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Complexation with diol host compounds. Part 14. Inclusion compounds of 2,2'-bis(9-hydroxy-9-fluorenyl)biphenyl with acetonitrile, cyclohexanone, di-*n*-propylamine and dimethylformamide

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Complexation with diol host compounds. Part 14. Inclusion compounds of 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl with acetonitrile, cyclohexanone, di-*n*-propylamine and dimethylformamide

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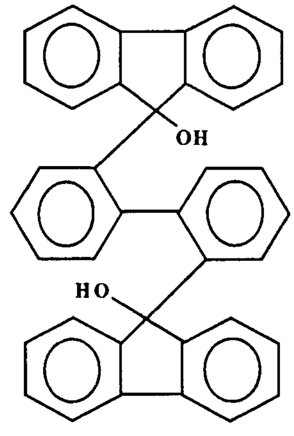
The structures of the inclusion compounds of 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl (H) with acetonitrile (1) (1:1), cyclohexanone (2) (1:2), di-*n*-propylamine (3) (1:1) and dimethylformamide (4) (1:2) are reported. Crystal data: (1) monoclinic, $P2_1/c$ with $a = 10.500(3)$, $b = 15.598(3)$, $c = 18.344(3)$ Å, $\beta = 96.66(2)°$, $Z = 4$, $D_C = 1.24$ g cm^{-3}. (2) monoclinic, $P2_1/c$ with $a = 13.980(3)$, $b = 11.768(5)$, $c = 23.49(1)$ Å, $\beta = 98.77(3)°$, $Z = 4$, $D_C = 1.24$ g cm^{-3}. (3) monoclinic, $C2/c$ with $a = 29.57(1)$, $b = 13.485(4)$, $c = 18.17(1)$ Å, $\beta = 107.94(4)°$, $Z = 8$, $D_C = 1.16$ g cm^{-3}. (4) monoclinic, $C2/c$ with $a = 30.123(9)$, $b = 13.391(6)$, $c = 19.177(6)$ Å, $\beta = 111.23(4)°$, $Z = 8$, $D_C = 1.22$ g cm^{-3}. Final R values for the four structures were 0.065, 0.120, 0.084 and 0.107 for 2937, 2830, 2071 and 3769 reflections, respectively. The host conformation is quite rigid and does not appear to be influenced by the shape and size of the guests studied. The host is held in a spiral conformation by means of an intramolecular hydrogen bond. In addition, host–guest hydrogen bonds are observed in all structures. Thermal analysis was used to evaluate the strength of binding of the guest molecules and confirmed that (1) is the most stable of the four compounds studied.



(H)

1. H . MeCN (1:1)
2. H . cyclohexanone (1:2)
3. H . $(n\text{-Pr})_2NH$ (1:1)
4. H . DMF (1:2)

Scheme 1

INTRODUCTION

Organic hosts that form crystalline inclusion complexes with various guests have been extensively studied.[1] Some are true clathrates[2] in which steric factors alone control their formation while others are co-ordinatoclathrates,[2,3] so called because their aggregates are held together by some co-ordination between host and guest. The hydrogen bond is frequently the link between host and guest in these compounds.[4,5] The new atropomeric host compound 2,2′-bis(9-hydroxy-9-fluorenyl)biphenyl (**H**) exists in the racemic and either of the two resolved forms. Our preliminary studies on these compounds show that they all have inclusion abilities for a wide variety of guests[6] and we are presently working on the crystallographic and thermal analysis of a number of these compounds with a view to understanding stability and selectivity.

We report here the structures of the racemic form of the host compound, **H**, with (**1**) acetonitrile (1:1); (**2**) cyclohexanone (1:2); (**3**) di-*n*-propylamine (1:1) and (**4**) dimethylformamide (1:2) (scheme 1).

RESULTS AND DISCUSSION

Details of data collection and structure refinement are given in Table 1. Final fractional atomic co-ordinates,

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Table 1 Crystal data, details of data collection and final refinement

