Complexation with Diol Host Compounds. Part 10.[1] Synthesis and Solid State Inclusion Properties of Bis(diarylhydroxymethyl)-substituted Benzenes and Biphenyls; X-Ray Crystal Structures of Two Host Polymorphs and of a Non-functional Host Analogue

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A new family of host molecules where the molecular axis of usual 'wheel-and-axle' compounds is replaced by aromatic units is described. These diol hosts form crystalline inclusions with a variety of uncharged organic molecules mainly of a polar nature (53 different species). The formation and stoichiometry depend in a systematic manner on structural parameters of the host allowing these hosts to be more selective than the parent compounds. Non-hydroxylic analogues do not function as host molecules. The crystal structures of two polymorphs of host compound **2** and of the inefficient compound **9** have been studied. Crystal data: **2** (polymorph α_1), monoclinic, $C2/c$, $a = 16.827(2)$, $b = 15.212(3)$, $c = 10.708$ Å, $\beta = 97.01(1)°$, $V = 2721$ Å^3, $Z = 4$; **2** (polymorph α_2), triclinic, $P\bar{1}$, $a = 8.807(2)$, $b = 10.687(6)$, $c = 16.263(3)$ Å, $\alpha = 100.97(3)°$, $\beta = 91.47(2)°$, $\gamma = 113.02(3)°$, $V = 1375$ Å^3, $Z = 2$; **9**, monoclinic, $P2_1/n$, $a = 12.781(3)$, $b = 7.773(2)$, $c = 28.405(17)$ Å, $\beta = 103.01°$, $V = 2749$ Å^3, $Z = 4$. Alignment of the axis of the molecular backbones was observed in all structures. Formation of host–host hydrogen bonds in the case of the α_2-polymorph of **2** resulted in a *gauche* conformation of the hydroxy moieties unlike the α_1-polymorph of **2** which is *anti*. The packing factors are 17.00, 17.18 and 18.09 Å^3 per non-hydrogen atom for **2** (α_1), **2** (α_2) and **9**, respectively.

Lattice-assisted inclusion compounds (clathrates) and crystalline complexes[2] are important topics of supramolecular chemistry[3] owing to their great promise in future technologies.[4] These co-crystalline systems consist of complementary chemical species, generally designated as host and guest molecule. The host component provides the nesting place or the binding site to the guest molecule, thus enabling selective co-crystallization. Therefore, the development of host molecules is a prime target.[2] Although *a priori* design of a co-crystalline structure still poses insurmountable problems,[5] there are some useful guidelines for the design of host molecules. These include a rigid basic framework, bulky substituents, strategically positioned functional groups and symmetry relations.[6]

Characteristic examples are the scissor-type,[6,7] the roof-shaped[6,8] or the small ring[9] dicarboxylic host molecules. Another important class of compounds following these principles and having a particular shape are the dog-bone- or wheel-and-axle-type diol host molecules (Fig. 1, **I**).[10] Normally they consist of a linear mono- or di-ethynylene central unit (A^1) and two bulky diarylmethanol terminal groups (B).[11] Host compounds of this type include a wide variety of guest molecules and provide a crystalline reaction framework for appropriately oriented guests.[11,12] In the crystal phase, the concave sites along the molecular axis may be occupied either by a convex fragment of an adjacent host molecule, or else by a complementary shaped guest molecule with which the host co-crystallizes.[11,13] In line with the 'coordination-assisted' clathrate tenet,[6] the hydroxy groups act as H bond sites for the guest, as well as encouraging host–host interaction, thus achieving high inclusion selectivity.[11,13] Enhanced inclusion ability is obtained owing to the larger voids created by bulky terminal groups.[11] On the other hand, little information exists on analogous compounds which have a modified molecular backbone.[11,14] In particular, analogues (Fig. 1) where the central ethynylene moieties of the parent (**I**) have been substituted by 1,4-phenylene building blocks (**II**) or other aromatic units (**III**)[15] are of interest, since it is well known that aromatic groups give rise to predictable packing structures.[16]

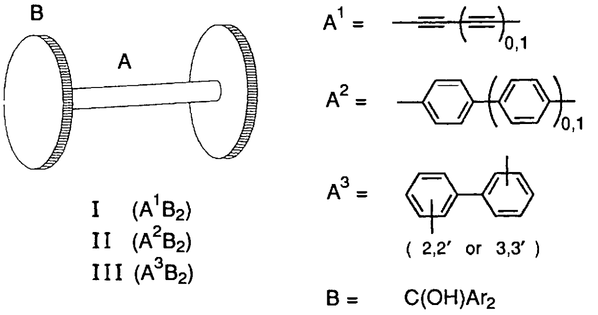
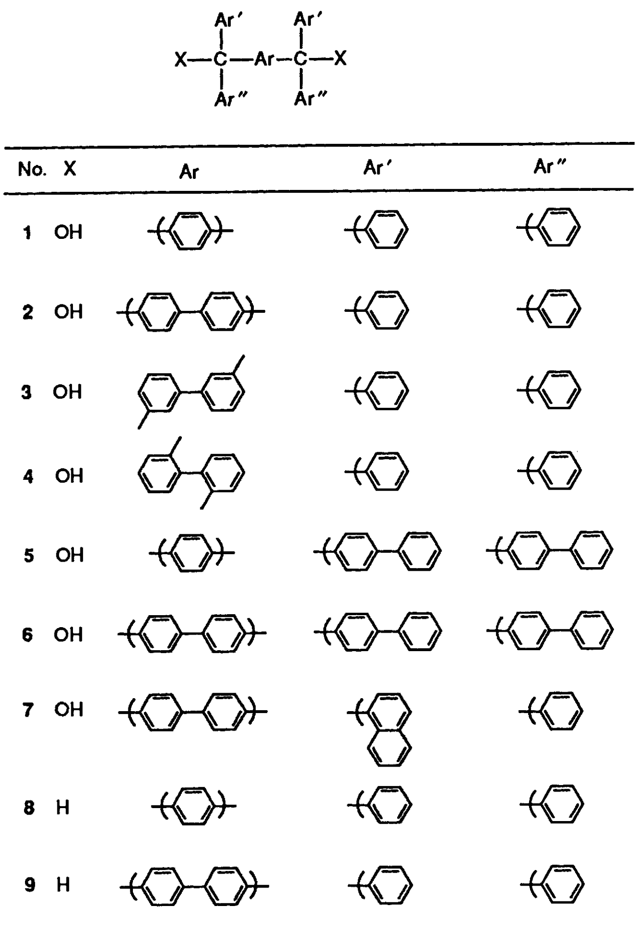


