.: CH/$\pi$ hydrogen bonds in crystals. CrystEngComm **6**, 130–158 (2004)
20. Dance, I.: $\pi$-$\pi$ Interactions: theory and scope. In: Atwood, J.L., Steed, J.W. (eds.) Encyclopedia of Supramolecular Chemistry, pp. 1076–1092. CRC Press, Boca Raton (2004)
21. Toda, F.: Inclusion by acetylenic alcohols and some other novel host compounds. In: Atwood, J.L., Davies, J.E.D., MacNicol, D.D. (eds.) Inclusion Compounds. Key Organic Host Systems, vol. 4, pp. 126–187. Oxford University Press, Oxford (1991)
22. Weber, E., Nitsche, S., Wierig, A., Csöregh, I.: Inclusion compounds of diol hosts featuring two 9-hydroxy-9-fluorenyl or analogous groups attached to linear spacer units. Eur. J. Org. Chem. 856–872 (2002)
23. Bacchi, A., Bosetti, E., Carcelli, M.: Engineering organic/inorganic diols that reversibly capture and release volatile guests. CrystEngComm **7**, 527–537 (2005)
24. Jetti, R.K.R., Kuduva, S.S., Reddy, D.S., Xue, F., Mak, T.C.W., Nangia, A., Desiraju, G.R.: 4-(Triphenylmethyl)benzoic acid: a supramolecular wheel-and-axle host compound. Tetrahedron Lett. **39**, 913–916 (1998)
25. Leonard, J., Lygo, B., Procter, G.: Praxis der Organischen Chemie, pp. 53–68. VCH, Weinheim (1994)
26. Braun, J.V., Irmisch, G., Nelles, J.: Synthesen in der Di- und Terphenylreihe. Ber. Dtsch. Chem. Ges. **66B**, 1471–1483 (1933)
27. Sheldrick, G.M.: A short history of SHELX. Acta Crystallogr. **A64**, 112–122 (2008)