Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Bourne, Susan A. , Nash, Katherine L. Gifford and Toda, Fumio(1997) 'Crystal Structures and Thermal Analysis of Hexakis(3-hydroxy-3,3-diphenyl-2-propynyl)benzene with 1,4-dioxane, and 1,3-dioxolan-2-one', Supramolecular Chemistry, 8: 2, 137 — 145

To link to this Article: DOI: 10.1080/10610279708233977

URL: http://dx.doi.org/10.1080/10610279708233977

SUPRAMOLECULAR CHEMISTRY, 1997, Vol. 8, pp. 137–145
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Crystal Structures and Thermal Analysis of Hexakis(3-hydroxy-3,3-diphenyl-2-propynyl)benzene with 1,4-dioxane, and 1,3-dioxolan-2-one

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(Received 19 June 1996)

Structures of the inclusion compounds of hexakis(3-hydroxy-3,3-diphenyl-2-propynyl)benzene with 1,4-dioxane (**1**) and 1,3-dioxolan-2-one (**2**) have been determined. **2** illustrates the selectivity of the host for carbonyl compounds as it was grown from a solution of 1,3-dioxolane with 1,3-dioxolan-2-one as a minor impurity. The thermal analysis (TG and DSC) of both compounds was carried out. Guest desorption from **1** was found to follow the F1 mechanism with an activation energy of 148(2) kJmol^{-1}.

INTRODUCTION

Hexakis(3-hydroxy-3,3-diphenyl-2-propynyl)benzene (**H**) is proving to be a very versatile host. It encompasses a number of the directed host design principles described by Toda *et al.*[1] It contains six hydroxyl moieties as hydrogen bonding donors. These are shielded by rigid bulky groups, which yield suitable spaces for the accommodation of selected guest molecules.

H has formed a number of inclusion compounds with a variety of small organic molecules. The structures with dimethyl formamide, methyl ethyl ketone, diethyl ketone and diethyl ether have been reported[2,3]. We now report the structures of **H** with 1,4-dioxane (**1**), and with 1,3-dioxolan-2-one (**2**). The latter, which was grown from a solution of **H** in 1,3-dioxolane, was a surprising result, and suggests that **H** has a higher selectivity for molecules with a carbonyl oxygen over those with an ether oxygen.

RESULTS AND DISCUSSION

Structure Solution and Refinement

The atomic labelling used in **1** and **2** is shown in scheme 1.

Both structures were solved by direct methods using SHELX-86[4] and refined by full-matrix least-squares using SHELX-93[5], refining on F^2.