Fig. 1

In order to explore the effect of this structural modification on the crystalline inclusion behaviour of wheel-and-axle compounds, we have synthesized a series of bis(diarylhydroxymethyl)-substituted benzenes and biphenyls, including non-hydroxy analogues, **1–9**, and carried out a systematic study of their inclusion properties. We report these results and give the X-ray crystal structure of compound **2**, in two polymorphic forms, and that of compound **9**.

Results and Discussion

Synthesis.—Diol compounds **1–7** can be made as required from simple starting materials (aromatic ketones or esters and aromatic bromides) using the Grignard method[17] under different solvent conditions (see Experimental section). Hydrocarbons **8** and **9** were prepared by Zn-powder reduction of diols **1** and **2**, respectively.



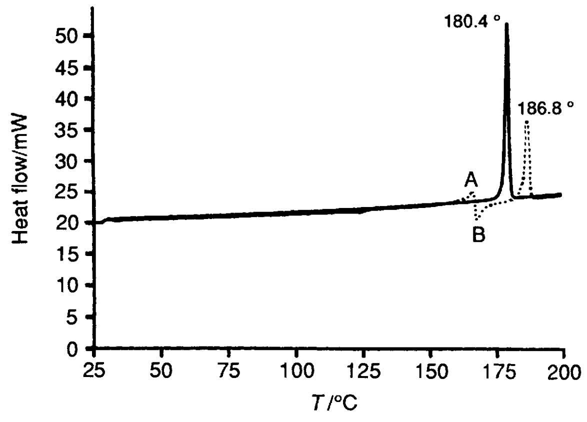


Fig. 2 Thermal analysis diagram (DSC traces) involving α_1 (broken line) and α_2 (solid line) polymorphs of **2**, carried out at 10 °C min^{-1}

Recrystallization of compound **2** from different solvents resulted in the discovery of two polymorphs. One, polymorph α_1, was obtained by evaporating a solution of **2** dissolved in Et_2O. The other, polymorph α_2, was obtained by evaporating a similar solution of **2** in *o*-xylene. Polymorphs are different crystal forms of the same compound and exhibit different physical and chemical properties including different melting points.[18] The two polymorphs gave distinct traces in differential scanning calorimetry (DSC) which are shown in Fig. 2. Polymorph α_1 melts at 186.8 °C and has an enthalpy of melting of 36.6 kJ mol^{-1}. The melting endotherm is preceded by a small endotherm and exotherm, labelled A and B, which may represent a phase change prior to melting. Polymorph α_2 exhibits only one sharp endotherm due to melting at 180.4 °C and has an enthalpy of melting of 49.7 kJ mol^{-1}.

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

	Host compound					
Guest solvent[b]	1	2	3	4	5	7
MeOH	—	—	1:2	1:1	—	—
EtOH	—	1:2	—	1:1	—	—
PrOH	—	1:2	—	—	—	—
Pr^{i}OH	3:2	1:2	—	1:1	—	—
Bu^{t}OH	2:1	—	—	*c*	—	—
Me_2CO	2:1	1:2	1:2	2:1	—	—
MeCN	2:1	1:1	3:2	1:1	—	1:1
$MeNO_2$	2:1	—	—	1:1	—	1:1
DMF	1:2	1:2	1:2	1:1	1:3	1:3
DMSO	1:2	1:2	*c*	1:1	1:3	1:2
THF	2:1	1:2	1:1	1:1	1:3	1:2
Dioxane	1:2	1:2	1:2	2:1	1:3	*c*
Morpholine	1:1	1:1	1:2	1:1	1:3	*c*
Piperidine	1:2	1:2	1:2	*c*	1:3	1:3
Benzene	—	—	—	2:1	—	—
p-Xylene	—	4:7	—	—	—	—

[a] See Experimental for methods of preparation, drying standard, and characterization. [b] BuOH, Bu^{s}OH, cyclohexanone, toluene, *o*-xylene, *m*-xylene and mesitylene, which were also tested as guest solvents, yielded no inclusion compounds. [c] Difficult to crystallize.

Inclusion Properties.—A variety of solvents (21 examples, see Table 1) were used to test the inclusion properties of potential host compounds **1**–**9**. These include alcohols of different molecular size and degrees of ramification, dipolar aprotic compounds of different polarities, heterocycles of different ring sizes and with different numbers and types of heteroatoms, as well as aromatic hydrocarbons. A similar selection of solvents was tested with the parent hosts (*cf.* **I**, Fig. 1),[11] thus making significant comparison between the previous and the present compounds possible. The ability of the modified wheel-and-axle compounds **1**–**9** to form crystalline inclusions is evident from Table 1, which specifies 53 different clathrates. However, they are not uniformly distributed among the individual molecules **1**–**9**. Compounds **1**–**4** are efficient inclusion hosts. Compounds **5** and **7** allow fewer inclusions, while compounds **8** and **9** have no host properties at all and compound **6** is inapplicable because of low solubility. The following general conclusions may be drawn.

