

## Crystalline Alcoholic Inclusions of Singly-bridged Triarylmethanol Hosts. Synthesis, X-Ray Crystal Structures and Binding Modes of Five Inclusion Compounds †

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Five alcoholic inclusion compounds of singly-bridged triarylmethanol hosts have been synthesized and investigated by X-ray diffraction. In four cases recognition of the alcoholic guest by the host is characterized by a coupled system of hydrogen bonds in the form of closed loops. The centrosymmetric hydrogen-bonded rings, with full hydrogen bond saturation, are created by four –OH groups belonging to two host and two guest molecules. In the fifth complex, however, 'anomalous' hydrogen-bonded 2:1 host:guest associates are formed without full saturation of hydrogen bonds. In the crystals the hydrogen-bonded units are held together mostly by ordinary Van der Waals' forces, occasionally supported by electrostatic C–H...O interactions.

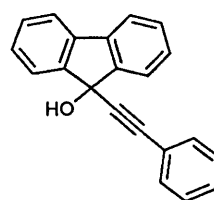
Considerable interest in crystalline inclusion compounds <sup>2</sup> has arisen in the past few years due to their potential uses in analytical <sup>3</sup> and materials sciences. <sup>4</sup> Bridged triarylmethanols have proven efficiency in crystalline inclusion formation involving organic guests of different compound classes. <sup>5</sup> Selectivities and stoichiometric ratios of the formed host-guest complexes depend in a systematic manner on structural parameters of the host including the nature and the position of substituents. <sup>5,6</sup> Some of these crystalline inclusions are true clathrates type, others have particular modes of binding typical of coordinatoclathrates. <sup>7</sup> A systematic structural study of a series of dioxane inclusions, previously done, <sup>1</sup> suggested characteristic features of dioxane recognition relating to the singly bridged triarylmethanol host family.

Here we present a similar study involving alcohols as the particular guest type under discussion, where binding between host and guest hydroxy groups with reference to different host constitutions is the key question. We report synthesis of the inclusion compounds **1a–4a** and **3b**, where **4** in **4a** refers to a newly synthesized host compound, and we describe X-ray crystal structures of the inclusions. We compare these new structures and discuss modes of binding as well as packing features, bringing to light recognition properties of the bridged triarylmethanol hosts for alcohol guests in the crystalline state, in view of the objectives mentioned at the beginning of the article.

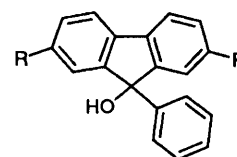
### Results and Discussion

**Synthesis.**—The synthesis of host compounds **1–3** has been described in a previous paper. <sup>5</sup> Host molecule **4** was prepared from ketone **5** and bromobenzene with phenyllithium. Inclusion compounds **1a–4a** and **3b** were obtained by recrystallization of the respective host compound from the corresponding guest solvent. The host-guest stoichiometries were determined by NMR integration of the isolated, dried crystals. <sup>5</sup>

**X-Ray Diffraction Analysis.**—Crystal data on compounds **1a–4a** and **3b** are given in Table 1. Selected conformational

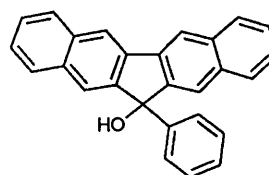


1

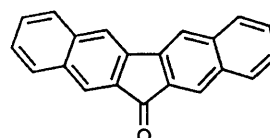


2 R = Me

3 R = Br



4



5

1a = 1•PrOH (1:1)

2a = 2•Bu'OH (1:1)

3a = 3•MeOH (1:1)

3b = 3•PrOH (1:1)

4a = 4•PrOH (1:1)

features of the host molecules are shown in Table 2. Table 3 lists the distances and angles in O–H...O hydrogen bonds and in possible C–H...O interactions. Perspective views of the stoichiometric units of compounds **1a–4a**, and **3b** are depicted in Figs. 1(a)–(e). The molecular packings and the hydrogen bond frameworks in crystals **1a–4a**, and **3b** are illustrated by the stereo plots of Figs. 2(a)–(e).

