Complexation with Diol Host Compounds. Part 20.† Kinetics of Desolvation of Inclusion Compounds of 2,2'-Bis(2,7-dichloro-9-hydroxy-9-fluorenyl)biphenyl with 1,4-Dioxane and 1,3-Dioxolane

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The structures of the inclusion compounds of 2,2'-bis(2,7-dichloro-9-hydroxy-9-fluorenyl)biphenyl with 1,4-dioxane and 1,3-dioxolane, with host: guest ratios of 1 : 3.5 and 1 : 2 respectively, have been elucidated. Their kinetics of desolvation have been studied and the dioxane inclusion compound desolvates in two distinct steps, each following the first-order kinetic model. The dioxolane inclusion compound desolvates in one step and follows a contracting area model. X-Ray powder photography shows that the dioxane inclusion compound forms a stable intermediate γ-phase before final desolvation to a non-porous α-phase.

Molecules which contain the fluorene moiety have proved to be successful hosts, capable of forming inclusion compounds with a variety of guests.[1] These hosts are often functionalized by an hydroxy group at position 9, and are sometimes dimerized *via* an aromatic moiety such as biphenyl, to yield a crowded diol host molecule. We have studied a number of substituted fluoren-9-ol hosts with 1,4-dioxane and elucidated their structures. We have also analysed the structures of 9,9'-dihydroxy-9,9'-bifluorene with ethanol, butan-1-ol and pyridine and measured their thermal stabilities.[2] A most versatile variation of the host compound is 2,2'-bis(9-hydroxy-9-fluorenyl)biphenyl, which includes a large number of guests, including aliphatic alcohols, nitriles, amines, ketones and pyridines. We have studied the crystal structures of this host with acetonitrile, cyclohexanone, dipropylamine and dimethylformamide and noted the rigidity of the host's conformation, irrespective of the guest species.[3] This host also includes selected guests from the vapour phase and we have elucidated the structure of the diethyl ether clathrate, which is remarkably stable, only releasing the guest at 125.8 °C, which is 91.3 °C above the normal boiling point of diethyl ether.[4] Substituting the fluorene moieties at the 2- and 7-positions with bulky groups such as halogens, also yields successful host compounds, which are often stabilized by hydrogen bonds between host and guest.[5] In this paper we present the structural results of the inclusion compounds of 2,2'-bis(2,7-dichloro-9-hydroxy-9-fluorenyl)biphenyl with two closely related guests, 1,4-dioxane (**1**) and 1,3-dioxolane (**2**) and analyse their kinetics of desolvation.

Experimental

The inclusion compounds were obtained by dissolving the host compound[5] in an excess of the appropriate guest. Crystals of diffraction quality were obtained by slow evaporation of the solutions over a period of 14 days. X-Ray diffraction data were measured on an Enraf–Nonius CAD4 diffractometer, using graphite-monochromated radiation, (λ = 0.7107 Å) and the ω–2θ scan mode. The selected crystals were sealed in Lindemann capillary tubes together with mother liquor in order to prevent desorption of the guest. During data collection three reference reflections were monitored periodically to check crystal stability. The data reduction included correction for Lorentz and polarization effects and for absorption.[6] Crystal data and structural refinement parameters are given in Table 1.

Differential scanning calorimetry (DSC) and thermal gravimetry (TG) were performed on a Perkin-Elmer PC7 series system. Fine powdered specimens, obtained from continuously stirred solutions, were blotted dry on filter paper and placed in open pans. Sample weight in each case was 2–5 mg. The temperature range was typically 30–300 °C, at a heating rate of 20 °C min^{-1}. The samples were purged by a stream of nitrogen flowing at 40 cm^3 min^{-1}. Data for the kinetics of desolvation were obtained from isothermal TG experiments done at selected temperatures in the range 50–70 °C, for the first stage and 100–125 °C, for the second stage, for compound **1**, and 60–72 °C for compound **2**.