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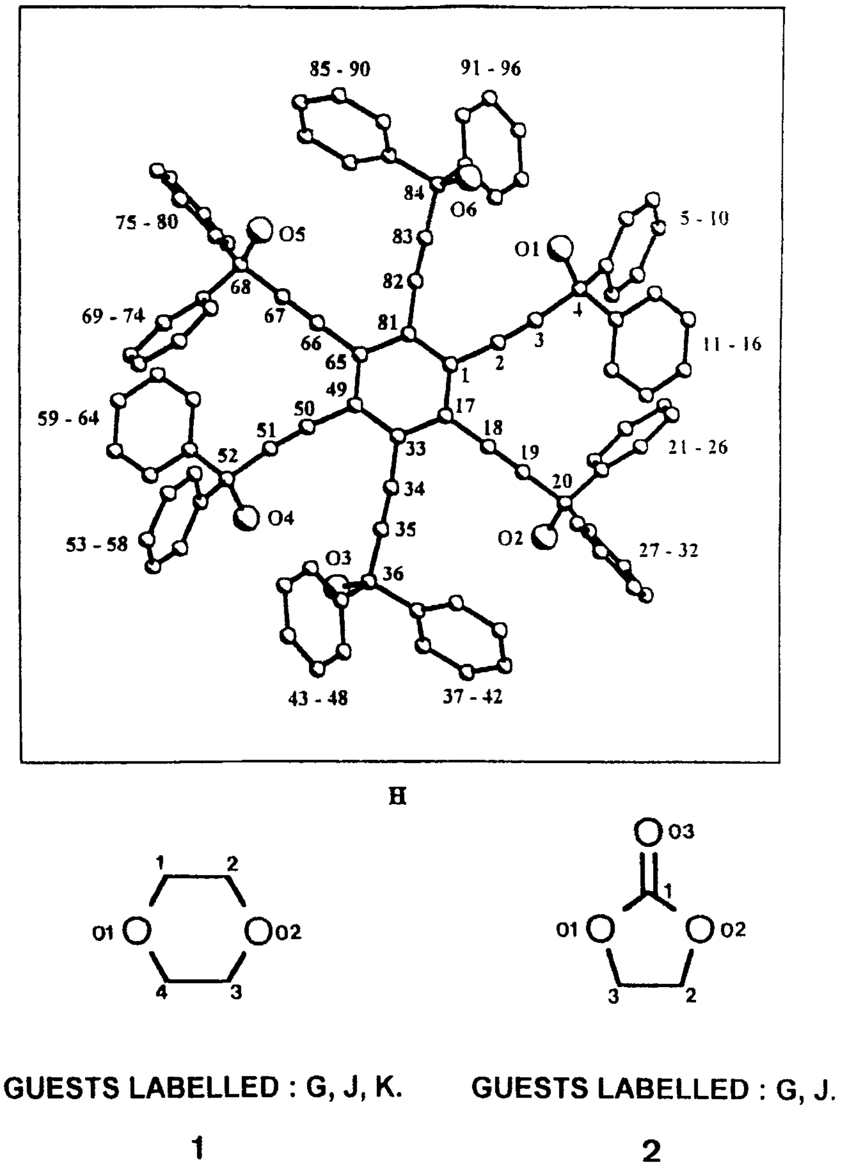

SCHEME 1

Details of the structure solutions and refinements are given in Table 1. Bond lengths and angles fall within expected ranges.[6]

All the non-hydrogen atoms of the host molecule in **1** were refined anisotropically and the aromatic hydrogens were placed in geometrically calculated positions. The hydroxyl hydrogens were located in the difference electron density maps and allowed to refine independently. The direct methods also located two and a half dioxane guests. One is located on a centre of inversion at Wyckoff position *b*. This guest (G) refined uneventfully and was allowed to refine with anisotropic temperature factors. The carbons of guest J were disordered over two positions as shown in Figure 1 (site occupancy factors A: 0.48, B: 0.52). The oxygens were refined anisotropically and the carbons isotropically. In

TABLE I Crystal data and refinement parameters

Parameter	1	2
Molecular formula	$C_{96}H_{66}O_6 \cdot 5C_4H_8O_2$	$C_{96}H_{66}O_6 \cdot 2C_3H_4O_3$
Molecular weight (g.mol^{-1})	1756.10	1491.70
Crystal system	Triclinic	Monoclinic
Space group	P $\bar{1}$	P2_1/n
a (Å)	12.203 (2)	18.095 (5)
b (Å)	14.384 (3)	12.563 (4)
c (Å)	15.827 (3)	34.18 (1)
α (°)	110.83 (1)	90.00 (3)
β (°)	104.82 (1)	97.14 (3)
γ (°)	100.68 (1)	90.00 (2)
Volume (Å^3)	2390 (25)	7710 (25)
Z	1	4
Density (calc) (g.cm^{-3})	1.220	1.285
Linear absorption coefficient μ (mm^{-1})	0.080	0.083
F(000)	930	3128
Colour	pale yellow	pale orange
Data collection		
Temperature (K)	293(2)	223(2)
Size of crystal (mm)	0.28 × 0.28 × 0.31	0.32 × 0.32 × 0.35
Scan width in ω (°)	0.8 + 0.35 tan θ	0.8 + 0.35 tan θ
Vertical aperture (mm)	4	4
Aperture width (mm)	1.12 + 1.05 tan θ	1.12 + 1.05 tan θ
Range scanned θ (°)	1–25	1–25
Range of indices *h,k,l*	−14, 14; −17, 17; 0, 18	−21, 21; 0, 14; 0, 40
Reflections measured	8747	13779
Unique reflections	8415	13539
R_{int}	0.030	0.044
Observed reflections $I_{rel} > 2\sigma I_{rel}$	4418	6598
Decay of standard reflections (%)	1.12	0.7
Final refinement		
R ($I_{rel} > 2\sigma I_{rel}$)	0.076	0.066
R (all data)	0.173	0.176
wR2 ($I_{rel} > 2\sigma I_{rel}$)	0.213	0.200
wR2 (all data)	0.286	0.480
w*	a = 0.1541, b = 0.91	a = 0.1413, b = 6.01
S	1.034	1.037
Extinction coefficient	–	0.0009(3)
Mean shift/esd	0.023	0.001
Max. height in difference electron density map (eÅ^{-3})	0.62	0.29
Min. height in difference electron density map (eÅ^{-3})	−0.52	−0.35