(1) The presence of hydroxy groups is essential, since in their absence (*cf.* **8** and **9**) no inclusion occurs.

(2) The presence of hydroxy groups makes inclusion of strong H-bond acceptor and donor solvents likely.[6] In practice, however, all hosts form inclusion complexes with different proton acceptor solvents (dipolar aprotic compounds and heterocycles); however, inclusion formation with typical proton donor solvents, represented by the alcohols, is limited (Table 1). Only morpholine and piperidine, which may also be conceived of as H-donor solvents, form crystal inclusions with virtually all of the hosts.

(3) As expected, apolar hydrocarbons are very rarely enclathrated by the present hosts, indicating that 'true clathrates'[19] are not favourable among these compounds. Exceptions are the *p*-xylene and benzene inclusions of **2** and **4**, respectively. The inclusion compound of **2** with *p*-xylene suggests a complex structure due to the unusual stoichiometric ratio (4:7); *o*-xylene and *m*-xylene are not included by **2**.

(4) Linear extension of the central spacer, *i.e.* changing from **1** to **2**, affects clathrate formation in favour of medium size alcohols, while **1** favours branched alcohols.

(5) Angular extension of the central spacer, *i.e.* changing from **1** to **3** or from **1** to **4**, causes reduced inclusion formation in the case of **3** (mostly for the alcohols) whereas **4** has enhanced inclusion formation.[15]

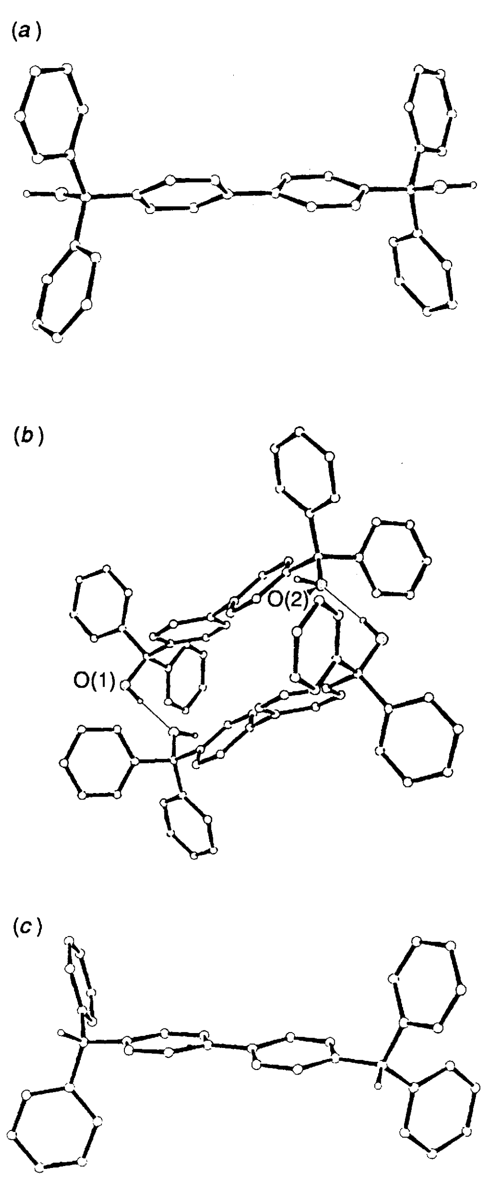


Fig. 3 Perspective views showing molecular conformations: (*a*) polymorph α_1 of **2** (stoichiometric unit); (*b*) polymorph α_2 of **2** (H-bonded molecular association, symmetry = $-x + 2,\ -y + 2,\ -z + 1$; H bonds as thin lines); (*c*) compound **9** (asymmetric unit). O atoms are shaded; H atoms related to the aromatic subunits are omitted for clarity.

Table 2 Relevant torsion angles /° for compounds **2**(α_1), **2**(α_2) and **9**

Atoms	Compound **2**(α_1)	 **2**(α_2)	 **9**
C(51)–C(1)–C(11)–C(12)	65	−68	67
C(51)–C(1)–C(21)–C(22)	48	24	27
C(61)–C(2)–C(31)–C(32)	65	43	21
C(61)–C(2)–C(41)–C(42)	48	−74	87
C(53)–C(54)–C(64)–C(63)	41	45	9
O(1)–C(1)–C(2)–O(2)	−6	16	—
H(1)–C(1)–C(2)–H(2)	—	—	54

(6) Reduced inclusion ability is obtained by increasing the bulkiness of the terminal groups (*cf.* **5** or **7** with **2**).

(7) Host:guest stoichiometric ratios are characteristic of the host structure, *e.g.*, the preferred stoichiometry of compound **2** is 1:2, but 1:1 for **4**, with two hydroxy groups in both molecules. Obviously, this is due to the hydroxy groups being at different distances in the two molecules. In the case of **4**, they are close to each other and may form an intramolecular H-bond.[15] Moreover, compound **5** is remarkable for the high host:guest ratio (1:3) which is universally seen for this host, and to a certain extent also for compound **7**. It may be explained by the fact that due to the bulkier terminal groups more lattice voids are created.