**Molecular Structures.**—No anomalous values of bond lengths and angles (Tables 5 and 6, Supplementary Data) were observed for the host molecules in compounds **1a–4a**, and **3b**. The semi-rigid 9-phenylfluorene-9-ol moieties of hosts **2** and **3** show the usual geometry <sup>1,5,8</sup> with a flat 13-membered fluorene group roughly perpendicular to the ring plane of the 9-phenyl

† Triarylmethanol Hosts and Analogues. Part 9. For Part 8 of this series see ref. 1.

**Table 1** Crystal data and selected details of the data reduction and structure refinement calculations<sup>a</sup>

	1a	2a	3a	3b	4a
Formula					
host	C <sub>21</sub> H <sub>14</sub> O	C <sub>21</sub> H <sub>18</sub> O	C <sub>19</sub> H <sub>12</sub> OBr <sub>2</sub>	C <sub>19</sub> H <sub>12</sub> OBr <sub>2</sub>	C <sub>27</sub> H <sub>18</sub> O
guest	C <sub>3</sub> H <sub>8</sub> O	C <sub>4</sub> H <sub>10</sub> O	CH <sub>4</sub> O	C <sub>3</sub> H <sub>8</sub> O	C <sub>3</sub> H <sub>8</sub> O
Host: Guest stoichiometry	1:1	1:1	1:1	2:1	1:1
<i>M<sub>w</sub></i>	342.44	402.53	448.15	892.32	418.53
Crystal system	triclinic	monoclinic	monoclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>I</i> 2/ <i>a</i> <sup>b</sup>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
Unit cell dimensions					
<i>a</i> /Å	9.478(1)	16.748 8(8)	9.028(1)	10.059(1)	8.459(8)
<i>b</i> /Å	9.558(1)	11.619 1(4)	17.052(2)	10.213(1)	12.319(12)
<i>c</i> /Å	12.192(1)	22.215 4(10)	12.507(2)	18.352(2)	13.071(13)
<i>α</i> /°	110.229(4)	90.0	90.0	100.402(7)	63.46(5)
<i>β</i> /°	98.146(5)	102.382(3)	106.59(1)	97.422(7)	72.43(3)
<i>γ</i> /°	104.035(4)	90.0	90.0	94.655(4)	74.61(3)
<i>V<sub>calc</sub></i> /Å <sup>3</sup>	974.1(2)	4241.6(5)	1945.2(4)	1828.2(3)	1148(2)
Refinement of the unit cell dimensions					
No. of reflections used	40	79	66	80	28
2 <i>θ</i> -range/°	38–55	20–36	19–37	20–40	10–23
<i>Z</i>	2	8	4	2	2
<i>D<sub>calc</sub></i> /g cm <sup>-3</sup>	1.167 5(2)	1.129 0(1)	1.613 2(4)	1.620 9(3)	1.211(3)
<i>F</i> (000)	364	1552	888	884	444
<i>T</i> /K	291(1)	193(1)	291(1)	173(1)	173(1)
Radiation	Cu-Kα	Mo-Kα	Mo-Kα	Mo-Kα	Mo-Kα
<i>μ</i> /cm <sup>-1</sup>	5.38	0.65	43.58	43.96	0.69
Range of 2 <i>θ</i> /°	3–140	3–50	3–60	3–50	3–50
No. of collected reflections	3761	7863	5862	8304	4053
No. of standard reflections	5	4	5	5	4
Time interval between the standards/min	90	90	90	90	90
Intensity instability	< 2%	< 1%	< 1%	< 2%	< 4%
No. of unique non-zero reflections	3162	3068	4058	8304	3357
No. of significantly observed reflections	2003	1477	1552	3011	1718
Criterion of significance	<i>I</i> / <i>σ</i> ( <i>I</i> ) > 3	<i>I</i> / <i>σ</i> ( <i>I</i> ) > 2	<i>I</i> / <i>σ</i> ( <i>I</i> ) > 2	<i>I</i> / <i>σ</i> ( <i>I</i> ) > 3	<i>I</i> / <i>σ</i> ( <i>I</i> ) > 2
No. of refined parameters	245	281	235	439	312
Final agreement factors					
<i>R</i> [= Σ Δ <i>F</i>  /Σ  <i>F<sub>o</sub></i>  ]	0.048	0.043	0.039	0.036	0.044
<i>wR</i> [= (Σ <i>w</i>  Δ <i>F</i>   <sup>2</sup> /Σ <i>w</i>   <i>F<sub>o</sub></i>   <sup>2</sup> ) <sup>1/2</sup> ]	0.067	0.048	0.042	0.041	0.048
<i>wR<sub>tot</sub></i>	0.076	0.068	0.058	0.067	0.056
Weighting: <i>w</i> = [σ <sup>2</sup> ( <i>F</i> ) + <i>gF</i> <sup>2</sup> ] <sup>-1</sup>					
with <i>g</i> =	0.000 50	0.000 76	0.000 35	0.000 34	0.000 40
Final Δ <i>ρ</i> <sub>max</sub> / <i>ρ</i> <sub>min</sub> [e <sup>-</sup> Å <sup>-3</sup> ]	0.31/–0.23	0.08/–0.11	0.47/–0.35	0.71/–0.50	0.08/–0.11