*$W = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (\max(F_o^2, 0) + 2F_c^2)/3$

guest K, the oxygens and carbons had high temperature factors and as a result were refined isotropically. All the guests' hydrogens were omitted from the model.

The host molecules are packed in layers with the central aromatic ring parallel to [110], and the guests are located in channels between these layers, centered at z = 0.5 (Figure 2). The hydro-

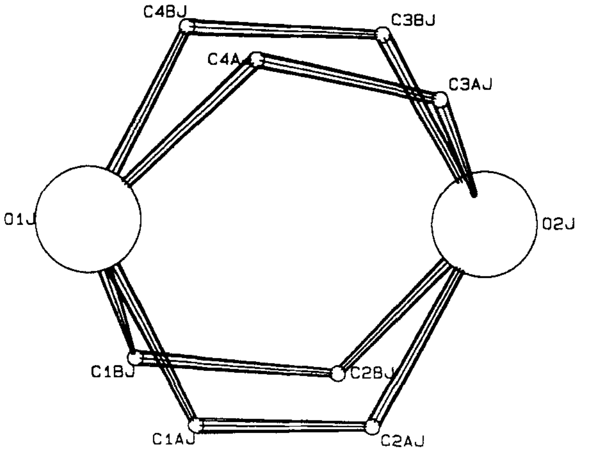

FIGURE 1 Disorder in guest J of **1**.

gen bonds observed in **1** are detailed in Table 2 and illustrated in Figure 3. Guest J is held in place by cooperative O-H...O hydrogen bonding with the host, while Guest G is hydrogen bonded so as to link adjacent layers of host molecules. Guest K has no short contacts.

The thermograms for **1** are shown in Figure 4. The DSC curve shows a single step for guest loss at *ca* 100°C, followed by an exothermic rearrangement of the host at *ca* 115°C. The host then melts with decomposition at 259°C. The TG curve confirms the single step guest loss and the host:guest ratio of 1:5 refined in the crystal structure (expected mass loss 25.08%, observed mass loss 24.27%).

X-Ray powder diffraction data for **1** and its desolvation product were collected (Figure 5). From these patterns it is clear that on desolvation **1** undergoes a phase change back to that of the uncomplexed host material.

The kinetics of desolvation and structural collapse of **1** was determined by a series of isothermal thermogravimetric experiments. Guest loss was found to take place in a single deceleratory step (Figure 6), and the first order (F1) reaction mechanism (-ln(1-α)) fits the data (α-range 0.05–

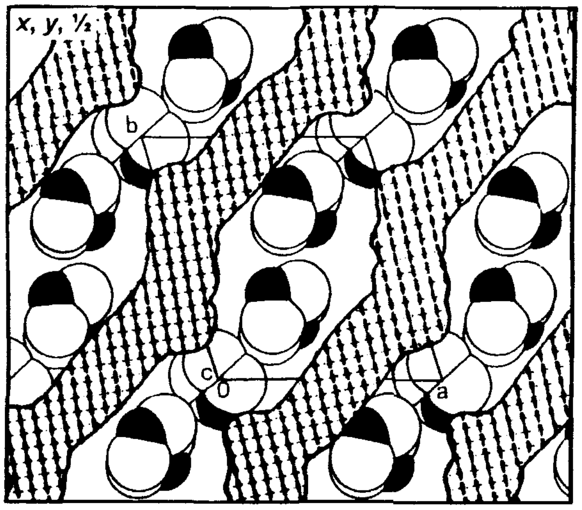

FIGURE 2 Cross section of **1** viewed along [001]. The hatched region is that occupied by host atoms. The guest molecules (with oxygens shaded) are shown in the channels.