The clathrating abilities of these host compounds are intimately related to their molecular shapes. We therefore undertook the crystal structure analyses of compounds **2** and **9**. In the case of compound **2**, two polymorphs were obtained by crystallization from different solvents, and yielded distinctly different crystal structures.

X-Ray Analysis. Structure Description of the Two Polymorphs (α_1 *and* α_2) *of* **2**, *and of compound* **9**.—Perspective views of the molecules under discussion are shown in Figs. 3(*a*)–(*c*) and packing diagrams are illustrated in Figs. 4(*a*)–(*c*); the labelling of atoms is specified in Fig. 5. Due to the space group symmetry (Table 3, see below) the asymmetric unit in the crystal structure of **2** (α_1) [Fig. 3(*a*)] comprises only one half of the formula unit. In the case of **2** (α_2) [Fig. 3(*b*)], a H-bond-related pair of molecules is shown (symmetry: $-x + 2,\ -y + 2,\ -z + 1$).

The bond lengths and angles in the three structures show good agreement with those found in similar structures.[14–20] By way of contrast, the conformations of the three molecules [**2** (α_1), **2** (α_2) and **9**] differ widely, as indicated by the torsion angles given in Table 2. Compound **2**, in the α_1-polymorph, shows a *trans* (ap) conformation of the hydroxy moieties as well as a staggered conformation of the two phenyl rings [C(51)–C(66)] along the backbone. In this respect, the polymorph α_1 of **2** corresponds to the parent molecule (**I** in Fig. 1).[21] In the α_2-polymorph of **2**, the phenyl backbone rings are once again staggered but the hydroxy moieties are almost eclipsed having adopted a *cis* (sp) conformation in order to achieve the host–host interaction evident in this crystal form [see Fig. 3(*b*)]. Thus α_1 and α_2 of **2** are 'conformational polymorphs'.[18] Relevant torsion angles of molecule **9** are close to the α_1-polymorph of **2** (*cf.* Table 2).

The packing of **2** in polymorph α_1 is shown in Fig. 4(*a*). The molecule is located on a diad at Wyckoff position e, with its molecular axis lying parallel to *a*. There is no hydrogen bonding in this structure. The second polymorph of **2**, α_2, is characterized by a hydrogen bonding scheme with O ··· O distances of 2.877(3) Å which joins the molecules in pairs as illustrated in Fig. 3(*b*). A stereo projection of the packing structure of **2** (α_2) is shown in Fig. 4(*b*) demonstrating the way in which the aromatic molecular axes align parallel to one another. Also, in the crystal packing of **9**, the axes of the molecular backbones are aligned running almost parallel to *c* [Fig. 4(*c*)].

The polymorph α_1 of **2** has a packing factor of 17.00 Å^3 per non-hydrogen atom, while the packing factor of polymorph α_2 of **2** is 17.18 Å^3 per non-hydrogen atom which implies that the molecules of **2** are slightly less efficiently packed in the α_2 form, although this structure has added stabilization due to hydrogen bonding contributions. Compound **9** has a packing factor of 18.09 Å^3 per non-hydrogen atom and is thus less tightly packed than the two polymorphs α_1 and α_2 of **2**. Nevertheless, compound **9** was found not to be able to include any molecular species as guests, for example apolar aromatic compounds.

Conclusions

Compounds derived from the 'wheel-and-axle' design[10,11] (see Fig. 1) but where the molecular axis is aromatic in character and perhaps not strictly linear have proved to be a source of new inclusion hosts. Compared with the parent molecules of type **I** (Fig. 1), they are more selective hosts since they capture

