Crystalline Inclusion Compounds of Substituted 2,2'-Bis(9-hydroxyfluoren-9-yl)biphenyls: Synthesis, X-Ray Crystal Structures and Thermal Analysis Study of Inclusion Compounds with Butyronitrile, Cyclohexanone, Cyclopentanol and Dimethylformamide†

Susan A. Bourne,*[a] **Luigi R. Nassimbeni,**[a] **Margaret L. Niven,**[a] **Edwin Weber***[b] **and Andreas Wierig**[b]
[a] *Department of Chemistry, University of Cape Town, Rondebosch 7700, South Africa*
[b] *Institut für Organische Chemie der Technischen Universität Bergakademie Freiberg, Leipziger Str. 29, D-09596 Freiberg/Sa., Germany*

The syntheses of 2,2'-bis(2,7-di-*tert*-butyl-9-hydroxyfluoren-9-yl)biphenyl (**2**), 2,2'-bis(2,7-dichloro-9-hydroxyfluoren-9-yl)biphenyl (**3**) and 2,2'-bis(2,7-dibromo-9-hydroxyfluoren-9-yl)biphenyl (**4**) are reported. Inclusion compounds were prepared with these hosts: **5** = **2**·butyronitrile (1:1), **6** = **3**·cyclohexanone (1:2), **7** = **3**·cyclopentanol (1:2), **8** = **4**·dimethylformamide (1:2). Crystal data: **5**, monoclinic, $C2/c$ with a = 17.174(2), b = 17.985(3), c = 17.333(3) Å, β = 113.73(1)°, Z = 4, D_c = 1.10 g cm^{-3}; **6**, monoclinic, $P2_1/n$ with a = 15.048(3), b = 16.106(4), c = 19.10(1) Å, β = 112.97(4)°, Z = 4, D_c = 1.32 g cm^{-3}; **7**, monoclinic, $P2_1/c$ with a = 14.576(2), b = 15.783(4), c = 19.561(4) Å, β = 111.72(1)°, Z = 4, D_c = 1.31 g cm^{-3}; **8**, triclinic, $P\bar{1}$ with a = 11.52(1), b = 11.825(1), c = 17.836(1) Å, α = 79.19(5), β = 71.15(7), γ = 60.85(7)°, Z = 4, D_c = 1.62 g cm^{-3}. Final R values for the four structures were 0.071, 0.062, 0.077 and 0.096 for 2489, 3270, 3432 and 3802 reflections, respectively. Host ··· guest hydrogen bonds are observed in all four structures and there is an intramolecular hydrogen bond in the hosts **5**–**7**. In addition, in compounds **6**–**8** there are a number of O ··· Cl, Cl ··· Cl, N ··· Br and Br ··· Br interactions. Thermal analysis was used to study the binding of the guest molecules and indicated that the guests in **5**–**7** were more strongly held than that in **8**.

Inclusion compounds formed between simple organic molecules serve as useful models for studying interatomic interactions and other aspects of molecular recognition.[2]

We recently published the synthesis, structure and thermal analysis of some inclusion compounds of 2,2'-bis(9-hydroxyfluoren-9-yl)biphenyl (**1**).[1,3] These compounds were defined as coordinatoclathrates[4] because their aggregates are held together by coordination between host and guest.[5] Many other examples of coordinatoclathrates have been reported[6–10] in which the most common linkage between host and guest is the hydrogen bond.

We have prepared several substituted versions of this host **1** in order to study the role played by the substituents in inclusion properties. To this end, host molecules **2**–**4** were synthesized containing *tert*-butyl, chloro and bromo groups at the 2- and the 7-positions on the fluorenyl moieties. The addition of chloro and bromo substituents has the added potential for a number of electrostatic interactions.[11]

Experimental

General Methods and Materials.—All temperatures are uncorrected. M.p.s were determined with a Reichert hot-stage apparatus. High-resolution mass spectra were obtained using an AEI MS 50 instrument. ^{1}H and ^{13}C NMR spectra were measured for CDCl$_3$ solutions (Me$_4$Si as internal standard) with Varian EM-360 (60 MHz) and Bruker WH-90 (90 MHz) spectrometers, respectively. Microanalyses were carried out by the Microanalytical Laboratory of the *Institut für Organische Chemie und Biochemie, Universität Bonn.* For column chromatography Al$_2$O$_3$ (grade II–III, Merck) and silica gel (0.063–0.1 mm, Merck) were used. All solvents were of reagent quality or purified by distillation before use. Starting compounds and all other reagents were purchased from Janssen unless otherwise stated.

2,2'-Dibromobiphenyl.—From 1,2-dibromobenzene with BuLi as described;[12] recrystallization from EtOH gave colourless crystals (44%), m.p. 79–81 °C (lit.,[12] 80–81 °C).

2,7-Disubstituted Fluorenones **9**–**11**.—*2,7-Di-*tert*-butylfluorenone* **9**. From 2,7-di-*tert*-butylfluorene[13] with oxygen as described;[14] chromatography (Al$_2$O$_3$, toluene) and recrystallization from isoamyl alcohol yielded a yellow powder (75%), m.p. 105–107 °C (lit.,[15] 107 °C).