<sup>a</sup> Esds, where given, are in parentheses. <sup>b</sup> *I*2/*a* is the same space group as *C*2/*c* but with a different choice of unit cell.

**Table 2** Selected conformational features of the singly bridged triarylmethanol hosts 1–4 in their inclusion compounds with alcohols, studied by X-ray diffraction<sup>a</sup>

	1	2	3 <sup>b</sup>	3 <sup>c,d</sup>	4 <sup>e</sup>
The ring atoms of the fused ring system <sup>f</sup> are co-planar within/Å	0.092	0.097	0.043	0.069	0.218
Dihedral angle <sup>f</sup> between the LS planes of the bridged phenyl rings of the fused ring system <sup>e</sup> /°	3.25(8)	1.9(1)	0.8(2)	1.7(2)	3.4(1)
The phenyl ring atoms in the single aryl substituent are co-planar within/Å	0.009	0.008	0.010	0.025	0.011
Dihedral angle <sup>f</sup> between the LS planes of the fused ring system <sup>e</sup> and the phenyl ring in the single aryl substituent <sup>f</sup> /°	68.50(7)	103.9(1)	86.0(2)	78.5(1)	85.7(1)
				77.6(2)	

<sup>a</sup> Esds, where given, are in parentheses. <sup>b</sup> In compound 3a [3-MeOH (1:1)]. <sup>c</sup> In compound 3b [3-Pr'OH (2:1)]. <sup>d</sup> The crystals of 3b contain two crystallographically independent host molecules (the unprimed and the primed one). <sup>e</sup> The bridged diaryl moiety in hosts 1–3 is a fluorene moiety with 13 ring atoms, whereas host molecule 4 contains a dibenzofluorene group with 21 ring atoms. <sup>f</sup> Following Nardelli.<sup>18</sup>

substituent. The methyl C atoms of the 2- and 7-substituents in 2 depart from the fluorene plane by 0.127(4) and 0.016(4) Å, respectively. The deviations of the bromine substituents from the respective fluorene plane in the three independent molecules of host 3 (in 3a and b) range between 0.002 and 0.129 Å, with a mean value of 0.06[4] Å (the dispersion around the arithmetic average is given in angular brackets). The dihedral angles

formed by the least-squares (LS) planes through the fluorene and the 9-phenyl groups in 2 and in the two independent host molecules in 3b deviate more than 10° from a right angle, in all probability due to packing effects. In host 1, containing the 9-phenylacetylene group, however, the increased distance between the fluorene moiety and the phenyl ring of the 9-substituent leads to a dihedral angle of only 68.50(7)° between

**Table 3** Bond distances (Å) and angles (°) in O–H...O bonds and in possible C–H...O interactions in compounds **1a–4a** and **3b**<sup>a</sup>