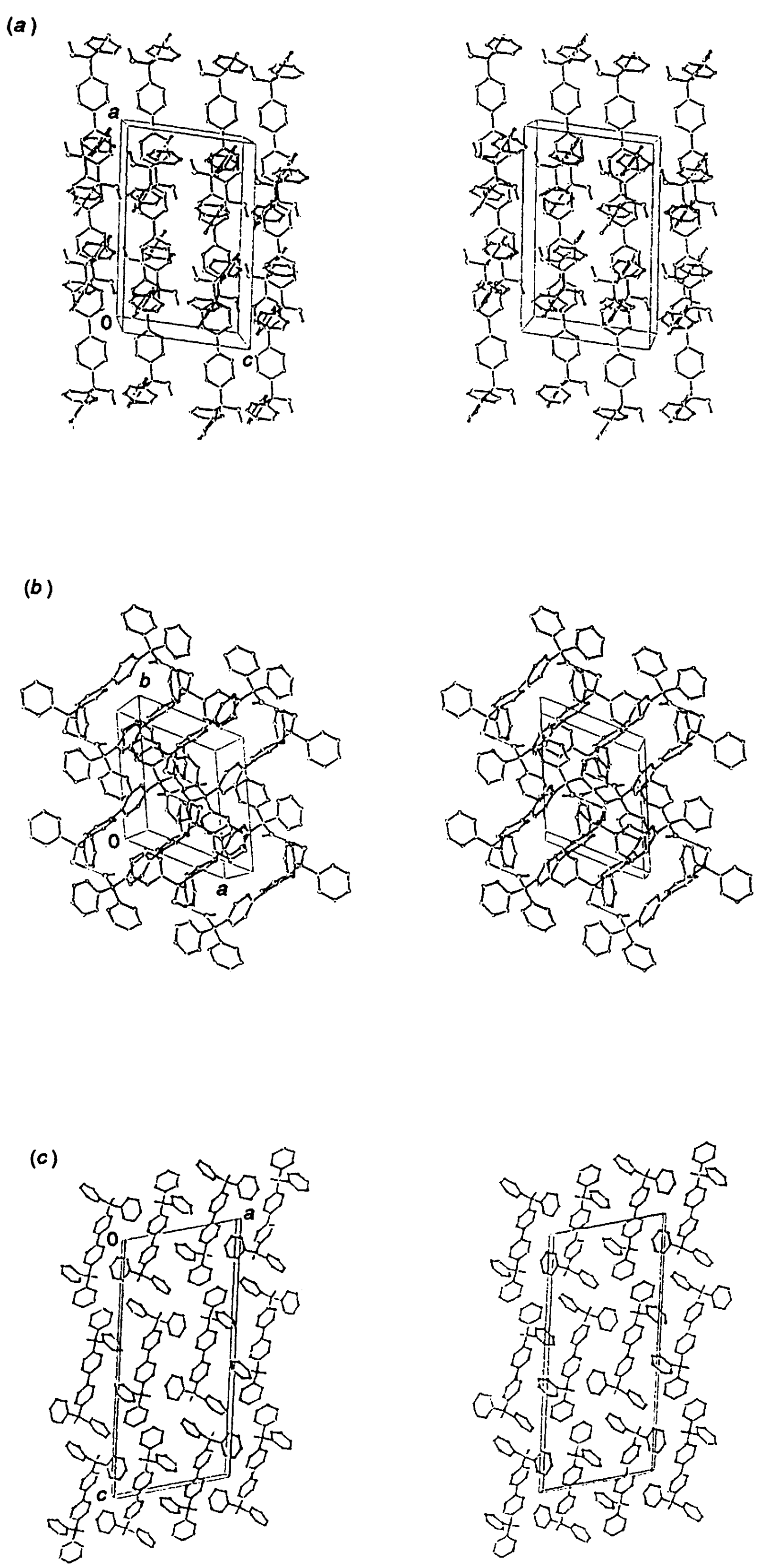
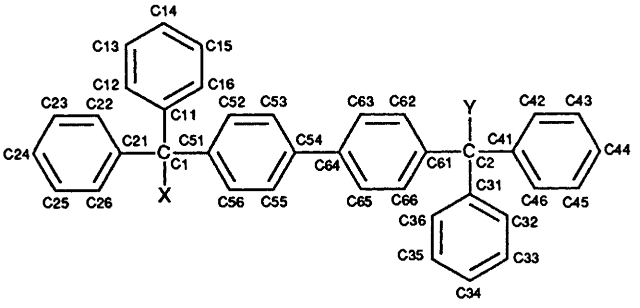


Fig. 4 Stereoscopic packing illustrations of (*a*) polymorph α_1 of **2**, (*b*) polymorph α_2 of **2** and (*c*) compound **9**. H atoms related to the aromatic subunits are omitted for clarity. The thin lines in (*b*) represent H bonds.

a somewhat smaller variety of guest molecules. Pre-eminence of hydrogen bonding in the formation of host–guest crystalline inclusions is supported by the behaviour of compounds **8** and **9** which are not able to include any molecular species as guests. This implies that van der Waals interactions alone are insufficient stabilizing forces in the formation of inclusion compounds with the molecules studied.

The relative flexibility of compound **2** not only appeared to introduce efficient host properties but also resulted in two polymorphic crystalline forms (α_1 and α_2). One may infer that



2 X = O(1)—H(1)
Y = O(2)—H(2)

9 X = H(1)
X = H(2)

Fig. 5

these polymorphs, to a certain degree, reflect the solution structures of **2** in polar or apolar solvents. Polymorph α_1 of **2**, with no hydrogen bonding between the molecules, is obtained from Et_2O which is a weak H bond acceptor and as such in principle capable of solvating individual molecules of **2**. On the other hand, polymorph α_2 with hydrogen bonded dimers of **2** in the crystal is obtained from *o*-xylene which is neither a H-bond acceptor nor a donor, thus promoting dimer formation. In this context, X-ray structural determination of crystalline inclusions with polar and apolar guest solvents,[15] particularly involving host compound **2**, will be of great interest in the future. This work is in progress.

Experimental

General Methods and Materials.—M.p.s were determined with a Reichert hot-stage apparatus. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC7 Dynamic Differential Calorimeter and PETA77/PC Thermal Analysis Instrument Controller, controlled by means of an Epson PCAX2 personal computer. For column chromatography, a silica gel (0.063–0.1 mm) was used. Solvents were dried by standard procedures. Starting compounds 1-bromonaphthalene and 4-bromobiphenyl were purchased from Janssen.

1,4-Dibenzoylbenzene,[22] 4,4′-dibenzoylbiphenyl,[23] dimethyl biphenyl-2,2′-dicarboxylate,[24] dimethyl biphenyl-3,3′-dicarboxylate[25] and dimethyl biphenyl-4,4′-dicarboxylate[26] were prepared according to literature procedures.

Host Compounds **1**–**7**.—Grignard solutions required for the synthesis of **1**–**7** were prepared in different ways and reactions of the Grignard solutions with the corresponding diketones or diesters as well as work-up of the reaction products were also performed differently for **1**–**7**. All Grignard reactions were done under an atmosphere of argon. For quenching of the reaction mixtures a saturated aqueous solution of NH_4Cl was used. Specific details for each compound are given below.

1,4-*Bis(diphenylhydroxymethyl)benzene* **1**. To a Grignard solution prepared from 33.0 g (210 mmol) bromobenzene and 6.07 g (250 mmol) Mg in dry Et_2O (100 cm^3) was added in small portions 20.0 g (69 mmol) powdered 1,4-dibenzoylbenzene. The mixture was diluted with dry Et_2O (50 cm^3) and refluxed for 2 h. Work-up included quenching, separation of the organic layer, washing with water, drying over $MgSO_4$, evaporation under reduced pressure and recrystallization from benzene to yield 26.0 g (85%) of colourless crystals; m.p. 168 °C (lit.,[27] m.p. 169 °C).