2,7-Dichlorofluorenone **10**. From fluorenone with *N*-chlorosuccinimide as described;[16] recrystallization from EtOH yielded yellow crystals (60%), m.p. 190–191 °C (lit.,[16] 189–190 °C).

2,7-Dibromofluorenone **11**. From dibromofluorene[17] with oxygen as described;[16] chromatography (Al$_2$O$_3$, toluene) and recrystallization from isoamyl alcohol yielded a yellow powder (81%), m.p. 200 °C (lit.,[18] 202 °C).

Substituted 2,2'-Bis(9-hydroxyfluoren-9-yl)biphenyls **2**–**4**. *General Procedure.*—2,2'-Dibromobiphenyl and BuLi were reacted with the corresponding 2,7-disubstituted fluorenone (**9**–**11**) following a described procedure.[3] Specific details for each compound including differences in preparation are given below.

*2,2'-Bis(2,7-di-*tert*-butyl-9-hydroxyfluoren-9-yl)biphenyl* **2**. Fluorenone **9** was reacted. Treatment of the product with hot MeOH (1 h) yielded a white powder (46%), m.p. > 300 °C (Found: C, 87.7; H, 8.0. C$_{54}$H$_{58}$O$_2$ requires C, 87.76; H, 7.91%); δ_C(90 MHz; CDCl$_3$) 152.78, 151.97, 151.51, 151.03, 142.06, 141.67, 137.60, 136.69, 132.35, 128.53, 127.08, 126.14, 125.65, 122.03, 121.64, 119.66, 118.95, 87.55, 35.12, 35.02 and 31.56; δ_H(60 MHz, CDCl$_3$) 1.09 (s, 18 H, Bu^t), 1.22 (s, 18 H, Bu^t), 3.38

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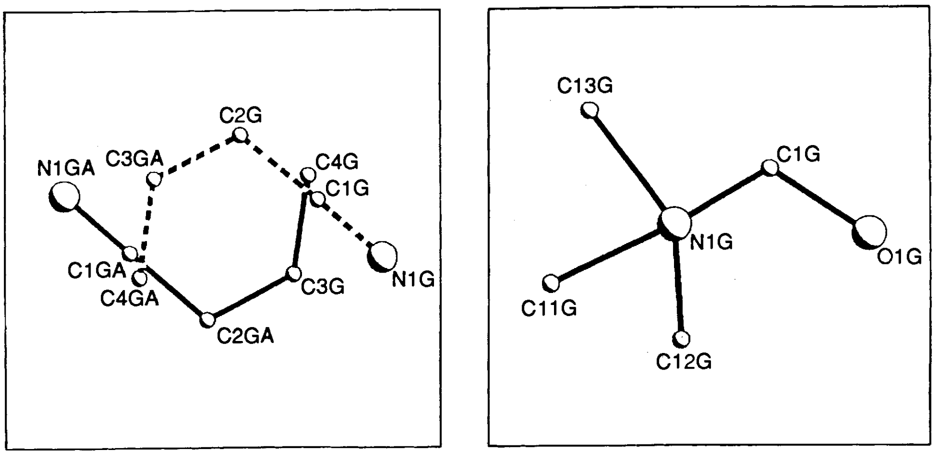
† Complexation with Diol Host Compounds, Part 15. For Part 14 of this series see ref. 1.



(*a*) (*b*)

Fig. 1 Disorder models of the guests in (*a*) compound **5** and (*b*) compound **8**

(s, 2 H, OH) and 6.44–7.62 (m, 24 H, Ar); (M^+, 738.4460. $C_{54}H_{58}O_2$ requires *M*, 738.4422).

2,2′-*Bis*(2,7-*dichloro*-9-*hydroxyfluoren*-9-*yl*)*biphenyl* **3**. Fluorenone **10**, added in portions as a solid, was reacted. Treatment of the crude product with hot MeOH and recrystallization of the solid residue from DMF yielded colourless crystals (34%), m.p. > 300 °C (Found: C, 67.9; H, 4.1. $C_{38}H_{22}Cl_4O_2$ requires C, 67.40; H, 3.70%); δ_C(90 MHz, [$^2H_6$]Me$_2$SO) 150.94, 150.86, 150.75, 148.21, 141.41, 139.59, 137.31, 135.01, 134.21, 130.65, 128.76, 128.65, 127.83, 127.39, 126.19, 124.78, 124.53, 121.81, 121.36 and 87.28; δ_H(60 MHz, [$^2H_6$]Me$_2$SO) 5.25 (s, 2 H, OH) and 7.13–7.63 (m, 20 H, Ar); [M^+ (FAB), 650. $C_{38}H_{22}Cl_4O_2$ requires *M*, 650.0366].

2,2′-*Bis*(2,7-*dibromo*-9-*hydroxyfluoren*-9-*yl*)*biphenyl* **4**. Fluorenone **11**, added in portions as a solid, was reacted. Dry THF was added to the reaction mixture to give a solution that was heated under reflux for 24 h. The solid precipitate which formed, and which did not dissolve on quenching with saturated aqueous NH_4Cl solution, was collected and treated with hot MeOH to remove impurities. Recrystallization from dimethylformamide (DMF) yielded colourless crystals (22%), m.p. > 300 °C (Found: C, 54.81; H, 2.6. $C_{38}H_{22}Br_4O_2$ requires C, 54.98; H, 2.67%); δ_C(90 MHz, [$^2H_6$]Me$_2$SO) 156.18, 150.14, 143.87, 140.14, 138.51, 137.54, 135.91, 133.43, 132.34, 132.21, 129.35, 128.59, 128.03, 127.08, 126.57, 123.79, 122.42, 122.30, 121.98 and 86.86; δ_H(60 MHz, [$^2H_6$]Me$_2$SO) 3.86 (s, 2 H, OH) and 6.62–8.05 (m, 20 H, Ar); (M^+, 830.172. $C_{38}H_{22}Br_4O_2$ requires *M*, 830.172).