Atoms involved	Symmetry	Distances			Angle
		Donor...O	Donor–H	H...O	∠ Donor–H...O
<b>1a: 1-Pr<sup>i</sup>OH (1:1)</b>					
O(9)–H(O9)...O(P)	1 – x, 1 – y, –z	2.717(4)	0.98	1.75	168
O(P)–H(OP)...O(9)	x, y, z	2.750(3)	1.00	1.75	177
<b>2a: 2-Bu<sup>i</sup>OH (1:1)</b>					
O(9)–H(O9)...O(B)	x, y, z	2.732(4)	1.00	1.73	180
O(B)–H(OB)...O(9)	1.5 – x, 0.5 – y, 0.5 – z	2.817(3)	1.00	1.82	180
<b>3a: 3-MeOH (1:1)</b>					
O(9)–H(O9)...O(M)	x, y, z	2.689(7)	1.01	1.71	161
O(M)–H(OM)...O(9)	–1 – x, 1 – y, –z	2.724(6)	0.96	1.77	180
<b>3b: 3-Pr<sup>i</sup>OH (2:1)</b>					
O(9)–H(O9)...O(P)	x, y, z	2.729(6)	0.95	1.78	180
O(9')–H(O9')...O(9)	x, y, z	2.819(5)	0.93	1.91	165
C(1)–H(1)...O(9')	x, y, z	3.410(8)	1.00	2.58	140
C(1')–H(1')...O(9)	x, y, z	3.327(7)	1.00	2.51	139
<b>4a: 4-Pr<sup>i</sup>OH (1:1)</b>					
O(13)–H(13)...O(P)	–x, 1 – y, 2 – z	2.785(5)	0.94	1.88	163
O(P)–H(OP)...O(13)	x, y, z	2.837(5)	1.06	1.78	175
C(11)–H(11)...O(13)	1 – x, 1 – y, 2 – z	3.470(6)	1.00	2.58	136

<sup>a</sup> Esds, where given, are in parentheses. The H atom positions were not refined (*cf.* the text).

these two LS planes. The same dihedral angles for **3** in **3a** and for host **4** are within the range of the corresponding ones in the related host molecules, observed in their guest free crystals,<sup>8</sup> and in their benzene<sup>5</sup> or dioxane<sup>1,5</sup> inclusions. The 21 ring atoms of the dibenzofluorene moiety in **4** are nearly co-planar; the dihedral angles between the planes of the fused benzene rings are 1.8(1)° [C(1a)...C(6a)] and 0.9(1)° [C(7a)...C(12a)].

The guest alcohols in general show the expected geometry. Nevertheless, the propan-2-ol guest in **1a** and the methanol in **3a** seem to have greater thermal motion than their hosts (*cf.* the displacement parameters in the Supplementary Data), thus yielding larger scatter in the bond lengths and angles for these guests. At the same time, the observed bond distances and angles of the *tert*-butanol in **2a**, and of the propan-2-ol in **3b** and **4a** generally conform to expected values. It is worth noticing, however, that the structures of **1a** and **3a** were solved using room temperature data, whereas the structural models of **2a**, **3b** and **4a** were derived from data collected at lower temperatures (*cf.* Table 1).

**Packing Relations and Host–Guest Interactions.**—In the present inclusion compounds both the host and the guest are equipped with an alcoholic –OH group, which gives them relatively strong proton donor/acceptor properties. Consequently, they are capable of forming closed loops of hydrogen bonds, which resemble those observed earlier in numerous alcoholic and carboxylic inclusions of different carboxylic hosts.<sup>9</sup> The eight-membered (including also the hydrogens) pseudo ring, closed *via* hydrogen bonds in four (**1a–4a**) out of the five inclusion compounds presented here (Fig. 2), involves four hydroxy groups of two host and two guest molecules, located around the centre of symmetry. In this way hydrogen-bonded centrosymmetric 2:2 host:guest associates are created with maximum saturation of hydrogen bonds. Hence, compounds **1a**, **2a**, **3a** and **4a** clearly demonstrate the conclusion, based on earlier X-ray studies of alcoholic inclusions of carboxylic hosts,<sup>9</sup> that the recognition pattern between hosts and guests, equipped with functional groups of strong or relatively strong hydrogen-donor/-acceptor properties is characterized by cooperativity,<sup>10</sup> which is indicated by the coupled system of hydrogen bonds between them.