4,4′-*Bis(diphenylhydroxymethyl)biphenyl* **2**. A Grignard solution prepared from 12.0 g (76 mmol) bromobenzene and 1.95 g (80 mmol) Mg in dry Et_2O (100 cm^3) was added dropwise to a suspension of 9.0 g (25 mmol) 4,4′-dibenzoylbiphenyl in dry benzene (100 cm^3). The violet coloured solution which formed was refluxed for 3 h. Work-up included addition of benzene (100 cm^3), quenching, separation of the organic phase, drying over Na_2SO_4, evaporation under reduced pressure to a volume of 100 cm^3, cooling (refrigerator), collection of the precipitated solid which formed, and recrystallization from benzene to give the 1:1 inclusion compound with benzene. Treatment of the inclusion crystals at 100 °C under 15 Torr for 2 h yielded 9.5 g (73.5%) of pure **2** as colourless powder; m.p. 160–161 °C (lit.,[23] m.p. 160–165 °C). Two polymorphous crystals of **2**, α_1 and α_2, have been obtained by recrystallization from Et_2O and *o*-xylene, respectively: α_1 are colourless crystals with m.p. 186.8 °C, α_2 are colourless crystals with m.p. 180.4 °C (see Fig. 2).

3,3′-*Bis(diphenylhydroxymethyl)biphenyl* **3**. A solution of 3.5 g (13 mmol) dimethyl biphenyl-3,3′-dicarboxylate in benzene (100 cm^3) was added dropwise to a Grignard solution prepared from 6.2 g (40 mmol) bromobenzene and 1.1 g (45 mmol) Mg in benzene (100 cm^3). The mixture was refluxed for 24 h. Work-up included quenching, separation of the organic layer, washing with water, drying over $MgSO_4$, and evaporation under reduced pressure to give a viscous oil. Chromatography on SiO_2 (eluent $CHCl_3$) yielded 4.1 g (72%) of colourless powder; m.p. 180 °C (lit.,[23] m.p. 183–184 °C).

2,2′-*Bis(diphenylhydroxymethyl)biphenyl* **4**. 18.0 g (110 mmol) bromobenzene and 2.9 g (120 mmol) Mg in dry Et_2O (100 cm^3), and 5.0 g (18 mmol) dimethyl biphenyl-2,2′-dicarboxylate in benzene (100 cm^3) were reacted as described for **3**. The same work-up yielded 5.2 g (65.5%) of colourless powder; m.p. 247 °C (lit.,[28] m.p. 251–253 °C).

4,4′-*Bis[di(4-biphenyl)hydroxymethyl]biphenyl* **6**. A mixture of 24.95 g (100 mmol) 4-bromobiphenyl and 5.0 g (200 mmol) Mg in dry THF (100 cm^3) was refluxed for 2 h. The excess of Mg was separated and the mixture diluted with dry THF (100 cm^3). To this Grignard solution was added in small portions 5.0 g (18 mmol) dimethyl biphenyl-4,4′-dicarboxylate and the mixture was refluxed for 4 h. Work-up included evaporation under reduced pressure, addition of Et_2O (200 cm^3), quenching, collection of the precipitate which formed and recrystallization from xylene to yield 6.9 g (45%) of colourless powder; m.p. 265 °C (lit.,[23] m.p. >260 °C).

4,4′-*Bis[(1-naphthyl)phenylhydroxymethyl]biphenyl* **7**. A solution of 5.4 g (15 mmol) 4,4′-dibenzoylbiphenyl in Et_2O (100 cm^3) was added dropwise to a Grignard solution prepared from 6.10 g (30 mmol) 1-bromonaphthalene and 0.72 g (30 mmol) Mg in dry Et_2O. The mixture was refluxed for 2 h. Work-up as described for **1** yielded 4.7 g (51%) of colourless powder; m.p. 258–259 °C (lit.,[28] m.p. 260–262 °C).

General Procedure: Compounds **8** *and* **9**.—To 15 mmol of diol **1** or **2** dissolved in hot acetic acid (150 cm^3) was added Zn-powder (12 g). The stirred suspension was refluxed for 3 h, then filtered while hot and the residue on the filter washed with hot acetic acid. On cooling the filtrate and washings, a solid precipitated which was treated with hot water, dried and recrystallized from acetone to yield pure products.

1,4-*Bis(diphenylmethyl)benzene* **8**. 95% yield; colourless powder; m.p. 170 °C (lit.,[27] m.p. 172 °C).

4,4′-*Bis(diphenylmethyl)biphenyl* **9**. 91% yield; colourless powder; m.p. 164–165 °C (lit.,[29] m.p. 163–165 °C).

Crystalline Inclusion Compounds.—The host compound was dissolved under heating in a minimum amount of the respective guest solvent. The solution was allowed to cool slowly in an oil bath in order to ensure crystallization of the inclusion compound. After storage for 12 h at room temperature, the crystals which formed were collected by suction filtration and dried (1 h, 15 Torr, room temperature). The host:guest stoichiometric ratios were determined by ^1H NMR integration. Data for each compound are given in Table 1.