Compound	1	2	3	4
Molecular formula	$C_{38}H_{26}O_2{\cdot}C_2H_3N$	$C_{38}H_{26}O_2{\cdot}(C_6H_{10}O)_2$	$C_{38}H_{26}O_2{\cdot}C_6H_{15}N$	$C_{38}H_{26}O_2{\cdot}(C_3H_7NO)_2$
Mass (g mol^{-1})	555.68	710.91	615.82	660.81
Space group	$P2_1/c$	$P2_1/c$	$C2/c$	$C2/c$
a (Å)	10.500 (3)	13.980 (3)	29.57 (1)	30.123 (9)
b (Å)	15.598 (3)	11.768 (5)	13.485 (4)	13.391 (6)
c (Å)	18.344 (3)	23.49 (1)	18.17 (1)	19.177 (6)
β (°)	96.66 (2)	98.77 (3)	107.94 (4)	111.23 (4)
Volume (Å^3)	2984 (7)	3819 (16)	6984 (5)	7211 (5)
Z	4	4	8	8
$F(000)$	1168	1512	2624	2800
μ (Mo Kα) (cm^{-1})	0.70	0.72	0.66	0.72
Crystal dimensions (mm)	0.50 × 0.50 × 0.50	0.31 × 0.25 × 0.43	0.42 × 0.50 × 0.40	0.50 × 0.50 × 0.5
D_c (g cm^{-3})	1.24	1.24	1.16	1.22
θ range scanned (°)	1–25	1–23	1–23	1–25
Range of h, k, l	±12, 18, 21	±15, 12, 25	±32, 14, 20	±15, ±19, 22
Decay during collection (%)	3.2	55.9[a]	0.2	3.8
Number of reflections collected	5634	5740	10,628	13,079
Number of reflections with $I_{rel} > 2\sigma I_{rel}$	2937	2830	2071	3769
Number of parameters	401	494	402	433
Max LS shift to e.s.d.	0.12	0.11	0.37	0.40
$R(\sum F_O - F_C/\sum F_O)$	0.0650	0.1200	0.0840	0.1066
R_w	0.0690	0.1110	0.0760	0.1066
$w(\sigma^2 F + gF^2)^{-1}$	0.03	0	0	1.00
Max/min residual electron density (eÅ^{-3})	0.32/−0.43	0.45/−0.42	0.27/−0.11	0.40[b]/−0.48

[a] Decay correction applied: Min, max, average % = 80.11, 99.96, 89.27. [b] Several peaks of 0.5 to 0.8 eÅ^{-3} are found near the methyl groups of molecule D.

anisotropic thermal parameters, bond lengths and angles and Tables of observed and calculated structure factors have been deposited.

A perspective view of the host, showing the atomic labelling used, is given in Figure 1. The host is well refined in all four structures. O–C distances are between 1.421(4) and 1.428(4) Å. Within the 5-membered ring in the fluorenyl moiety, C(1AX)–C(9X) and C(8AX)–C(9X) are between 1.51(2) and 1.55(1) Å (where X may be A or B as shown in Fig 1). C(4AX)–C(5AX) is in the range 1.45(2)–1.47(1) Å. C(9)–C(10) bonds are between 1.53(2) and 1.540(5) Å and C(11A)–C(11B) are in the range 1.50(2)–1.508(4) Å. Bond lengths within the aromatic rings fall in the range 1.33(3) to 1.43(2) Å. These are all in agreement with values tabulated by Allen *et al.*[7]

Bond angles within the 5-membered ring are between 108.2(3) and 111.1(9)° except at C(9) where the internal angle is between 100.8(3)° and 101.4(6)°. The remainder of the angles around C(9) are between 108.6(7) and 112.9(3)°. Angles within the aromatic rings are in the range 117.5(3) to 122.9(3)°.

The fluorenyl moieties are planar to within 0.02 Å within each ring and have a maximum dihedral angle between the rings of 8.2(4)°. The biphenyl aromatic rings are also planar, with a maximum deviation from the least squares plane of 0.02 Å.

The conformation of the host molecules may be described by means of the torsion angles which define the orientation of the fluorenyl and biphenyl moieties. These angles are C(10A)–C(11A)–C(11B)–C(10B) (τ_1) to describe the orientation of the biphenyl group and the two angles O(9X)–C(9X)–C(10X)–C(11X) (τ_2 and τ_3 where X = A and B, respectively) which define the orientation of the fluorenyl group with respect to its adjacent phenyl ring. τ_1, τ_2 and τ_3 are listed in Table 2.

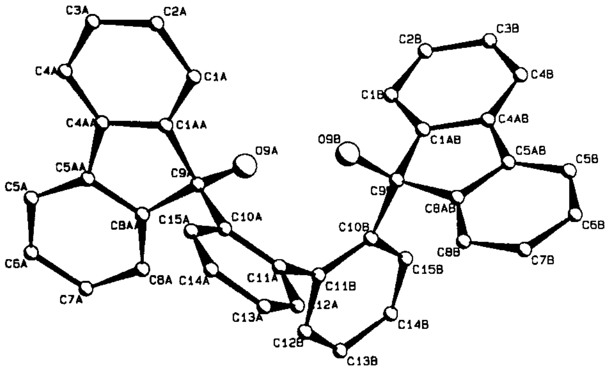


Figure 1 Perspective view of the host (H), showing the atomic labelling used.