TABLE II Hydrogen bond details for **1**

(D)onor	(A)cceptor	D-H (Å)	D...A (Å)	D-H...A (°)
O1	O1G	0.74(5)	2.809(5)	172(5)
O2	O3	0.87(5)	2.958(4)	158(4)
O3	O1J[a]	0.83(6)	2.759(5)	171(6)

[a] $x, 1 + y, z$

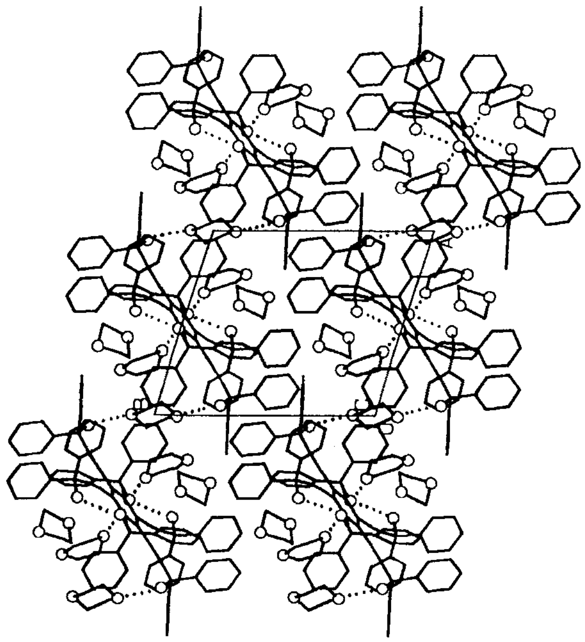

FIGURE 3 Crystal packing in **1** viewed down [001]. The hydrogen bonds are indicated by dashed lines.

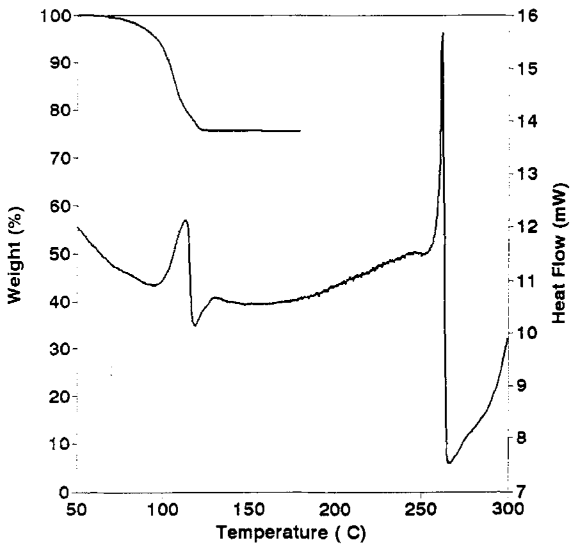

FIGURE 4 Thermograms (TG and DSC) of **1**.

0.95). The semilogarithmic plot of ln *k* vs 1/T yields an activation energy of 148(2) kJ.mol^{-1} (Figure 7).