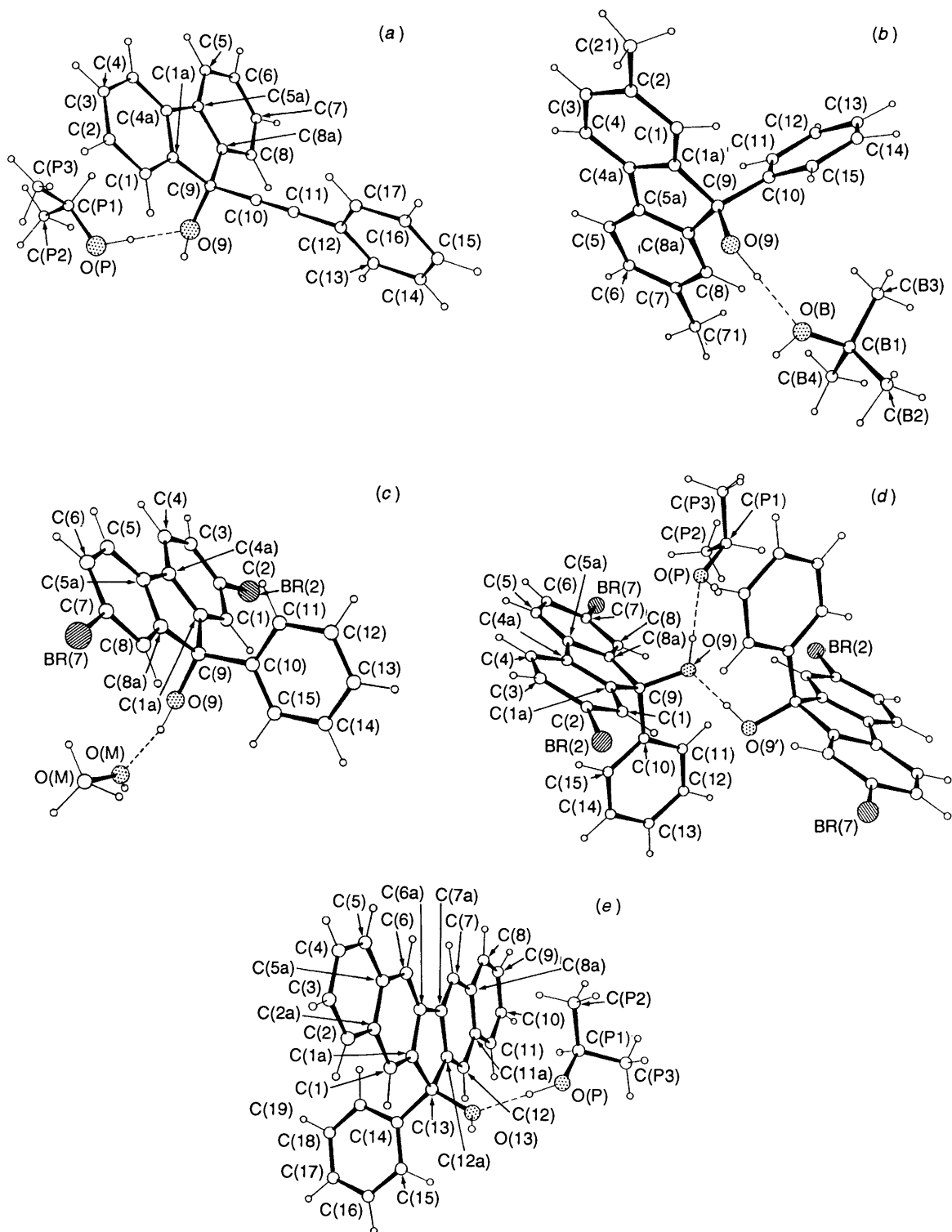
Similar hydrogen bond topology, *i.e.* closed loops of hydro-

gen bonds involving four hydroxy groups, has been found recently in the solvent free structure of 9-methylfluoren-9-ol host<sup>8</sup> and also in the 9-phenylfluoren-9-ol-benzene (8:3) complex.<sup>5</sup> Comparison and analogy with the present alcoholic inclusions suggests that the tetramer aggregates of 9-methyl- and 9-phenyl-fluoren-9-ols can be regarded as results of self-inclusion, where the 9-substituted fluorenol molecules act both as host and guest alcohol. In the case of the 9-phenyl derivative, however, the huge hydrogen-bonded tetramers cannot reach sufficiently high packing density due to their inconvenient shape.<sup>8</sup> Therefore, an additional component, such as benzene, has to be included in order to fill up the voids between the hydrogen-bonded aggregates and thus, make the crystal energetically stable.<sup>5</sup> On the contrary, in the absence of a suitable space filling guest, some of the hydrogen bonds cannot be formed, and as we have seen, the solvent free crystal of 9-phenylfluoren-9-ol is built up from smaller units of hydrogen-bonded dimers, which are able to reach acceptable packing density without a guest.<sup>8</sup>