The overall host conformation is a spiral; the two hydroxy groups form an intramolecular hydrogen bond in the centre of the spiral and are surrounded by bulky aromatic groups.

The guest molecules in all four structures displayed greater thermal motion than the host and were therefore more difficult to model successfully. The acetonitrile molecule in compound **1** refined well with a C–N bond length of 1.115(6) Å and a C–C distance of 1.450(9) Å. The N–C–C angle of 176.5(6)°, close to the required linear conformation.

Compound **2** contains two molecules of cyclohexanone per host molecule. C=O and C–C bond lengths are within normal limits,[7] internal bond angles are between 109(1)° and 118(2)° while C–C=O bond angles are between 120(1) and 123(2)° for both molecules. Both cyclohexanone molecules adopt the chair conformation. C(1) is 0.41 and −0.55 Å out of the mean plane in molecules C and D, respectively, while C(4) shows a deviation from the plane of −0.50 and 0.63 Å.

The propyl chains of the guest in compound **3** showed a great deal of thermal motion. The C–N bond lengths are 1.45(3) Å and 1.58(2) Å and the angle around the nitrogen is 118(2)°. C–C bond lengths are between 1.29(5) and 1.48(3) Å and angles about the carbons are between 106(2) and 114(4)°.

In compound **4** one dimethylformamide molecule is hydrogen bonded to the host. This molecule was successfully modelled and had bond lengths and angles in close agreement with expected values.[7] The modelling of the second guest was more difficult. It is located close to the diad at $(\frac{1}{2}y\frac{1}{4})$ and is thus disordered about this diad. There is some residual electron density close to this molecule, particularly in the region of the methyl groups. This could not be incorporated into a model for dimethylformamide.

In each of compounds **1** to **4**, the host coils around to form an intramolecular hydrogen bond between its two hydroxy groups. The second hydroxy hydrogen [H(9B)] then points outwards to hydrogen bond to an oxygen or nitrogen atom on the guest. Details of these hydrogen bonds are given in Table 3.

Table 2 Torsion angles defining host conformation

Compound	τ_1 (°)	τ_2 (°)	τ_3 (°)
1	90.9 (5)	−23.5 (5)	−21.8 (5)
2	91.8(16)	−23.5 (15)	−19.3 (14)
3	93.4(16)	−18.9 (15)	−13.2 (16)
4	93.3(12)	−17.5 (12)	−18.7 (12)