Table 3 Crystal data, experimental parameters and selected details of the refinement calculations[a]

Compound	**2** (α_1)	**2** (α_2)	**9**
Formula	$C_{38}H_{30}O_2$	$C_{38}H_{30}O_2$	$C_{38}H_{30}$
M	518.65	518.65	486.66
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$
a/Å	16.827(2)	8.807(2)	12.781(3)
b/Å	15.212(3)	10.687(6)	7.773(2)
c/Å	10.708(2)	16.263(3)	28.405(17)
α/°	90	100.97(3)	90
β/°	97.01(1)	91.47(2)	103.05(3)
γ/°	90	113.02(3)	90
Z	4	2	4
V/Å^3	2721(1)	1375(1)	2749(2)
D_c/g cm^{-3}	1.27	1.25	1.18
D_m/g cm^{-3}	1.22(4)	1.23(3)	1.16(1)
μ Mo-Kα/cm^{-1}	0.41	0.40	0.15
F(000)	1096	548	484
Data collection (21 °C)			
Crystal dimensions/mm	0.28 × 0.31 × 0.47	0.38 × 0.44 × 0.47	0.38 × 0.38 × 0.47
Range scanned θ/°	1–25	1–23	1–25
Range of indices h,k,l	±20, +18, +12	±9, ±11, +17	±15, +9, +33
Reflections for lattice parameters no., θ range/°	24, 15–17	24, 16–17	24, 16–17
Instability of standard reflections (%)	2.9	9.0	0.8
Scan mode	ω–2θ	ω–2θ	ω–2θ
Scan width/°	0.85 + 0.35 tan θ	0.60 + 0.35 tan θ	0.80 + 0.35 tan θ
Vertical aperture length/mm	4	4	4
Aperture width/mm	1.12 + 1.05 tan θ	1.12 + 1.05 tan θ	1.12 + 1.05 tan θ
Number of reflections collected (unique)	2072	3462	3874
Number of reflections observed with $I_{rel} > 2\sigma I_{rel}$	1593	2930	2712
Final refinement			
Number of parameters	186	370	352
R	0.053	0.046	0.055
wR	0.057	0.054	0.054
w	$[\sigma^2(F_o) + 0.001F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.001F_o^2]^{-1}$	$[\sigma^2(F_o) + 0.001F_o^2]^{-1}$
S	3.23	0.71	1.44
Max. shift/esd	0.166	0.002	0.002
Max. height in difference electron density map/e Å^{-3}	0.23	0.21	0.15
Min. height in difference electron density map/e Å^{-3}	−0.30	−0.25	−0.22

[a] Esds are given in parentheses.

Table 4 Fractional atomic coordinates (× 10^4) with esds in parentheses for compound **2** (polymorph α_1)

Atom	x/a	y/b	z/c
O(1)	3024(1)	643(1)	723(2)
H(1)	3565(13)	615(30)	436(2)
C(1)	2980(1)	694(2)	2050(2)
C(11)	3327(1)	1577(2)	2577(2)
C(12)	3601(2)	2197(2)	1805(3)
C(13)	3906(2)	2991(2)	2285(3)
C(14)	3922(2)	3181(2)	3532(3)
C(15)	3647(2)	2575(2)	4318(3)
C(16)	3347(2)	1772(2)	3849(3)
C(21)	3426(2)	−107(2)	2658(3)
C(22)	3103(2)	−938(2)	2404(3)
C(23)	3504(2)	−1687(2)	2855(3)
C(24)	4246(2)	−1620(2)	3562(3)
C(25)	4580(2)	−807(2)	3798(3)
C(26)	4173(2)	−52(2)	3350(3)
C(51)	2087(1)	674(2)	2186(2)
C(52)	1527(2)	961(2)	1206(2)
C(53)	718(2)	964(2)	1328(2)
C(54)	436(1)	702(2)	2432(2)
C(55)	1002(2)	425(2)	3416(2)
C(56)	1807(2)	409(2)	3300(2)

Crystal Structure Determination.—Sample preparation. Colourless crystals of polymorph α_1 of diol host compound **2** (m.p. 186.8 °C), suitable for X-ray diffraction were obtained by slow evaporation of a solution of the compound dissolved in Et_2O. The second polymorph (α_2) of **2** (m.p. 180.4 °C) was obtained by evaporating a similar solution from *o*-xylene. Crystals of compound **9** were grown by slow evaporation from an acetone solution.

Data collection and processing. For all three structures, unit cell parameters and space group assignments were first obtained photographically, and later by least squares analysis of 24 reflections measured on an Enraf-Nonius CAD4 diffractometer, in the range $16 < \theta < 17$ °. Intensity data were collected on the diffractometer at 293 K using graphite monochromated Mo-Kα radiation (λ = 0.7107 Å) and the ω–2θ mode. During each data collection three reference reflections were monitored periodically to check crystal stability. The data were corrected for Lorentz and polarization effects but not for absorption. Crystal data and some experimental details are summarized in Table 3.

Structure analysis and refinement. All three structures were solved by direct methods using SHELXS-86[30] and refined by full matrix least squares using SHELX-76.[31] Refinement proceeded in parallel for the three structures. Non-hydrogen atoms were refined anisotropically and the hydrogen atoms were subjected to constrained refinement. The hydroxy hydrogens were located in Fourier maps and allowed to refine independently. When they were involved in hydrogen bonding they were constrained to fixed distances from their parent oxygens according to a function of O–H *versus* O · · · O distance.[32] The final reliability indices together with selected details of the

Table 5 Fractional atomic coordinates ($\times 10^4$) with esds in parentheses for compound **2** (polymorph α_2)