Crystalline Inclusion Compounds **5–8**.—The procedure, as described[14] was used. Stoichiometric ratios of the inclusion compounds were determined by ^1H NMR integration of dissolved probes.

Crystal Structure Determination of **5–8**.—*Sample preparation and data collection.* Single crystals for diffraction measurements were grown 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 298 K using graphite monochromated Mo-Kα radiation (λ = 0.7107 Å). Accurate cell parameters were obtained by least-squares analysis of the setting angles of 24 reflections in the range $16° \leq \theta \leq 17°$. The ω–2θ mode was used at a maximum recording time of 40 s. The scan width chosen was (0.85 + 0.35 tan θ) and an aperture width of (1.12 + 1.05 tan θ) and vertical aperture length of 4 mm were used. Three standard reflections were checked periodically for intensity and orientation control. Intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to compounds **6** and **8**.

Structure analysis and refinement. The structures were solved by direct methods using SHELXS-86[19] and refined using SHELX-76.[20] Refinement of the host molecules was similar in all structures. All non-hydrogen atoms were treated anisotropically. The aromatic hydrogens were placed in the calculated positions with a common temperature factor. For compounds **6**, **7** and **8** 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 hydroxy hydrogen atoms in compound **5** could not be located in the difference Fourier map and it was thus omitted from the final model.

The butyronitrile guest in **5** was located close to the centre of inversion at (0 1/2 0) and was disordered in that the corresponding butyl chains overlapped as shown in Fig. 1(*a*). The nitrogen and four carbon atoms were refined isotropically with site occupancy factors of 0.5 and no hydrogen atoms were modelled. The cyclohexanone molecules in **6** were anisotropically refined. Hydrogen atoms were fixed in calculated positions and treated isotropically with a common temperature factor. The two cyclopentanol molecules in **7** were modelled isotropically because of their high temperature factors. Hydrogen atoms were placed in calculated positions and refined with a common temperature factor. The methyl groups of the DMF guests in **8** showed a great deal of thermal motion and a simple disorder model was chosen to account for the smearing of electron density in the region of the guests. This is shown in Fig. 1(*b*): three carbon positions were modelled for each DMF, each with a site occupancy factor of 0.66. The DMF molecules were refined isotropically with no hydrogen atoms.

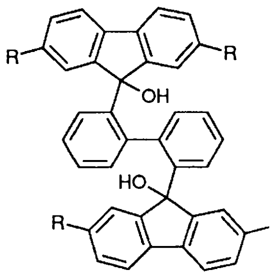
Thermal Analysis.—Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a Perkin-Elmer PC7 Series System. Crystals were removed from their mother liquor, blotted dry on filter paper and crushed before analysis. Sample weight in each case was *ca.* 5 mg. The temperature was raised from ambient to 350 °C at a heating rate of 20 °C min^{-1}. The purge gas was dry nitrogen flowing at 40 cm^3 min^{-1}.

Results and Discussion

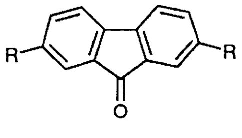
Synthesis.—Compounds **2–4** can be made by reaction of the corresponding fluorenones **9–11** with lithium reagent,[21] prepared from 2,2′-dibromobiphenyl in 22–50% (see Experimental). The starting fluorenones **9–11** were obtained by O_2

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

	5	**6**	**7**	**8**
Formula unit	$C_{54}H_{58}O_2 \cdot C_4H_7N$	$C_{38}H_{22}Cl_4O_2 \cdot (C_6H_{10}O)_2$	$C_{38}H_{22}Cl_4O_2 \cdot (C_5H_{10}O)_2$	$C_{38}H_{22}Br_4O_2 \cdot (C_3H_7NO)_2$
Formula weight	808.163	848.694	824.672	976.418
Space group	$C2/c$	$P2_1/n$	$P2_1/c$	$P\bar{1}$
a/Å	17.174(2)	15.048(3)	14.576(2)	11.52(1)
b/Å	17.985(3)	16.106(4)	15.783(4)	11.825(1)
c/Å	17.333(3)	19.10(1)	19.561(4)	17.836(1)
α/°	90	90	90	79.19(5)
β/°	113.73(1)	112.97(4)	111.72(1)	71.15(7)
γ/°	90	90	90	60.85(7)
V/Å^3	4901(28)	4263(65)	4181(2)	2006(87)
Z	4	4	4	2
F(000)	1744	1768	1720	976
μ (Mo–Kα)/cm^{-1}	0.60	3.21	3.26	41.46
Crystal dimensions/mm	0.28 × 0.28 × 0.34	0.45 × 0.50 × 0.50	0.35 × 0.36 × 0.30	0.44 × 0.50 × 0.50
D_c/g cm^{-3}	1.10	1.32	1.31	1.62
D_m/g cm^{-3}	1.10	1.38	1.29	1.65
θ range scanned/°	1–25	1–25	1–25	1–25
Range of h, k, l	± 20, 21, 20	± 17, 19, 22	± 17, −18, 23	± 13, ± 14, 21
Decay during collection (%)	0.3	14.8	2.1	15.0
Number of reflections collected	4625	8038	7879	7279
Number of reflections with $I_{rel} > 2\sigma I_{rel}$	2489	3270	3432	3802
Number of parameters	293	538	456	456
Max LS shift to e.s.d.	< 0.5	0.3	0.2	0.2
R ($\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$)	0.071	0.062	0.077	0.096
R_w	0.071	0.062	0.091	0.116
g ($w = \sigma^2F + gF^2)^{-1}$	1	1	0.005	0.20
Max/min residual electron density/e A^{-3}	0.27/−0.20	0.50/−0.39	0.60/−0.49	0.71/−0.60