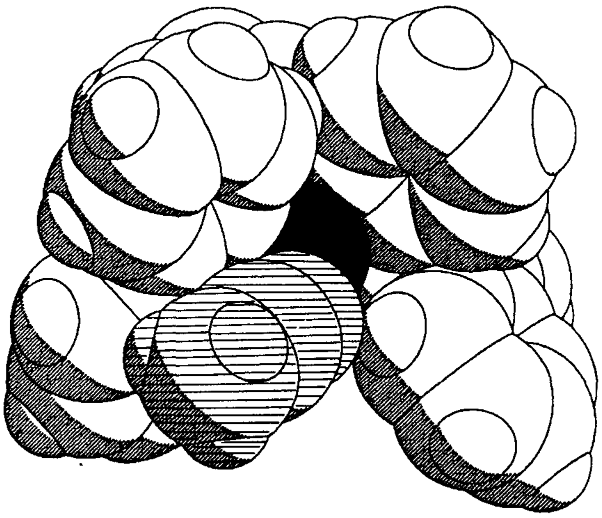


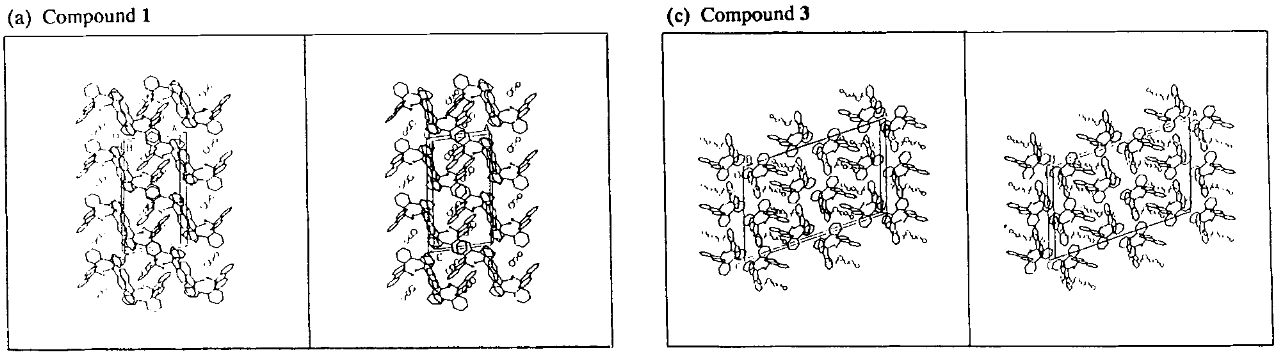
Figure 2 Space-filled diagram of the host–guest unit in compound **1**. The host's exposed hydroxy group is shaded and the acetonitrile guest is striped.

The molecular assembly of host and guest unit involves the approach of a guest to the free hydroxy moiety of the host. The guest is then held between the bulky aromatic groups of the host. The close fit of this arrangement is illustrated in Figure 2 for compound **1**. Guests in compounds **2–4** hydrogen bond to the host in a similar fashion but because they are not as small or as linear as acetonitrile, they do not fit as well.

The molecular packing diagrams of the four compounds studied are shown in Figure 3. The guests are held in cavities formed between the bulk host molecules. The cavity-like nature of the guest environment was confirmed by an analysis (using OPEC[8]) of the volume of occupied space in the unit cells. In compound **1** the acetonitrile is captured within a cavity of approximate dimensions 5.4 × 5.5 × 9.1 Å. Compound **2** has a more open arrangement. Two cyclohexanone molecules are present for each host—one is hydrogen bonded in a similar position to the acetonitrile in **1** while the other occupies the cavity formed by the scissor-like arrangement of phenyl and fluorenyl groups on two adjacent hosts. The dimensions of the cavities in **2** are approximately 6.1 × 7.1 × 10.6 Å.

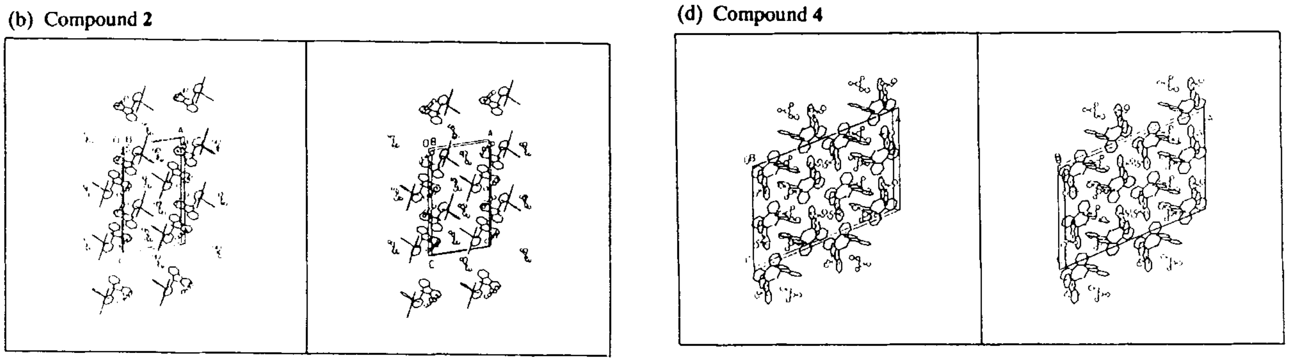
Table 3 Hydrogen bonding

Compound	*1*	*2*	*3*	*4*
O(9A)–H(9A) (Å)	1.03 (6)	0.995 (7)	1.00 (6)	0.99 (5)
O(9A)...O(9B) (Å)	2.826 (4)	2.76 (1)	2.93 (1)	2.773 (9)
O(9A)–H(9A)...O(9B) (°)	150 (6)	157.0 (5)	155 (10)	161 (10)
O(9B)–H(9B) (Å)	0.97 (4)	1.00 (9)	1.00 (9)	1.01(6)
O(9B)...N/O(1C) (Å)	2.897 (5)	2.77 (1)	2.83 (2)	2.662 (9)
O(9B)–H(9B)...N/O(1C) (°)	162 (4)	155 (9)	162 (8)	150 (7)



(a) Compound 1

(c) Compound 3



(b) Compound 2

(d) Compound 4

Figure 3 Packing diagrams of compounds **1**–**4**.