Results and Discussion

Structure Solution and Refinement.—The structures were solved by direct methods using SHELX-86[7] and refined by full-matrix least-squares methods on F^2, with SHELX-93.[8] The absorption correction program used, generates F data, and this was utilized for the structure determination and refinement. The weighting scheme used is shown in eqn. (1), where a and b are defined for each structure and $P = [0.333\,33 \times \text{max. of } (0 \text{ or } F_o^2) + (1 - 0.333\,33) \times F_c^2]$.

$$w = q/[\sigma^2(F_o^2) + (a \times P)^2 + b \times P] \qquad (1)$$

For compound **1**, the host molecule and three dioxane molecules are located in general positions, while one guest dioxane lies on a centre of inversion, thus yielding a host : guest ratio of 1 : 3.5. This was confirmed by the TG analysis (mass loss of 32%). Careful analysis of difference electron density maps showed that two of the guests were partially disordered. Thus, the final model employed two positions for C(32) of G3 [C(32) and C(32A) with a fractional site occupancy factor of 0.5 each] and of C(43) and C(46) for G4 [C(43) and C(46) with fractional site occupancy factors of 0.65 each and C(43A) and C(46A) at 0.35 each]. Refinement was carried out with the non-hydrogen atoms of the host and one of the dioxane molecules (G1) treated anisotropically, while the remaining guests were refined isotropically. Hydrogen atoms were all located in difference electron density maps and were refined in constrained positions.

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† For Part 19, see L. J. Barbour, M. R. Caira and L. R. Nassimbeni, *J. Chem. Crystallogr.*, 1994, **24**, 539.

Table 1 Crystal data, experimental and refinement parameters

Compound	**1**	**2**
Molecular formula	$C_{38}H_{22}Cl_4O_2{\cdot}3.5C_4H_8O_2$	$C_{38}H_{22}Cl_4O_2{\cdot}2C_3H_6O_2$
M_r/g mol^{-1}	980.72	800.51
Crystal data		
Space group	$P\bar{1}$	$C2/c$
a/Å	12.878(4)	21.954(3)
b/Å	13.221(3)	11.423(2)
c/Å	15.784(13)	18.157(3)
α(°)	102.95(4)	90
β(°)	100.53(4)	123.63(2)
γ(°)	108.82(2)	90
Z	2	4
V/Å^3	2382(2)	3791.3(1)
D_c/g cm^{-3}	1.339	1.402
μ(Mo-Kα)/cm^{-1}	0.305	0.36
F(000)	996	1656
Data collection (293 K)		
Crystal dimensions/mm	0.34 x 0.31 x 0.31	0.50 x 0.40 x 0.40
Range scanned θ(°)	1.38–24.97	2.10–25.05
Range of indices h, k, l	±15; ±15; 0, 18	−21, 25; −13, 0; −21, 0
Reflections for lattice parameters no., θ range (°)	24; 15–17	24; 15–17
Instability of standard reflections (%)	−3.6	6.3
No. of reflections collected (unique)	8350	3277
No. of reflections observed with $I_{rel} > 2\sigma I_{rel}$	4123	2034
Final refinement		
No. of parameters	540	225
$R1(I_{rel} > 2\sigma I_{rel})$	0.0907	0.068
$wR2(I_{rel} > 2\sigma I_{rel})$	0.2792	0.2023
Goodness of fit for F	1.011	1.073
Max. shift/e.s.d.	0.117	0.003
Mean shift/e.s.d.	0.003	0.000
Max. height in electron density map/e Å^{-3}	0.82[a]	0.67[a]
Min. height in electron density map/e Å^{-3}	−0.69	−0.62
Extinction coefficient	0.009(2)	

[a] In the region of the guest molecules.

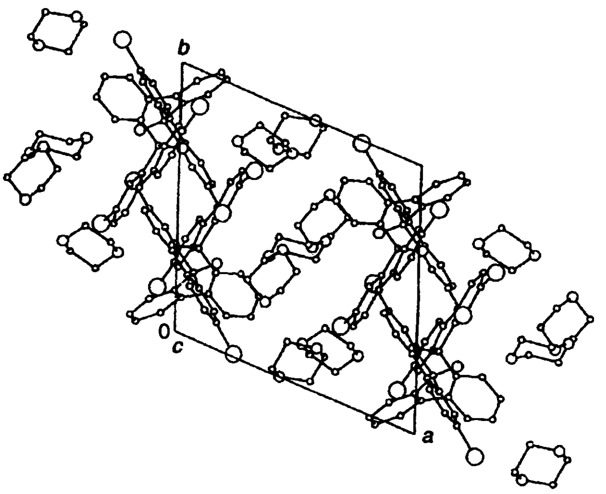

Fig. 1 Crystal packing in compound **1** as viewed down [001]

The hydroxy hydrogens, which were also located in a difference map, were refined with a simple bond length constraint according to a function of O–H *versus* O···O distances.[9] Only two of the dioxane molecules are hydrogen-bonded to the host. One dioxane molecule, G1, is bonded *via* one oxygen [O(9B)–H···O(14), with O···O = 2.766(5) Å] and G3, the dioxane molecule located on the centre of inversion, has two hydrogen bonds [O(9A)–H···O(31), with O···O = 2.846(7) Å]. The packing, shown in Fig. 1, is such that the guests lie in two distinct channels running parallel to [001].