Atom	x/a	y/b	z/c
O(1)	4 183(2)	6 400(1)	1 949(1)
H(1)	5 149(24)	6 306(31)	2 130(17)
C(1)	4 700(2)	7 788(2)	1 815(1)
O(2)	12 768(2)	13 758(2)	7 519(1)
H(2)	11 876(30)	13 377(34)	7 878(17)
C(2)	12 225(3)	14 519(2)	7 018(1)
C(11)	5 529(2)	7 907(2)	1 002(1)
C(12)	5 921(3)	9 091(2)	675(1)
C(13)	6 635(3)	9 192(2)	−68(1)
C(14)	6 966(3)	8 102(2)	−504(1)
C(15)	6 583(3)	6 924(2)	−192(1)
C(16)	5 876(3)	6 824(2)	556(1)
C(21)	3 107(2)	8 025(2)	1 702(1)
C(22)	1 732(3)	6 960(2)	1 208(1)
C(23)	310(3)	7 165(3)	1 044(2)
C(24)	223(3)	8 416(3)	1 377(2)
C(25)	1 567(3)	9 464(3)	1 879(2)
C(26)	3 003(3)	9 272(2)	2 035(1)
C(31)	11 512(3)	15 402(2)	7 598(1)
C(32)	10 003(3)	15 452(2)	7 416(1)
C(33)	9 464(3)	16 314(3)	7 967(2)
C(34)	10 423(3)	17 110(3)	8 712(2)
C(35)	11 903(3)	17 045(3)	8 899(2)
C(36)	12 466(3)	16 210(2)	8 354(1)
C(41)	13 769(3)	15 424(2)	6 670(1)
C(42)	14 040(3)	16 769(2)	6 595(2)
C(43)	15 402(3)	17 536(2)	6 222(2)
C(44)	16 495(3)	16 986(3)	5 927(2)
C(45)	16 237(3)	15 649(3)	6 002(2)
C(46)	14 873(3)	14 876(2)	6 363(1)
C(51)	5 836(2)	8 797(2)	2 600(1)
C(52)	7 359(3)	9 856(2)	2 574(1)
C(53)	8 314(3)	10 739(2)	3 310(1)
C(54)	7 786(3)	10 592(2)	4 093(1)
C(55)	6 266(3)	9 505(2)	4 123(1)
C(56)	5 307(3)	8 645(2)	3 389(1)
C(61)	10 975(3)	13 476(2)	6 275(1)
C(62)	10 731(3)	13 903(2)	5 547(1)
C(63)	9 673(3)	12 975(2)	4 858(1)
C(64)	8 821(3)	11 576(2)	4 867(1)
C(65)	9 049(3)	11 159(2)	5 597(1)
C(66)	10 109(3)	12 092(2)	6 287(1)

Table 6 Fractional atomic coordinates ($\times 10^4$) with esds in parentheses for compound **9**

Atom	x/a	y/b	z/c
C(1)	7 044(2)	6 455(3)	1 185(1)
H(1)	7 717(21)	5 861(34)	1 297(9)
C(2)	8 408(2)	14 094(4)	−1 526(1)
H(2)	8 674(19)	13 322(35)	−1 757(9)
C(11)	6 833(2)	7 537(3)	1 603(1)
C(12)	7 646(2)	8 611(4)	1 851(1)
C(13)	7 501(3)	9 593(4)	2 237(1)
C(14)	6 552(3)	9 534(4)	2 382(1)
C(15)	5 737(3)	8 499(4)	2 138(1)
C(16)	5 873(2)	7 507(3)	1 751(1)
C(21)	6 235(2)	4 992(3)	1 054(1)
C(22)	6 341(2)	3 567(3)	1 357(1)
C(23)	5 607(2)	2 257(4)	1 274(1)
C(24)	4 736(2)	2 333(4)	886(1)
C(25)	4 625(2)	3 720(4)	581(1)
C(26)	5 367(2)	5 046(4)	662(1)
C(31)	9 338(2)	15 312(3)	−1 315(1)
C(32)	9 905(2)	16 034(4)	−1 627(1)
C(33)	10 729(2)	17 178(5)	−1 468(1)
C(34)	11 005(3)	17 636(4)	−992(2)
C(35)	10 468(3)	16 919(4)	−674(1)
C(36)	9 633(2)	15 756(4)	−832(1)
C(41)	7 462(2)	15 075(4)	−1 826(1)
C(42)	6 844(3)	14 320(5)	−2 239(1)
C(43)	5 969(3)	15 192(7)	−2 515(2)
C(44)	5 700(3)	16 774(8)	−2 384(2)
C(45)	6 303(3)	17 549(6)	−1 982(1)
C(46)	7 182(2)	16 713(5)	−1 703(1)
C(51)	7 174(2)	7 562(3)	761(1)
C(52)	8 000(2)	7 264(4)	536(1)
C(53)	8 153(2)	8 273(4)	158(1)
C(54)	7 483(2)	9 651(3)	−13(1)
C(55)	6 649(2)	9 951(3)	214(1)
C(56)	6 499(2)	8 932(3)	594(1)
C(61)	8 110(2)	12 927(4)	−1 147(1)
C(62)	7 331(3)	13 310(5)	−905(1)
C(63)	7 125(3)	12 266(5)	−545(1)
C(64)	7 679(2)	10 768(3)	−413(1)
C(65)	8 445(3)	10 385(4)	−662(1)
C(66)	8 648(3)	11 435(4)	−1 021(1)

refinement calculations are listed in Table 3. Final atomic coordinates for the three structures are given in Tables 4–6.

Supplementary data. Lists of bond lengths and bond angles involving the non-H atoms, anisotropic thermal parameters, and hydrogen atom coordinates have been deposited at the Cambridge Crystallographic Data Centre.* Lists of the observed and calculated structure factors may be obtained from the authors (L. R. N.).

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