Table 4 Thermal analysis

Compound	*1*	*2*	*3*	*4*
Host:guest ratio	1:1	1:2	1:1	1:2
Boiling point of guest (°C)	81.6	155.6	110	153
TG				
Weight loss expected (%)	7.39	27.61	16.43	22.12
Weight loss obtained (%)	7.49	26.78	17.14	21.73
DSC				
Guest loss endotherm temperature range (°C)	149–189	120–144	154–188	133–196
Host melting endotherm onset temperature (°C)	299	302	300	300

The $C2/c$ structures have very similar cell parameters and their packing motifs are almost identical. Figure 3 shows the packing diagrams of **3** and **4**, both viewed along [010]. The arrangement of the host molecules remains the same but three dimethylformamide molecules fit into the cavities which hold two di-*n*-propylamine molecules. The cavities in these structures, calculated by OPEC, are elongated with approximate dimensions 5.4 × 5.8 × 22 Å.

A similar host to **H**, 2,2′-bis-(diphenylhydroxymethyl)-1,1′-diphenyl was prepared and its (2:1) inclusion compound with acetone reported by Toda *et al.*[9] The host conformation was comparable with that of **H**, having an intramolecular hydrogen bond with O–O distance 2.76(2) Å. A very different mode of packing was observed however. Six hosts are arranged around a $\bar{3}$ centre and are alternately bridged by the acetone guests to form a hydrogen-bonded cluster with hydrophobic phenyl and methyl groups lining the outside surface.

The results of the thermal analyses are summarized in Table 4 and the Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG) traces are shown in Figure 4. There is close agreement between the calculated and observed weight losses in the TG for all four compounds, thus confirming the host to guest ratios modelled. The DSC curves of **1**–**4** are characterized by an initial endotherm which corresponds to the guest loss observed in the TG. This is followed by a second, sharper endotherm caused by the melting