1 R = H
2 R = Bu^t
3 R = Cl
4 R = Br
5 = **2** • butyronitrile (1:1)
6 = **3** • cyclohexanone (1:2)
7 = **3** • cyclopentanol (1:2)
8 = **4** • DMF (1:2)



9 R = Bu^t
10 R = Cl
11 R = Br

oxidation of the corresponding fluorenes (for **9** and **11**)[14] or by chloro substitution of fluorenone with *N*-chlorosuccinimide.[16] Inclusion compounds **5**–**8** were obtained by recrystallization of host compounds **2**–**4** from the respective guest solvent.[14]

X-Ray Diffraction Analysis.—Details of data collection and structure refinement are given in Table 1. Final fractional atomic coordinates, anisotropic thermal parameters, bond lengths and angles, and tables of observed and calculated structure factors have been deposited.*

Molecular structure. A perspective view of the host backbone, showing the atomic labelling used, is given in Fig. 2. Bond lengths and angles with the hosts are within expected ranges.[22]

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 for the four compounds are illustrated and listed in Table 2. The values obtained for the unsubstituted host **1** (determined in a previous study[1]) have been included for comparison. Although the orientation of the biphenyl group remains much the same for the four compounds (τ^1), the conformation with respect to the fluorenyl moieties (τ^2, τ^3) is quite different. In the unsubstituted form, the overall host conformation was found to be a spiral,[1] the two hydroxy groups formed an intramolecular hydrogen bond in the centre of the spiral and were surrounded by bulky aromatic groups. The same conformation is found in the cases of compounds **5**–**7**. However, in compound **8**, the host appears to uncoil itself so that no intramolecular hydrogen bonding is possible.

The guest molecules in the four structures have greater thermal motion than their respective hosts and thus presented greater difficulties in modelling. Fig. 1(*a*) shows the two-fold disorder observed for the butyronitrile guest in compound **5**. The C–N bond length is 1.10(2) Å and C–C distances are

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

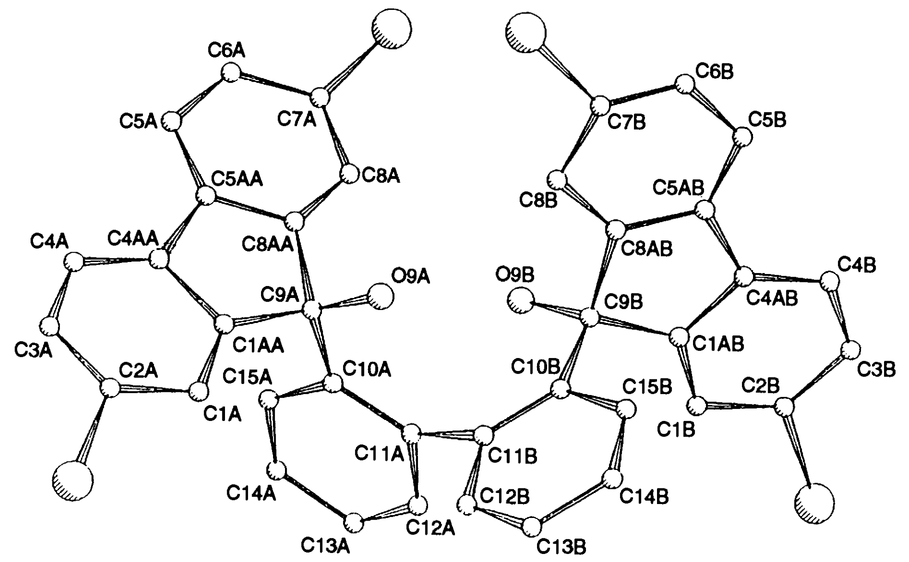


Fig. 2 Perspective view of the host backbone showing the labelling used. Substituent groups are labelled according to their parent carbon atom.

