

Inclusion by a diol host compound: structure and dynamics of volatile guest exchange

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1,1,6,6-Tetraphenylhexa-2,4-diyne-1,6-diol (H) forms inclusion compounds with furan (**1** and **2**), tetrahydrofuran (**3**) and thiophene (**4**). **1**, H·½FUR (H : G = 1 : ½), is a true clathrate, with the furan guest located in a cage formed by the host. The remaining structures (H : G = 1 : 2) **2**, H·2FUR, **3**, H·2THF and **4**, H·2THIO are isostructural with guests located in channels. Selectivity and guest exchange reactions have been analysed and correlated to the topologies of the inclusion compounds.

Introduction

The synthesis, structure and thermal stability of organic inclusion compounds have been widely studied,^{1–4} but there are relatively few detailed studies of guest-exchange. The recent literature yields the following studies. (a) The dynamics of ethane and methane exchange in an organic host consisting of a substituted durene† dimer, a so-called “tennis ball”, have been studied by NMR methods.⁵ (b) The rate of dissociation and dimerisation of tetraurea calixarenes and the rate of exchange between included and free benzene have also been studied by NMR.⁶ (c) Cholic acid has proved to be a useful host for single-crystal to single-crystal transformations induced by guest exchange.⁷ (d) Bulky hosts containing the fluorenyl moiety have been shown to be responsive to volatile guests, forming inclusion compounds with a tubulate topology. The exchange between EtOH and *n*-PrOH guests was monitored as a function of time on the powdered inclusion compounds using X-ray powder diffraction.⁸ (e) Guest exchange of ammonium with alkylammonium ions has been carried out on tetranuclear adamantanoid complexes and the process monitored by ¹H and ¹³C NMR spectroscopy.⁹ (f) A bis-resorcinol derivative of anthracene has been shown to undergo guest-exchange which is concomitant with an adjustment of the structure while retaining crystallinity.¹⁰

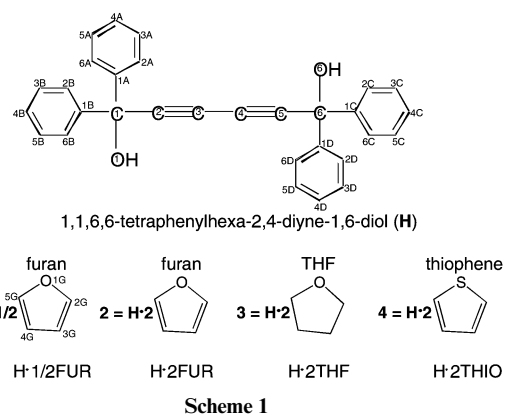
We now present the results of the structural analyses, competition experiments and guest exchange dynamics obtained from the inclusion of furan, tetrahydrofuran and thiophene by the host 1,1,6,6-tetraphenylhexa-2,4-diyne-1,6-diol (see Scheme 1). The study is novel in that it demonstrates, by the changing pattern of the DSC traces, the relative ease of guest exchange in three tubulate inclusion compounds.

Results and discussion

Structures

Crystal and experimental data are given in Table 1.

Compound **1**, H·½FUR, grown from a solution of the host in liquid guest, crystallises with 8 host and 4 guest molecules in the unit cell. Intensity reflection conditions indicated the space group to be either *C2/c* or *Cc*. We initially attempted the structure solution in *C2/c* because the E statistics strongly indicated



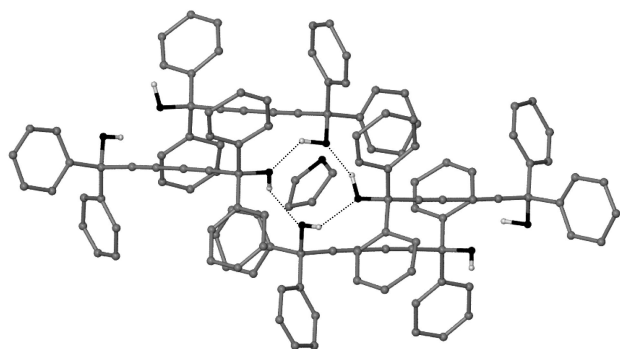
a centrosymmetric structure. Direct methods yielded the positions of all the non-hydrogen atoms of the host and some possible electron density peaks which could be attributed to the guest. However, further refinement yielded very poor positions of the guest atoms, with high values of the thermal parameters and bond lengths and angles, which were not credible. We therefore repeated the structure solution in *Cc*, and the refinement yielded credible positional and thermal parameters for both host and guest molecules, with a reasonable geometry of the furan guest. In the final stages of the refinement, all the hydroxy hydrogens were located in a difference electron density map and were refined with a simple bond length constraint and independent isotropic thermal parameters. The remaining hydrogen atoms were geometrically constrained and were assigned isotropic thermal parameters 1.2 times the U_{eq} of their parent atoms.