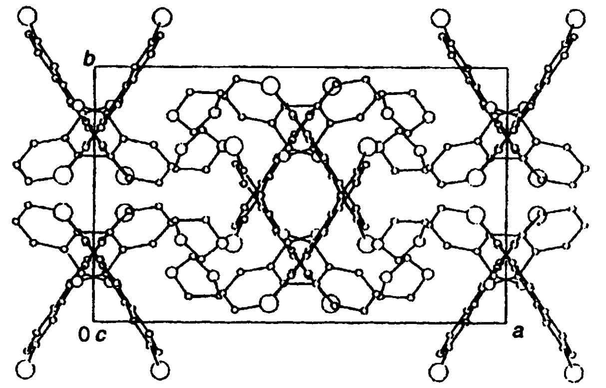

Fig. 2 Crystal packing in compound **2** as viewed down [001]

The structure of **2** was refined in a similar manner and no disorder was found in the positions of the dioxolane guests. There are four host molecules in the unit cell, and these were located on the diads, thus fulfilling the symmetry requirements for the space group $C2/c$. The packing, given in Fig. 2, shows the dioxolanes located in channels running along the screw diads. Each guest exhibits one hydrogen bond to the host [O(9A)–H···O(13), with O···O = 2.868(6) Å].

The conformation of the host molecules is governed by three torsion angles, τ_1, τ_2 and τ_3, shown in Fig. 3. The two benzene rings in the central biphenyl are at approximate right angles and Table 2 compares the torsion angle around this bond, τ_1 and the other torsion angles for host molecules derived from similar structures.[5] Torsion angle τ_1 varies from 88.4 to 101.4°,

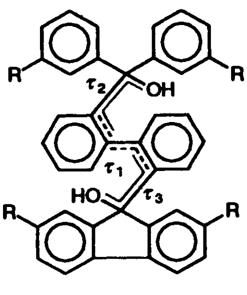

Fig. 3 Schematic of the general host, showing relevant torsion angles

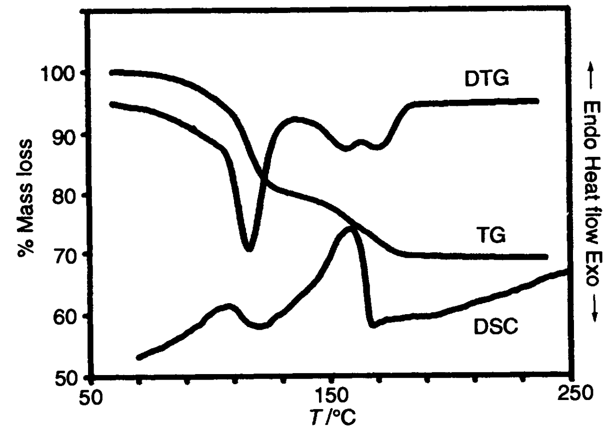

Fig. 4 Thermograms showing the desolvation of compound **1**

Table 2 Torsion angles (°) describing host conformation

Compd.	R	Guest (H:G)	τ_1	τ_2	τ_3
1	Cl	1,4-Dioxane (2:7)	101.4(6)	−2.0(7)	−8.5(7)
2	Cl	1,3-Dioxolane (1:2)	94.2(7)	−10.9(5)	−10.9(5)
3[a]	Bu^t	Butyronitrile (1:1)	88.4(6)	−28.5(7)	−28.5(7)
4[a]	Cl	Cyclohexanone (1:2)	89.0(9)	−22.4(8)	−28.1(8)
5[a]	Cl	Cyclopentanol (1:2)	90.8(9)	−25.2(8)	−27.1(9)
6[a]	Br	DMF (1:2)	92(2)	−1(2)	−3(2)
7[b]	H	Acetonitrile (1:1)	90.9(5)	−23.5(5)	−21.8(5)

[a] Ref. 5. [b] Ref. 3.

while τ_2 and τ_3 range considerably from −28.5 to −1°. The bond lengths and angles in the host molecules are in the accepted range for structures of this kind.[3,5,10]

Kinetics of Desolvation.—The thermal analytical results for the desolvation of compound **1** are shown in Fig. 4. The TG and DTG curves show that the guest loss reaction takes place in three steps, with onset temperatures of 66, 114 and 145 °C, corresponding to the loss of two, one-half and one guest molecules. The three mass loss steps can be more sharply differentiated when the experiment is carried out on small crystallites. The DSC trace shows two diffuse endotherms, corresponding to overlapping desolvation processes.