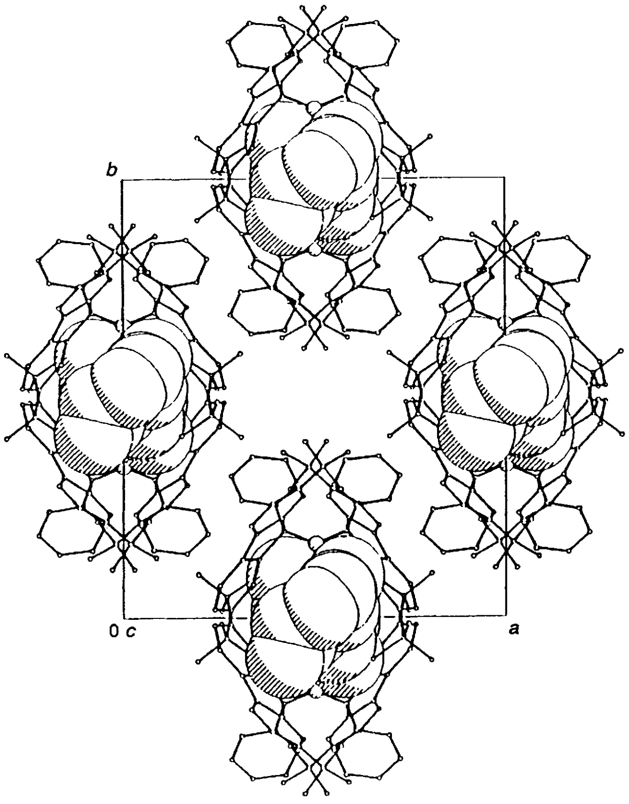
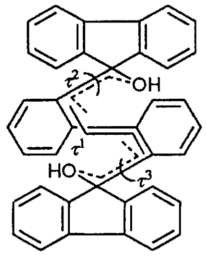


Fig. 3 Packing diagram of compound **5** viewed down [001]. In Figs. 3–6, guest molecules are shown as having van der Waals radii while the host is drawn in stick form.

1.45(3), 1.43(2) and 1.65(4) Å. The N–C–C angle is 174(2)° while the C–C–C angles are 110(2)° and 115(2)°. Compound **6** contains two molecules of cyclohexanone per host molecule. C=O and C–C bond lengths are within normal limits,[22] internal bond angles are between 105(1)° and 119(1)° while O=C–C angles are between 118(1) and 124(1)° for both molecules. The cyclohexanone molecule hydrogen bonded to the host adopts a chair conformation; C(1C) and C(4C) are 0.80 Å above and below the mean plane. The second cyclohexanone also adopts a chair conformation, but it is not as symmetrical as the first. C(1D) lies 0.46 Å above the mean plane and C(4D) is 0.64 Å below it. A similar situation is observed in compound **7**. Bond lengths and angles are within their expected ranges.[22] Both cyclopentanol molecules adopt the envelope conformation but the out-of-plane atoms differ in the two molecules. In molecule C, it is C(4C) which is raised above the mean plane by 0.30 Å while in molecule D, C(2D) is 0.59 Å above the plane. There are two DMF molecules in compound **8**. In each, the O=C–N fragment is well defined with O=C bonds of 1.39(8) and 1.43(3) Å and C–N bonds of 1.29(5) and 1.41(5) Å, O=C–N angles are 117(5) and 101(2)°. The methyl groups, however, displayed a high degree of thermal motion. In each case, three methyl carbons were refined with site occupancies of 0.66 each.

Table 2 Torsion angles describing host conformation



Compound	τ^1/°	τ^2/°	τ^3/°
5	88.4(6)	−28.5(7)	−28.5(7)
6	89.0(9)	−22.4(8)	−28.1(8)
7	90.8(9)	−25.2(8)	−27.1(9)
8	92(2)	−1(2)	−3(2)
1[a]	90.9(5)	−23.5(5)	−21.8(5)

[a] Ref. 1.

As is common with compounds of this type, hydrogen bonding is the dominant non-bonded interaction. In our study of the unsubstituted host **1** we found that the host adopted a spiral conformation to accommodate an intramolecular hydrogen bond between its two hydroxy groups.[1] The same conformation is found in this study for compounds **5**, **6** and **7**. However, the substitution of bromine onto the fluorene moieties appears to prevent sufficiently close approach of the hydroxy groups. This results in the host adopting an open 'uncoiled' conformation. In addition to the intramolecular hydrogen bonding observed in **5**–**7**, there are intermolecular hydrogen bonds between host and guest in all four compounds. Details of all the hydrogen bonds are given in Table 3.