The configuration of the host molecules is unusual in that the hydroxy moieties are *gauche*. The torsion angles O(1)–C(1)···C(6)–O(6) are 55.8° and 54.8° for the two host molecules, respectively. In **1**, self-association between the host molecules creates a cavity in which the furan guest is trapped (Fig. 1). The network formed by the host–host hydrogen bonding results in tetramers between which the guest species is sandwiched. This packing motif has been observed in the crystal structures of the host with cyclohexane and the xylene isomers.¹¹ We have mapped the cavity using program SECTION¹² and found it to have approximate dimensions of 6.0 × 6.2 × 5.5 Å. There is no host–guest hydrogen bonding.

† IUPAC name for durene is 1,2,4,5-tetramethylbenzene.

Table 1 Crystal data, experimental and refinement parameters

Complex	1	2	3	4
Molecular formula	2C ₃₀ H ₂₂ O ₂ ·C ₄ H ₄ O	C ₃₀ H ₂₂ O ₂ ·2C ₄ H ₄ O	C ₃₀ H ₂₂ O ₂ ·2C ₄ H ₈ O	C ₃₀ H ₂₂ O ₂ ·2C ₄ H ₄ S
<i>M_r</i> /g mol ⁻¹	897.08	550.65	558.72	582.79
<i>T</i> /K	172(2)	172(2)	172(2)	172(2)
<i>λ</i> /Å	0.71069	0.71069	0.71069	0.71069
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>Cc</i>	<i>P2₁/c</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
<i>a</i> /Å	21.959(2)	8.305(2)	8.291(1)	8.204(1)
<i>b</i> /Å	13.723(1)	15.391(1)	16.072(1)	16.019(1)
<i>c</i> /Å	17.149(1)	11.452(1)	11.423(1)	11.483(1)
<i>β</i> /°	108.22(1)	94.89(1)	93.06(1)	94.52(1)
<i>V</i> /Å ³	4908.8(1)	1458.5(1)	1519.8(1)	1504.4(1)
<i>Z</i>	4	2	2	2
<i>D_c</i> /Mg m ⁻³	1.214	1.254	1.221	1.266
<i>μ</i> (Mo-K _α)/cm ⁻¹	0.80	0.80	0.78	2.45
<i>F</i> (000)	1888	580	596	610
Crystal size/mm	0.50 × 0.20 × 0.17	0.25 × 0.47 × 0.15	0.70 × 0.50 × 0.40	0.35 × 0.20 × 0.12
Range scanned <i>θ</i> /°	2–28	2–28	2–28	2–25
Range of indices	<i>h</i> – 26 – 20 <i>k</i> ± 16 <i>l</i> ± 20	<i>h</i> ± 10 <i>k</i> ± 17 <i>l</i> ± 15	<i>h</i> ± 10 <i>k</i> ± 19 <i>l</i> ± 14	<i>h</i> ± 9 <i>k</i> ± 18 <i>l</i> ± 11
No. reflections collected	10421	4981	5754	6644
No. reflections observed <i>I</i> > 2σ <i>I</i>	6502	3002	3412	2545
No. parameters	574	189	175	190
<i>S</i>	1.074	1.081	1.066	1.067
<i>R</i> ₁	0.1042	0.0583	0.0880	0.0723
<i>wR</i> ₂	0.2700	0.1430	0.2444	0.2119
<i>Δρ</i> excursions/e Å ⁻³	0.91; –0.63	0.24; –0.72	0.72; –0.60	1.16; –0.60