Crystals of **2** were grown from a solution of **H** in 1,3-dioxolane. Direct methods located the host and two guest molecules. However, these proved to be, not 1,3-dioxolane, but 1,3-dioxolan-2-one. As this was a most unexpected result, several analytical techniques were performed to confirm the identity of the guest compound. Both ^{1}H and ^{13}C NMR established that 1,3-dioxolane was not present as the guest. 1,3-dioxolane is a puckered molecule, and as a result none of the hydrogens are equivalent. If the guest had been 1,3-dioxolane very complicated coupling should have been visible in the ^{1}H NMR spectrum. The hydrogens on 1,3-dioxolan-2-one are, however, equivalent since this molecule is far more rigid and planar. The measured ^{1}H NMR spectrum showed only one singlet for the guest compound, suggesting that it is 1,3-dioxolan-2-one. In the ^{13}C NMR spectrum only one guest peak was observed. Had the guest been 1,3-dioxolane (scheme 2) two peaks should have present for C(a) and C(b). However, if C(a) was a carbonyl carbon (as in 1,3-dioxolan-2-one) the peak would have been shifted far down

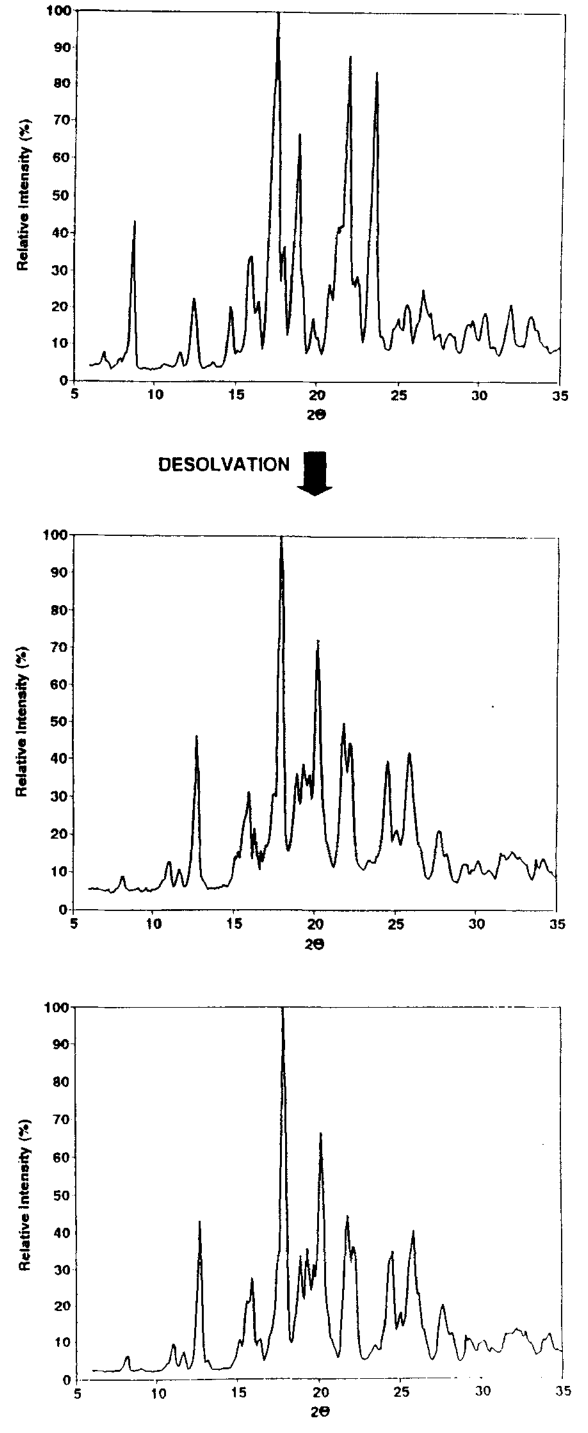

FIGURE 5 X-Ray powder diffraction traces of **1** (a) before desolvation; (b) after complete desolvation; (c) X-Ray powder diffraction trace of **H** (uncomplexed).