Compounds **6**, **7** and **8** contain halogen ··· halogen and

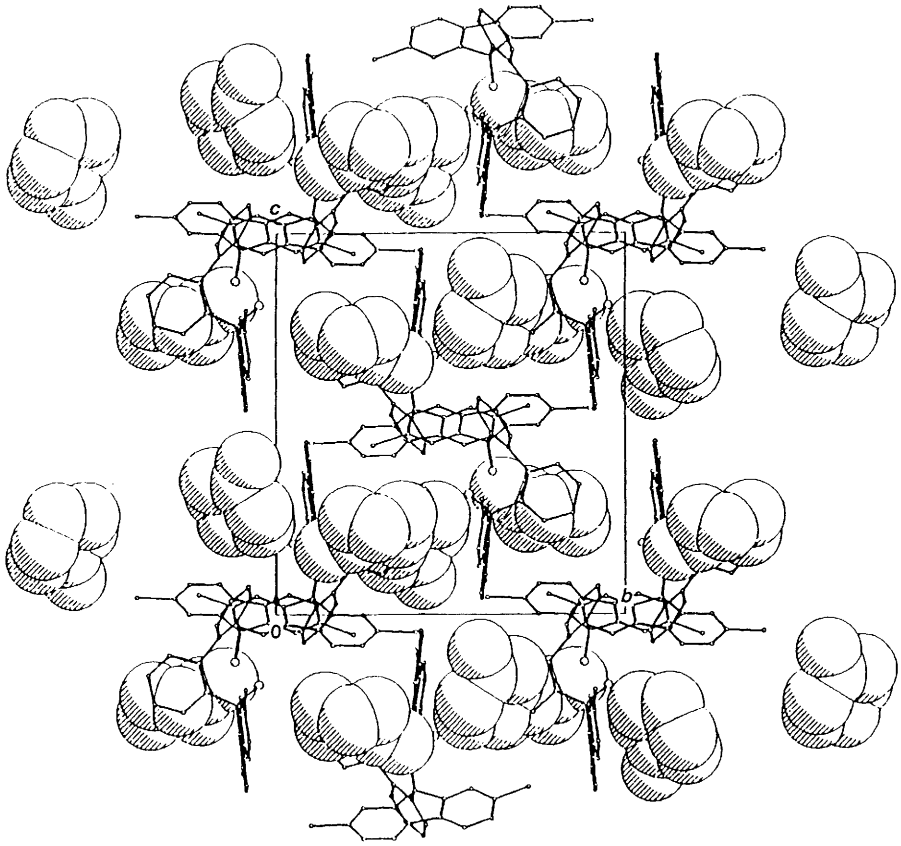


Fig. 4 Packing diagram of compound **6** viewed down [100]

Table 3 Hydrogen bonding

Compound	Donor	Acceptor	D–H/Å	D···A/Å	D–H···A/°
5	O(9)	O(9)[a]		2.729(5)	
	O(9)	N(1G)[a]		2.82(1)	
6	O(9A)	O(9B)	0.97(6)	2.697(7)	163(5)
	O(9B)	O(1C)	0.95(3)	2.685(7)	172(4)
7	O(9A)	O(9B)	0.99(3)	2.698(6)	158(4)
	O(9B)	O(1D)	1.01(22)	2.661(1)	128(13)
	O(1D)	O(1C)	0.97(4)	2.790(5)	163(5)
8	O(9A)	O(2G)	0.9(4)	2.70(2)	144(5)
	O(9B)	O(1G)	0.9(2)	2.75(2)	114(5)

[a] *via* $-x, y, -z + \frac{1}{2}$.

Table 4 Intermolecular contacts

Compound	Atom 1	Atom 2	r/Å
6	O(1D)	Cl(7B)	3.236
	O(1D)	Cl(2B)	4.141
	O(1D)	Cl(2A)	3.996
	Cl(2A)	Cl(7B)	3.820
7	Cl(2B)	Cl(7A)	3.690
	O(1C)	Cl(7B)	3.544
8	Br(2A)	Br(2A)	4.459
	Br(2A)	Br(7A)	4.664
	Br(7A)	N(1G)	4.072
	Br(2B)	Br(2B)	4.451
	Br(2B)	Br(7B)	4.665
	Br(7B)	N(2G)	4.036

Table 5 Thermal analysis data

	5	**6**	**7**	**8**
Host:guest ratio	1:1	1:2	1:2	1:2
B.p. (guest)/°C	117.5	155.6	140.9	153
TG:				
Weight loss expected (%)	8.55	23.13	20.89	14.97
Weight loss observed (%)	8.29	25.24	20.49	14.36
DSC:				
Desorption endotherm onset temperature/°C	136	173	160	119
Host melting endotherm onset temperature/°C	334	335	335	190–240[a]

[a] Broad peak with no clear onset.

O/N··· halogen interactions. These are listed in Table 4. The criterion for recognition of such interactions is that the interatomic distance should be close to the sum of the van der Waals radii of the two atoms. Thus, the interactions listed in Table 4 are all of medium to weak strength. However, the existence of even weak forces such as these may have a profound influence on the overall structure. Also, a view which takes into account only the size of the substituents cannot be valid since a *tert*-butyl group is bigger than a bromine, but does not force the host into a different conformation. Thus electronic effects must be of importance.