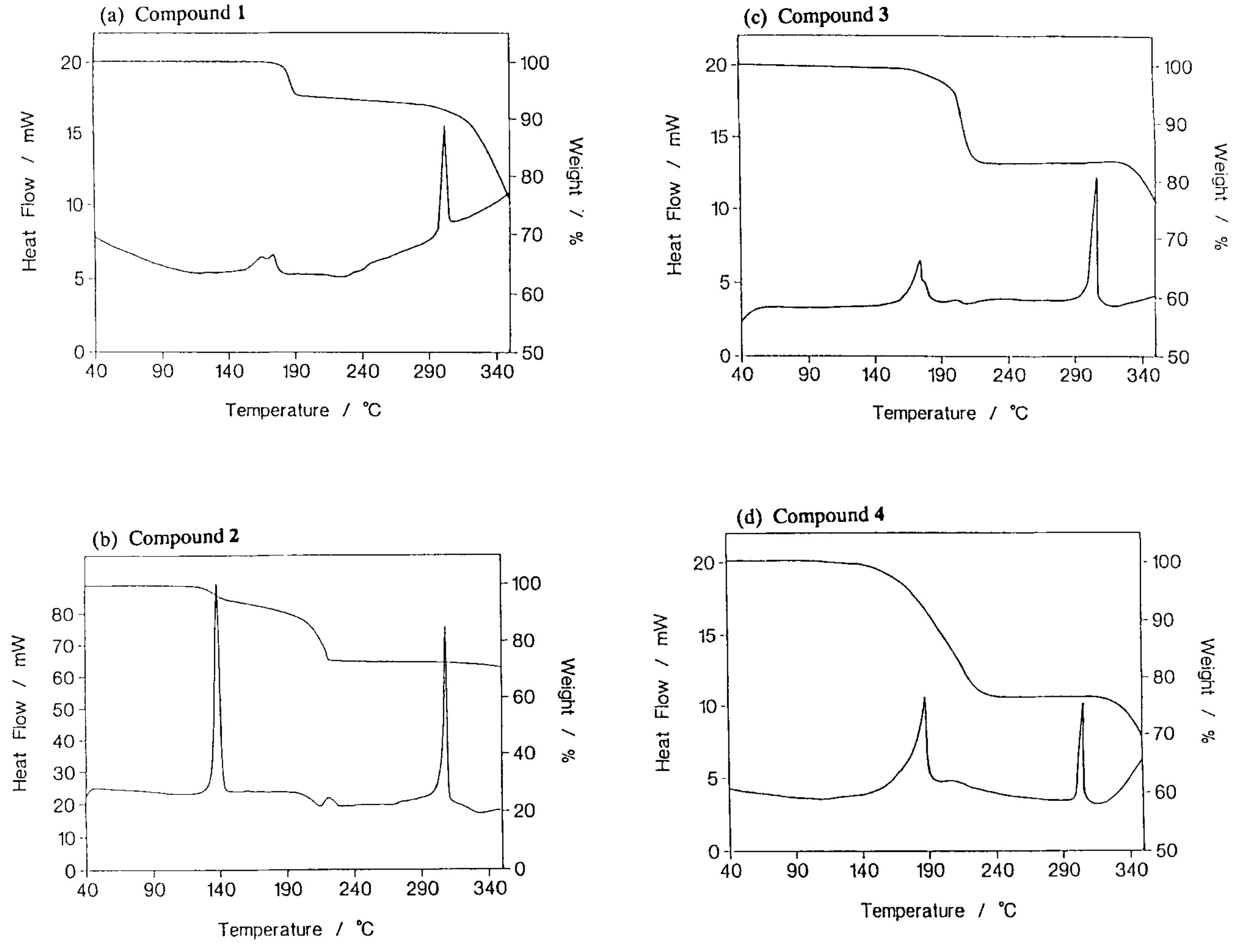


Figure 4 DSC and TG curves for compounds **1**–**4**.

of the host compound. At this heating rate, the host melts at 299–302°C. For compounds **2**, **3** and **4** the guest is released close to the boiling point of the pure guest liquid. In compound **1** however, the guest is held *ca.* 70°C beyond the boiling point of acetonitrile.

EXPERIMENTAL

The synthesis of the free host compound is described elsewhere.[10] The inclusion compounds were obtained as transparent angle crystals by slow evaporation of solutions of the host in guest. A suitable crystal of each compound was sealed in a Lindemann glass capillary (surrounded by mother liquor) and mounted on an Enraf-Nonius CAD4 diffractometer. Intensity data were collected at 298K using graphite monochromated Mo Kα radiation ($\lambda = 0.7107$ Å). Accurate cell parameters were obtained by least squares analysis of the setting angles of 24 reflections in the range $16° \leqslant \theta \leqslant 17°$. The ω–2θ scan mode was used at a maximum recording time of 40 s. The scan width chosen was ($0.85 + 0.35 \tan\theta$) with an aperture width of ($1.12 + 1.05 \tan\theta$) and vertical aperture length of 4 mm. Three standard reflections were checked periodically for intensity and orientation control. Intensities were corrected for Lorentz and polarization effects but not for absorption. A linear decay correction was applied to the data of compound **2**.

The structures were solved by direct methods using SHELXS-86[11] and refined using SHELX-76.[12] Refinement of the host molecules was similar in all structures. All non-hydrogen atoms were treated anisotropically. The aromatic hydrogens were placed in calculated positions with a common temperature factor. The hydroxy hydrogens were located in the difference Fourier map and the O–H bond length was constrained to 1.00(3) Å in each case.

The acetonitrile guest (compound **1**) was allowed to refine anisotropically. The hydrogens were treated as a rigid group and tied to a single temperature factor. The cyclohexanone molecules in compound **2** were anisotropically refined. Hydrogen atoms were fixed in calculated positions and treated isotropically with a common temperature factor. The di-*n*-propylamine molecule in compound **3** was modelled with isotropic temperature factors because of the high thermal motion of the propyl chains. The amine hydrogen was located in a difference Fourier map and was constrained to 1.00(3) Å from its parent nitrogen atom. Two dimethylformamide molecules are included per host molecule in compound **4**. One of the DMF molecules is hydrogen bonded to the host. This molecule refined uneventfully and was modelled anisotropically but without hydrogen atoms. The second DMF molecule was found close to the diad at ($\frac{1}{2}y\frac{1}{4}$). This molecule showed a great deal of thermal motion and it was difficult to model. Consequently, all atoms were modelled isotropically and no hydrogen atoms were placed.

Thermal analysis

DSC and TG were performed on a Perkin Elmer PC7 Series System. Crystals were removed from their mother liquor, blotted dry on filter paper and crushed before analysis. Sample weight in each case was *ca.* 5 mg. The temperature was raised from ambient to 350°C at a heating rate of 20°C min^{-1}. The purge gas was dry nitrogen flowing at 40 ml min^{-1}.

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