We separated the first two desolvation steps from the third by appropriate selection of temperatures for the isothermal kinetic runs. A typical example is shown in Fig. 5, in which we exhibit the mass loss *versus* time curve plotted with the temperature program used. The two resultant desolvation steps are clearly visible. Isothermal TG experiments were done at temperature intervals of 2 to 5 °C over a range of 50–70 °C (first step) and 100–125 °C (second step). The data, for each step, were reduced to curves of fractional reaction (α) *versus* time. Various kinetic models[11] were fitted to the data. The first combined desolvation step, corresponding to the loss of 2.5 mol of dioxane, was deceleratory. The first order (F1) reaction mechanism fitted this reaction over an α-range of 0.1 to 0.95. The first portion of the curves (α-range 0 to 0.1) were linear, corresponding to surface evaporation. The second desolvation step, corresponding to the loss of the third dioxane molecule, also fitted the F1 mechanism (α-range 0 to 0.9). The semilogarithmic plots of ln k *versus* $1/T$ are shown in Fig. 6(*a*) and (*b*), which yield activation energies of 34 (3) and 111 (9) kJ mol^{-1} for the first and second desolvation steps respectively.

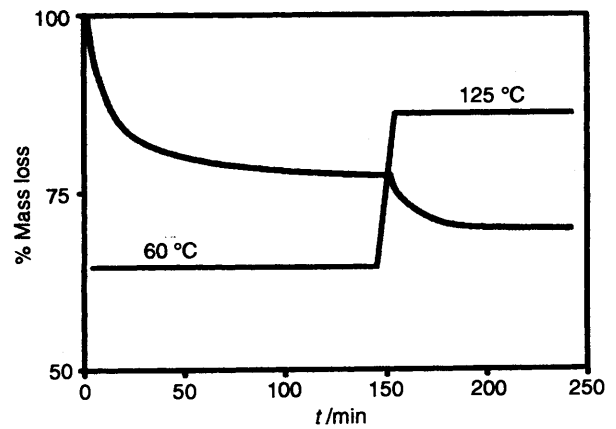

Fig. 5 Example of a set of isothermal TG runs done on compound **1**, showing the temperature program used

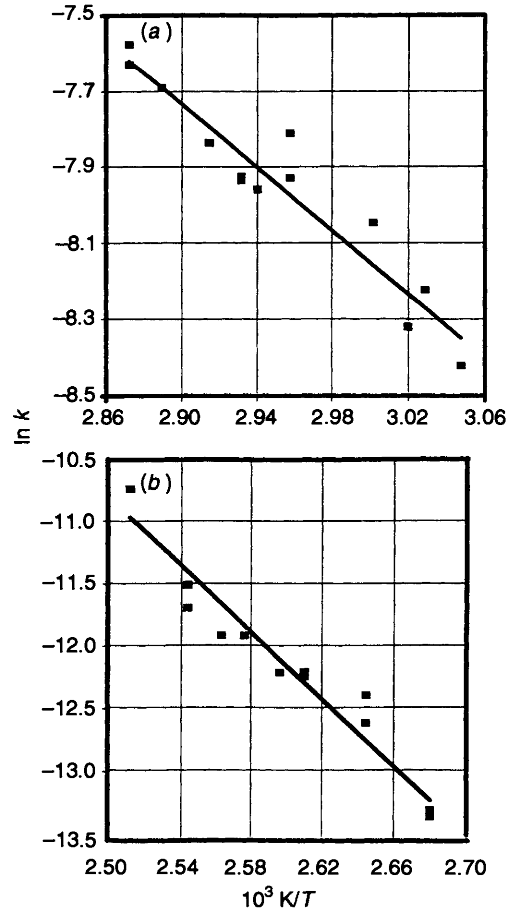

Fig. 6 Arrhenius plot for (*a*) the first stage and (*b*) the second stage of desolvation of compound **1**