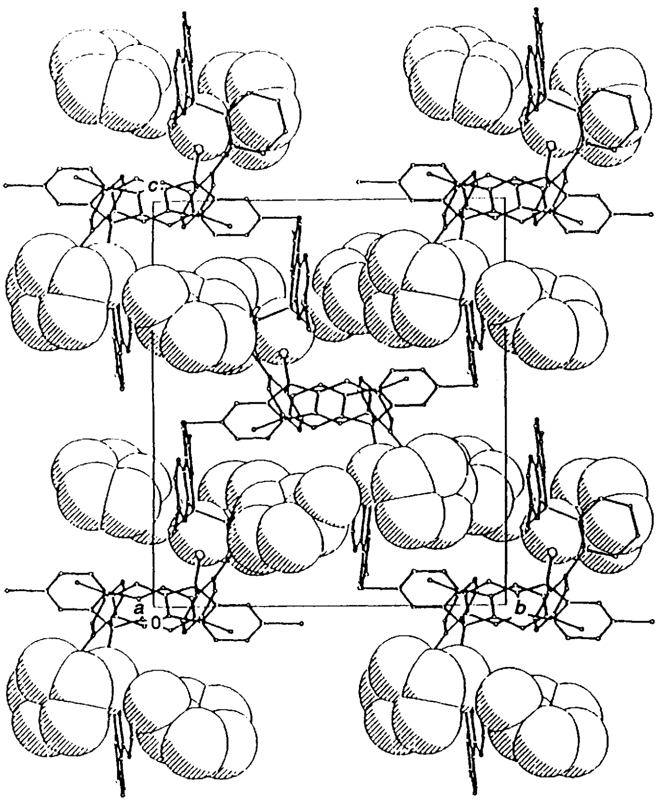


Fig. 5 Packing diagram of compound **7** viewed down [100]

Packing. The packing of these four compounds is illustrated in Figs. 3–6. In these, the host molecules have been drawn in stick form while the guests have been shown as having van der Waals radii. This depicts the cavity-like nature of the guests' environment.

Compounds **6** and **7** demonstrate an interesting point. In each, the host (the chloro-derivative) and one guest form a spiral hydrogen bonding network. The second cyclopentanol guest (compound **7**) is oriented with its hydroxy group toward this network so that it is able to participate in the hydrogen bonding scheme. In **6** however, the second cyclohexanone molecule is positioned so that its oxygen is pointing away from this network and it instead interacts with the chlorine atoms on neighbouring hosts. This is clearly seen in Fig. 7 which shows stereo plots of **6** and **7** with the relevant guest circled.

Thermal Analysis.—Thermal analysis results are shown in Fig. 8. TG was used to establish the host:guest ratios in the compounds. The observed weight losses are in agreement with those calculated for the stoichiometries used in the crystal structure refinements.

DSC traces showed two endotherms for compounds **5**–**8**. The first peak corresponds to the desolvation step while the second is caused by the host's melting. Onset temperatures for these peaks are listed in Table 5. Desolvation onset temperatures for **5**–**7** are higher than the boiling points of their pure guest liquids, which is an indication that these guests are strongly held within the host lattice. The guest release temperature in **8**, however, is 34 °C lower than the boiling point of DMF, implying that the DMF molecules are rather weakly bound. The 'uncoiled' conformation of the host in this compound may be responsible for this observation.

Acknowledgements

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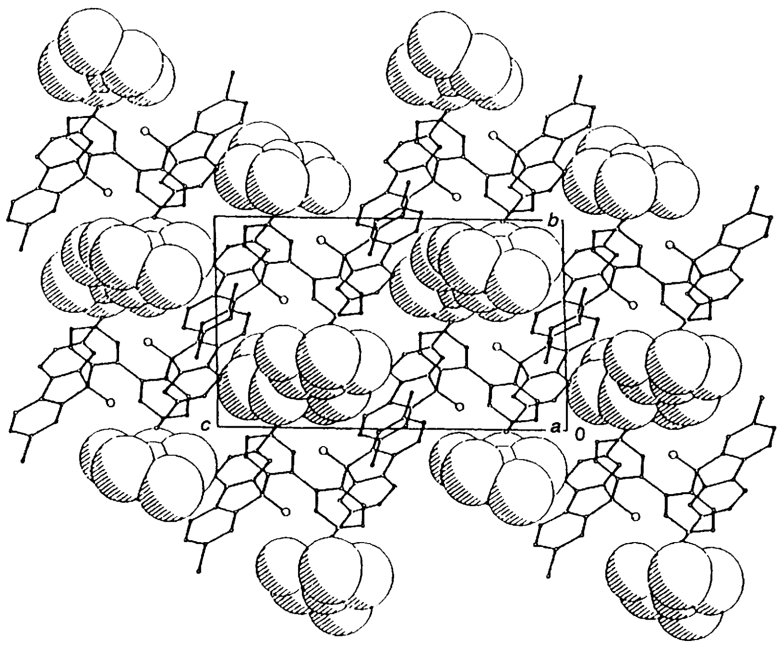

Fig. 6 Packing diagram of compound **8** viewed down [100]