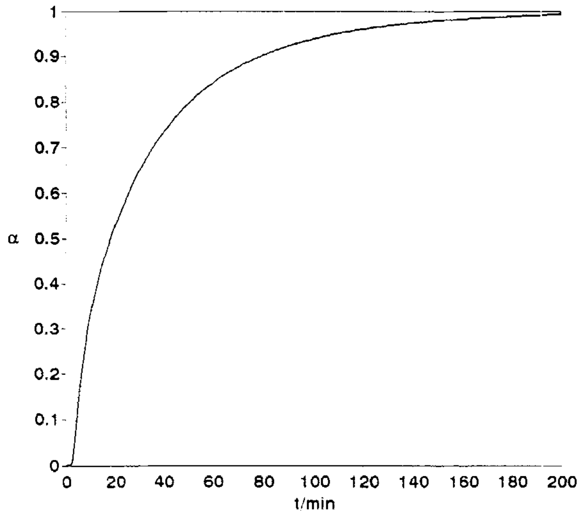

FIGURE 6 An example of an isothermal α *vs* time curve obtained for **1**.

field, and difficult to pick up. Mass spectrometry confirmed the guest compound's identity. The mass spectrum was recorded at 70eV, 50°C. This temperature was chosen so that the guest was volatised before the host. The M^+ peak and route of decomposition corresponds to 1,3-dioxolan-2-one: m/z 88 (M^+, 100), 43 (M-COOH, 68), 29 ($M\text{-}CH_2COOH$, 62).

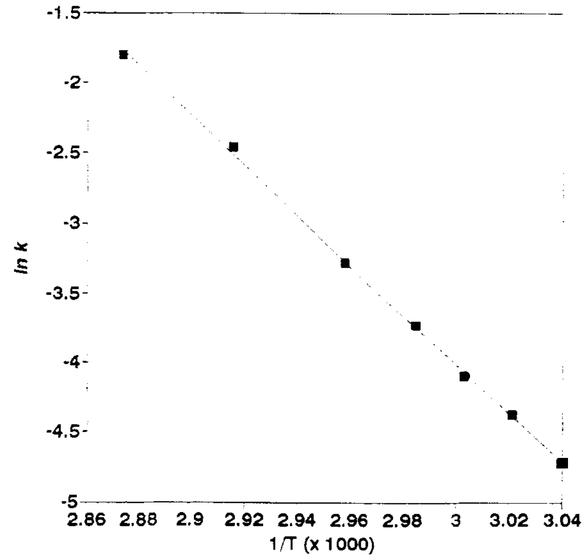

FIGURE 7 Arrhenius plot for the desolvation of **1**.

1,3-dioxolane **1,3-dioxolan-2-one**

SCHEME 2

Gas chromatography was performed to analyse the sample of 1,3-dioxolane that had been used to grow these crystals. Two peaks were observed, that for 1,3-dioxolane (b.p. = 78°C) which was followed by a much smaller peak (*ca.* 2%). 1,3-dioxolan-2-one (b.p. = 152°C) is not commercially available, so its retention time under these conditions could not be determined. Nevertheless, we are confident that it was this small impurity in our 1,3-dioxolane solvent that was selectively included by **H**.

The crystal structure of **H**.$(1,3\text{-dioxolan-2-one})_2$ was refined, allowing all non-hydrogen atoms to refine anisotropically; the aromatic and guest hydrogens were placed in geometrically calculated positions. The hydroxyl hydrogens were located in the difference electron density map, and allowed to refine independently, except for H1O, which was placed in a geometrically calculated position and allowed to refine with an isotropic temperature factor linked to O1.

In compound **2**, the host molecules are packed in a herringbone pattern (Figure 8), and the guests are situated in channels parallel to [010] and centered at $x = 0$ and $x = 0.5$ (Figure 9). The hydrogen bonding scheme observed is shown in Figure 10. The guests are held in place by hydrogen bonds from two of the host hydroxyl moieties. There is also a short contact between O2 and an adjacent phenyl ring (C5–C10) and O5 and an adjacent phenyl ring (C59–C64) in the same molecule. Details of the hydrogen bonds are given in Table 3.