This latter observation seems to be relevant also for compound **3b**, which has a different host:guest stoichiometry than the other four inclusions in this study, possibly indicating a different way of complexation of the alcoholic guest for this crystal. Indeed, X-ray structure analysis revealed an unexpected mode of interaction between the dibromo-9-phenylfluoren-9-ol host and its propan-2-ol guest. Instead of a coupled hydrogen bonding system of closed loops or endless chains, 2:1 host:guest aggregates are formed *via* hydrogen bonds [Fig. 2(d)] in this crystal, where neither the requirement of maximum saturation of hydrogen bonds, nor the 'maximum acceptor rule'<sup>11</sup> postulated a few years ago, is fulfilled. Accordingly, **3b** proved to be a unique exception with respect to the recognition pattern and hydrogen bonding topology among the numerous alcoholic inclusions of carboxylic or alcoholic hosts known to the authors.<sup>2,9,12</sup>

In the crystals of the presented inclusion compounds the hydrogen-bonded units are then held together mostly by ordinary Van der Waals' forces, occasionally supported by electrostatic C–H...O interactions (Table 3).

**Summary and Conclusions.**—Singly bridged triarylmethanols **1–4** have proved to be useful hosts for the inclusion of alcohols. The prominent recognition pattern appearing in four (**1a–4a**) out of five inclusion compounds with alcohols is an eight-



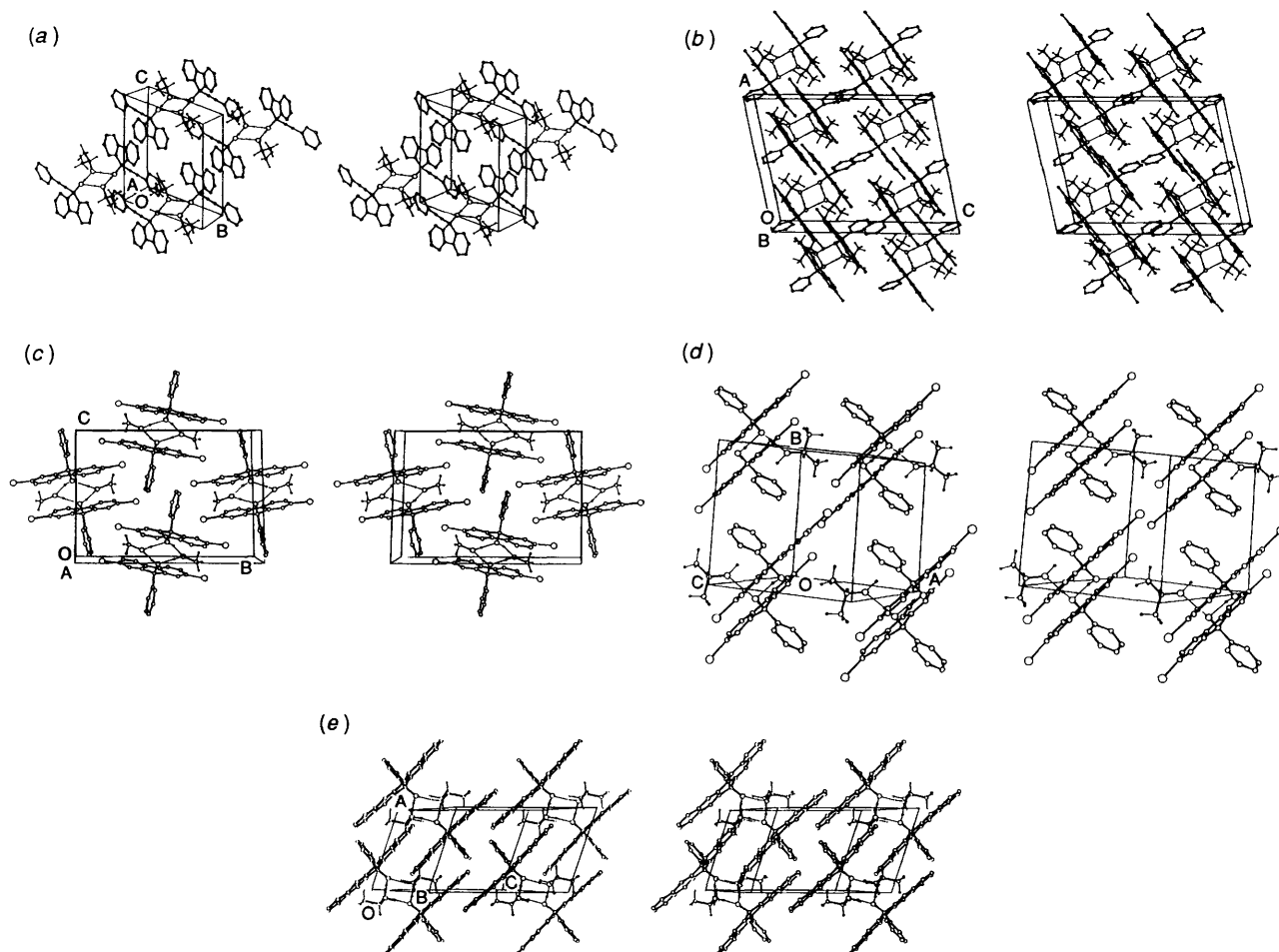
**Fig. 1** Perspective views of the stoichiometric units with labelling of the atoms in the inclusion compounds: **1a** [1-propan-2-ol (1 : 1)] (a); **2a** [2-*tert*-butanol (1 : 1)] (b); **3a** [3-methanol (1 : 1)] (c); **3b** [3-propan-2-ol (2 : 1)] (d); and **4a** [4-propan-2-ol (1 : 1)] (e). Solid and dashed lines represent covalent and hydrogen bonds, respectively. Heteroatoms are shaded.