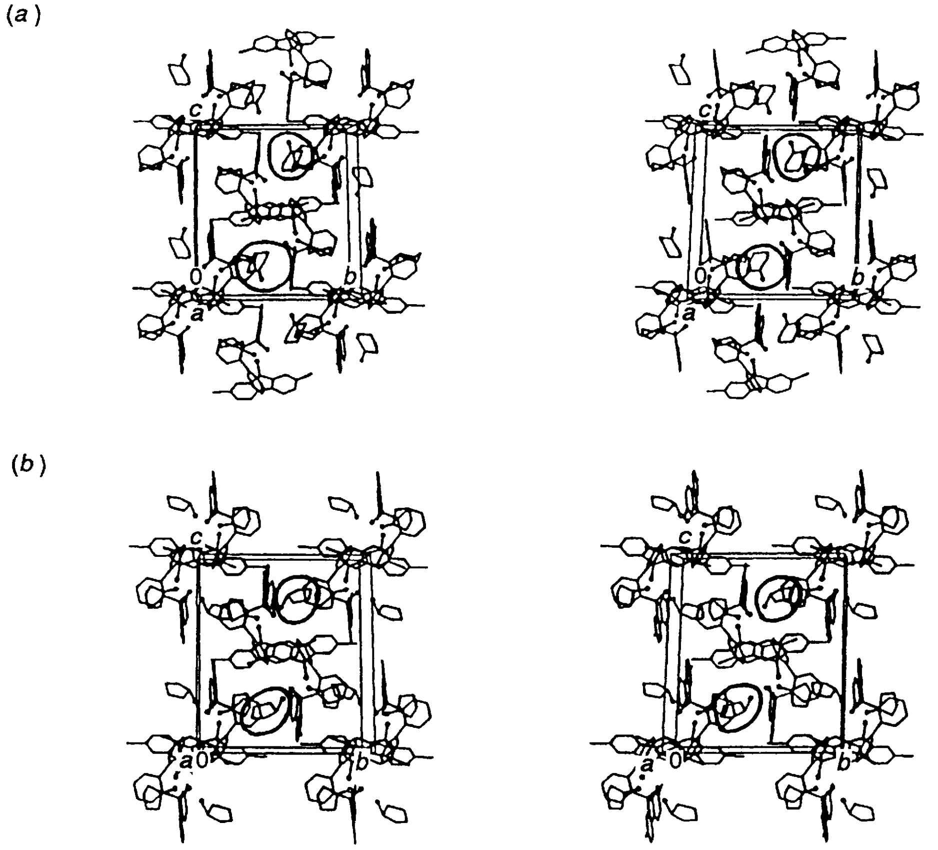

Fig. 7 Stereo plots of (*a*) compound **6** and (*b*) compound **7** viewed down [100]. The difference in packing of the guests is highlighted.

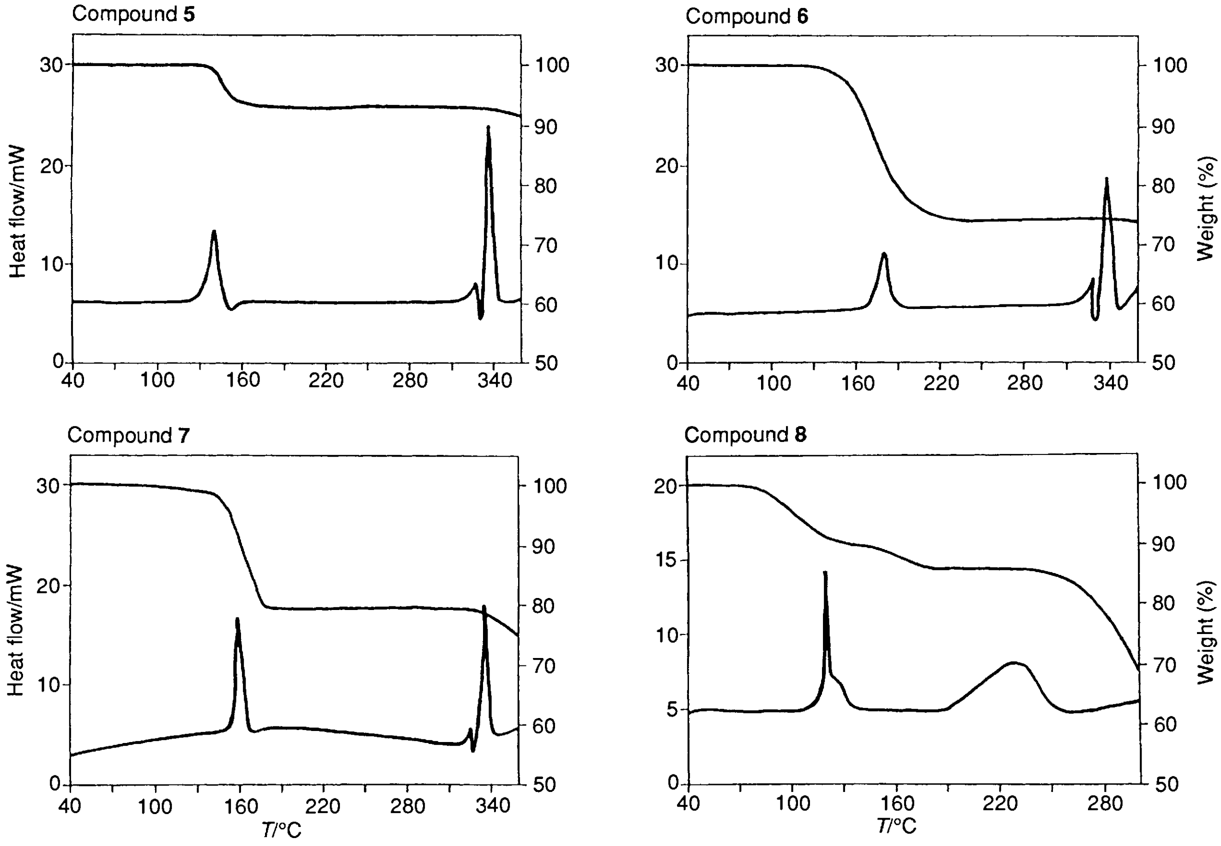

Fig. 8 Thermal analysis (DSC and TG) of compounds **5**–**8**

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