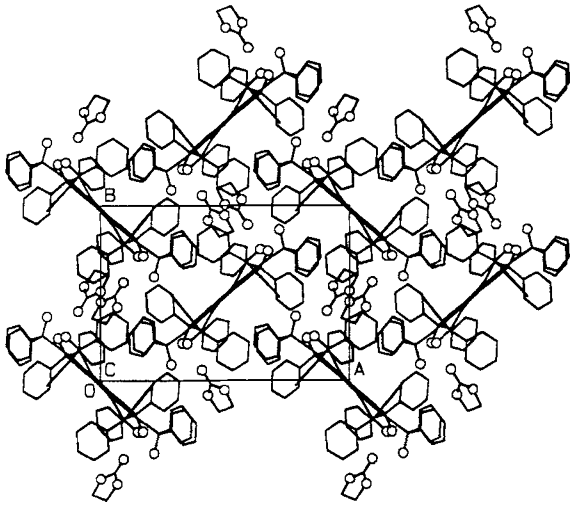

FIGURE 8 Crystal packing in **2** viewed down [001].

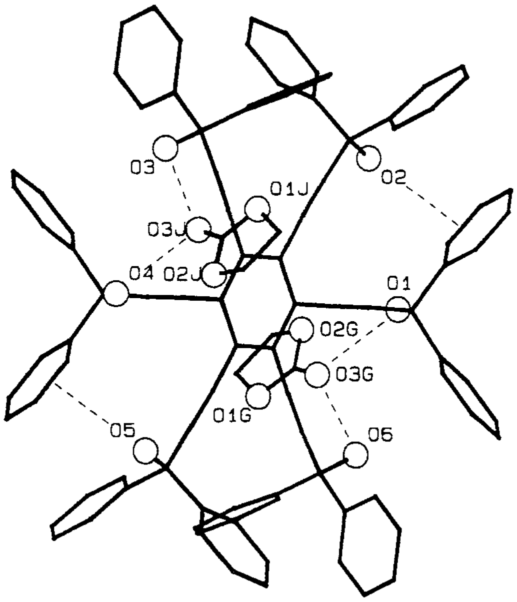

FIGURE 10 The hydrogen bonding scheme of **2**.

The thermograms of **2** are shown in Figure 11. The DSC curve shows a broad endotherm at *ca* 150°C corresponding to guest loss, followed by a sharper endotherm at 240°C due to the host melting. The host then immediately decomposes exothermically. The TG curve shows a single step guest loss and confirms the 1:2 stoichiometry modelled in the crystal structure (expected mass loss: 11.81%, observed mass loss: 11.87%).

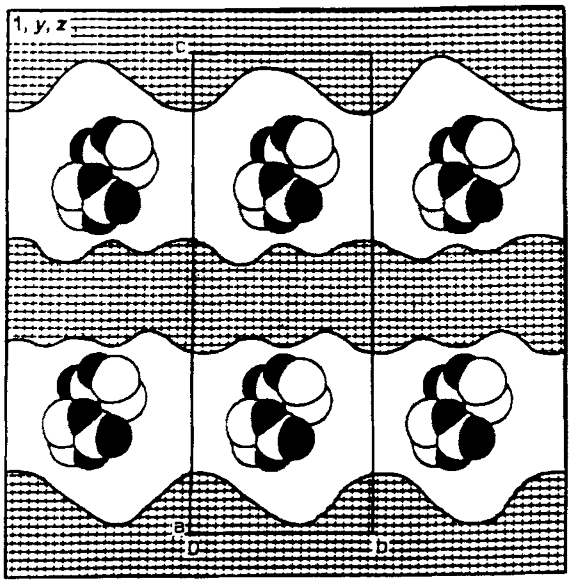

FIGURE 9 Cross section of the host molecules of **2** viewed along [100], showing the channels at $x = 0$. The guest molecules, with the oxygens shaded, are shown in the channels.

EXPERIMENTAL

Crystal Structure

Suitable crystals, grown by slow evaporation from solution of **H** in 1,4-dioxane (**1**) and 1,3-dioxolane (**2**), were mounted in Lindemann capillary tubes. X-Ray diffraction data were collected on an Enraf Nonius CAD4 diffractometer with graphite-monochromated MoK_α radiation ($\lambda = 0.7107$Å) in the ω-2θ scan mode. Three reference reflections were monitored periodically to check orientation and crystal stability. The data reduction included correction for Lorentz and polarisation effects but not for absorption. The crystal data and data collection parameters are listed in Table 1.