membered hydrogen-bonded ring comprising two host and two guest hydroxy groups to yield centrosymmetric 2:2 host-guest associates. This type of aggregate with maximum saturation of hydrogen bonds is formed in the crystalline state if packing density allows, thus corresponding to alcoholic inclusions of other hydroxylic hosts.<sup>12</sup> Summing up, the results of this study have potential for the development of chemical materials to be used in separation, stabilization, storage and sensing of alcohols.<sup>3c,7b</sup>

### Experimental

**Synthesis.**—Compounds 1–3 were synthesized from the respective tricyclic ketones and corresponding Grignard reagents according to the general procedure (i) given in literature.<sup>5</sup>

**9-Phenyldibenzo[b,h]fluoren-9-ol 4.** To a stirred suspension of ketone **5**<sup>13</sup> (0.8 g, 2.9 mmol) in dry Et<sub>2</sub>O was added dropwise during 20 min at room temperature a solution of phenyllithium, prepared from granulated lithium (0.7 g, 100 mmol) and



**Fig. 2** Stereoscopic packing illustrations and hydrogen bonding schemes of the inclusion compounds **1a** [1-propan-2-ol (1:1)] (a); **2a** [2-tert-butanol (1:1)] (b); **3a** [3-methanol (1:1)] (c); **3b** [3-propan-2-ol (2:1)] (d); and **4a** [4-propan-2-ol (1:1)] (e). The carbon bonded hydrogens of the host molecules are omitted for clarity. The hydrogen bonds are drawn as thin lines.