The TG, DTG and DSC traces for the desolvation of compound **2** are shown in Fig. 7. The host:guest ratio of 1:2 was confirmed by the TG experiment, showing a single mass loss step of 18.8%. A series of isothermal TG experiments were carried out over a temperature range of 60–72 °C. The data was

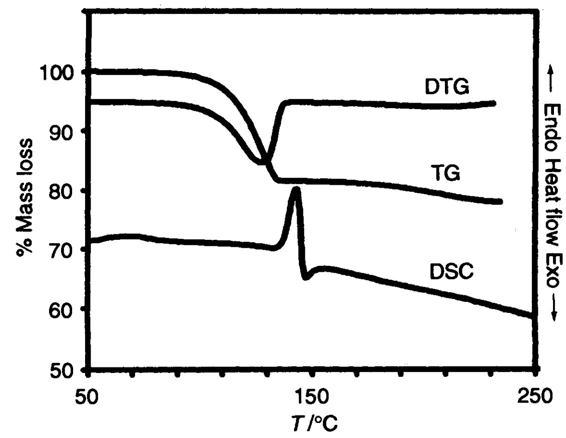

Fig. 7 Thermograms showing the desolvation of compound **2**

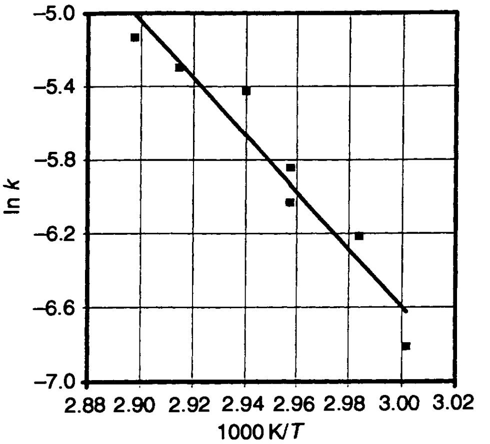

Fig. 8 Arrhenius plot for the first stage of desolvation of compound **2**

best described by the contracting area (R2) kinetic model. An activation energy of 129 (16) kJ mol^{-1} was obtained for this reaction over an α-range of 0 to 0.95. A curve of ln *k versus* $1/T$ is shown in Fig. 8.

X-Ray Powder Diffraction.—We have monitored the phase changes which occur upon desolvation of compound **1** by X-ray powder diffraction. Fig. 9 shows the photometric traces of the powder photographs we obtained for the inclusion compound **1** [trace (*a*)], while trace (*b*) was obtained after the first desolvation step. The final trace (*c*) is that achieved after complete desolvation and corresponds to the α-phase of the pure host. It is clear that trace (*b*) is different from the other two and thus corresponds to a new crystalline phase, γ. We have obtained similar results by analysing the desolvation of other inclusion compounds which yielded intermediate phases upon partial guest loss.[12,13]

Conclusions

The dioxane inclusion compound has a host:guest stoichiometry of 1:3.5. The crystal structure shows that two of the dioxane guests are not hydrogen-bonded and one would predict that the first desolvation step would be assigned to the loss of these two guests. However, using the temperature ramping technique for obtaining isothermal mass loss *versus* time data, we could not separate the three desolvation steps and we could only isolate the first two steps as a single process, corresponding to the loss of 2.5 dioxane molecules. The resultant product is the γ-phase, with a host:guest ratio of 1:1. The latter has been confirmed by X-ray powder diffraction.

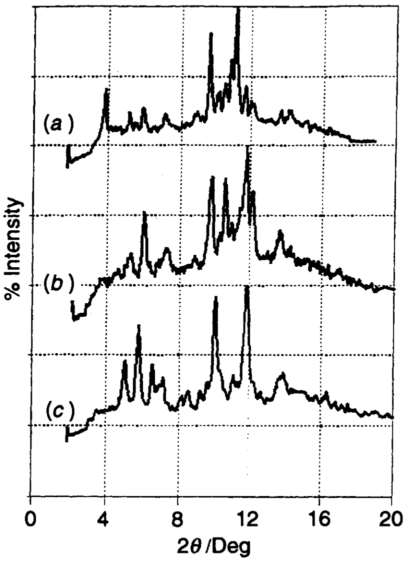

Fig. 9 Photometric traces of XRD photographs taken of compound **1**: (*a*) before desolvation; (*b*) after the first desolvation step (*i.e.* γ-phase); (*c*) after complete desolvation (*i.e.* α-phase)

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