TABLE III Hydrogen bond details for **2**

(D)onor	(A)cceptor	D-H (Å)	D...A (Å)	D-H...A (°)
O1	O3G	0.83	2.873(5)	172(5)
O6	O3G	0.92(7)	3.053(6)	173(6)
O3	O3J	0.88(5)	2.995(6)	174(5)
O4	O3J	0.99(6)	2.881(5)	156(5)
O2	centroid (C5–C10)	0.84(6)	3.55(1)	143(13)
O5	centroid (C59–C64)	0.87(6)	3.50(1)	164(17)

Thermal Analysis

Differential scanning calorimetry (DSC) and thermogravimetry (TG) were performed on a Perkin-Elmer PC7 system. Crystals were removed from the mother liquor, blotted dry and lightly crushed before analysis. Sample masses in the range 2-5mg were analysed over the temperature range 30–300°C, at a heating rate of $10°C min^{-1}$, and with dry nitrogen purge gas flowing at *ca.* $40\ cm^3 min^{-1}$.

Kinetics of Desolvation

Data for the kinetics of desolvation of **1** were obtained from a finely powdered sample grown by continuous stirring. The desorption reactions were carried out under isothermal thermogravimetric conditions at temperature intervals of 2 to 5°C over the range 56–75°C. The resultant percentage mass loss versus time curves were reduced to extent of reaction (α) versus time curves. Various appropriate kinetic models were fitted to the data[7], and the one which most nearly approached linearity over the largest α-range was chosen. Values of *k* thus obtained were used to produce Arrhenius plots for the estimation of the activation energy of desolvation.

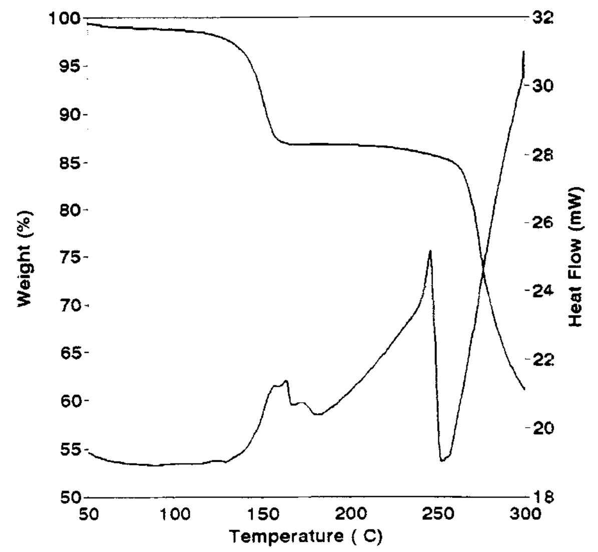

FIGURE 11 Thermograms (TG and DSC) of **2**.

X-Ray Powder Diffraction

Samples were packed in aluminium sample holders. The powder patterns were measured using a Philips vertical goniometer with Ni-filtered CuK_α radiation, and automatic receiving and divergence slits. Step scans (0.1° 2θ, with 2s counting times) were performed from 6 to 35° 2θ.

Nuclear Magnetic Resonance

Samples were dissolved in deuterated chloroform. ^1H and ^{13}C spectra were recorded at 200MHz, at 25°C on a Varian VXR-200 spectrometer with tetramethylsilane as the reference. The spectra were recorded with a sufficient pulse delay time to ensure quantitative resonance integrals to accurately estimate host:guest ratios.

Mass Spectrometry

The mass spectrum of **2** was recorded using a VG-Micromass 16F mass spectrometer with a VG system 2000 PDP-8/a microprocessor. Accurate mass determination was performed by peak matching using a Kratos High Resolution mass spectrometer.

Gas Chromatography

The 1,3-dioxolane was analysed for impurities using a Carlo Erba Fractovap 4200 gas chromatograph equipped with a BP255 capillary column (0.25mm diameter, 25m length) and with a Spectra-Physics SP4290 integrator.

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