bromobenzene (4.47 g, 28.0 mmol).<sup>14</sup> The mixture was stirred for 1 h and then refluxed for 1.5 h. Work-up of the reaction mixture, including hydrolysis (saturated  $\text{NH}_4\text{Cl}$  solution), extraction with  $\text{Et}_2\text{O}$ , washing (brine), drying ( $\text{MgSO}_4$ ) and evaporation of the solvent under reduced pressure yielded the crude product as a viscous red oil which was dissolved in light petroleum (b.p. 40–60 °C). After a few hours an off-white precipitate separated, which was collected and recrystallized from chloroform to give a white powder (69%), m.p. 192–194 °C;  $\delta_{\text{C}}$ (90 MHz;  $\text{CDCl}_3$ ) 148.92, 144.81, 137.30, 134.39, 134.26, 128.72, 128.37, 128.24, 127.20, 126.59, 126.14, 125.65, 124.36, 119.21 and 82.89;  $\delta_{\text{H}}$ (60 MHz;  $\text{CDCl}_3$ ) 2.50 (1 H, s, OH) and 7.20–8.40 (17 H, m, Ar); ( $M^+$  358.1360;  $\text{C}_{27}\text{H}_{18}\text{O}$  requires  $M$ , 358.1357).

Inclusion compounds **1a–4a** and **3b** were obtained by recrystallization of the respective host compound from the corresponding guest alcohol.

**Crystal Structure Determination.**—**Sample preparation.** Crystals of **1a–4a** and **3b**, suitable for X-ray analysis, were grown by slow evaporation of solutions of the host in the guest. The selected single crystals were coated with epoxy glue in order to prevent possible solvent evaporation during the X-ray data collection.

**Data collection and processing.** The intensity data were collected with a STOE/AED2 diffractometer, equipped with a graphite monochromator, using either Mo-K $\alpha$  ( $\lambda = 0.71069 \text{ \AA}$ ) or Cu-K $\alpha$  radiation ( $\lambda = 1.54183 \text{ \AA}$ ) and  $\omega$ - $2\theta$  scan tech-

nique. Calculation of the observed structure factors,  $F_{\text{obs}}$ , included corrections for background, decay, Lorentz and polarization effects, and for compounds **3a** and **b** also allowance for absorption effects. The empirical absorption correction, applied to compound **3a**, was based on  $\psi$  scans of ten reflections within the range  $71 < \chi < 89^\circ$  and  $12 < 2\theta < 46^\circ$ . The transmission factors varied between 0.134 and 0.397. The same correction for compound **3b**, however, was carried out by the numerical absorption correction program of the SHELX system.<sup>15</sup> The minimum and maximum values of the transmission factors in the latter case were 0.337 and 0.598, respectively. Crystal data and further details of the data reduction and structure refinement calculations are shown in Table 1.

The structures were solved by application of direct methods<sup>16</sup> and refined by full-matrix least-squares refinements based on  $|F|$  (SHELX).<sup>15,17</sup> The host and guest hydroxy hydrogens in each structure were located from difference electron density ( $\Delta\rho$ ) calculations and were held riding on their 'parent' atoms during the subsequent calculations. The carbon bonded H atoms, however, were either located from  $\Delta\rho$  maps and were treated as the hydroxy ones, or were assumed to be in geometrically idealized positions, recalculated after each cycle of the refinement. In the last stage of the refinements, the non-hydrogen atoms were allowed to vibrate anisotropically, whereas isotropic displacement parameters were refined for the hydrogen positions. A few reflections (10 for **1a**, 7 for **2a**, 6 for **3a**, and 4 for **3b**), with considerably lower  $F_{\text{obs}}$  than  $F_{\text{calc}}$ , most likely depending on extinction effects, have been omitted from the last refinement calculations, which yielded the reliability

indices  $R$  and  $wR$ , shown in Table 1. The  $wR_{\text{tot}}$  values were calculated for the final structural models using all unique non-zero reflections. Refined fractional atomic coordinates of the non-hydrogen atoms and those of the hydroxy H atoms have been deposited.\*

**Supplementary data.** Lists of fractional atomic coordinates of the non-hydrogen atoms (Table 4), bond lengths and angles involving the non-hydrogen atoms (Tables 5 and 6), fractional atomic coordinates of the hydrogen positions (Table 7) and bond distances and bond angles involving the H atoms (Tables 8 and 9) have been deposited as supplementary data at the Cambridge Crystallographic Data Centre. Lists of anisotropic displacement parameters of the C, O, and Br atoms (Table 10) and of the observed and calculated structure factors are available directly from the authors (I. C.).

\* For details of the CCDC deposition scheme, see 'Instructions for Authors,' *J. Chem. Soc., Perkin Trans. 2*, 1994, issue 1.

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