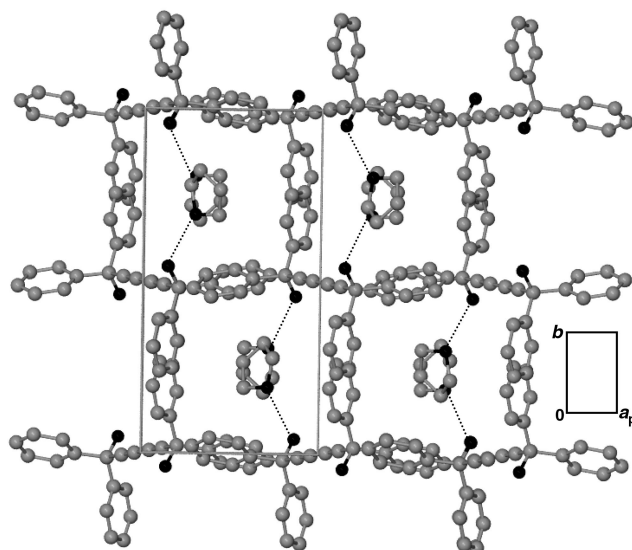
**Fig. 1** Hydrogen bonding scheme for 1.

Compounds **2**, **3** and **4** all have a host : guest ratio of 1 : 2 and crystallise in the space group *P2₁/c* with two host and four guest molecules per unit cell. Symmetry requirements located the host molecules at a centre of inversion at Wyckoff position *a* and these three compounds are isostructural with respect to the host atom positions. They differ, however, in respect of the precise location of the guest atoms.

Compound **2**, H·2FUR, grown from host powder exposed to furan vapour at 25 °C, has the furan molecules located in channels running parallel to [001]. However, careful placing of the guest atoms revealed that the furan oxygen is not located in the vicinity of a host hydroxy group and that there is no host–guest hydrogen bonding.

For compound **3**, H·2THF, the THF molecule is disordered with two alternative conformations, twist and envelope, present at a single site. The guest molecules are again located in channels, and are stabilised by (Host)–O–H···O(Guest) hydrogen bonds.

For compound **4**, H·2THIO, the thiophene guest is also disordered. The sulfur atom is disordered over two positions (S1G and S3G) with site occupancy factors of 60% and 40%, respectively. The guest molecules are once again located in channels running parallel to [001] and the disordered sulfur atom, at position S1G, is hydrogen bonded to the host with an O···S distance of 3.416 Å and angle of 158°. This is typical of O–H···S hydrogen bonds which have been surveyed in the Cambridge Structural Database.¹³

**Fig. 2** Projection of **3** along [001] (only guest envelope conformation shown for clarity).

A typical projection of these three structures is shown in Fig. 2, while a space filling projection, with guest molecules omitted is shown in Fig. 3. The cross sectional areas of the channels for **2**, **3** and **4** were determined using program SECTION and they are from 4.3 × 4.0 Å to 4.9 × 6.9 Å for **2**, from 4.3 × 4.3 Å to 4.9 × 7.1 Å for **3** and from 4.3 × 4.0 Å to 4.9 × 6.8 Å for **4**.

Details of the relationship of the guest positions with respect to the host molecules are summarised in Fig. 4. This shows the general position of the guest with respect to the hydroxy oxygen of the host. The guest centroid to hydroxy oxygen distance, *d*₂, is shown in contrast to the hydrogen bonding distance *d*₁. These are summarised in Table 2. For **1**, the centroid guest distance, which varies from 6.045 Å to 7.221 Å, shows that the guest is located between layers of the host–host hydrogen bonding networks. For **2**, **3** and **4**, however, the distance *d*₂ is practically invariant (*av* = 3.83 Å) showing the general similarities of guest position. Fig. 4(a), (b) and (c) clearly show that the disordered thiophene takes up an averaged position with respect to the

Table 2 Hydrogen-bonding parameters

Compound	Donor (D)	Acceptor (A)	D–H/Å	D···A (d_1)/Å	D···H–A/ $^\circ$	d_2 /Å
1	O1B	O6A	0.82(3)	2.679(2)	137(4)	6.203
	O1A	O6A ^a	0.97(3)	2.688(2)	145(5)	7.158
	O6A ^a	O6B ^a	0.82(3)	2.688(3)	144(5)	6.045
	O6B ^a	O1B	0.82(3)	2.692(2)	137(4)	7.092
2	—	—	—	—	—	3.748
3	O1	O1GA	0.97(3)	2.639(3)	152(3)	3.813
	O1	O1GB	0.97(3)	2.774(3)	156(3)	3.744
4	O1	S1G	0.97(3)	3.416(2)	158(3)	3.950

^a $x, 1 - y, z - 1/2$.

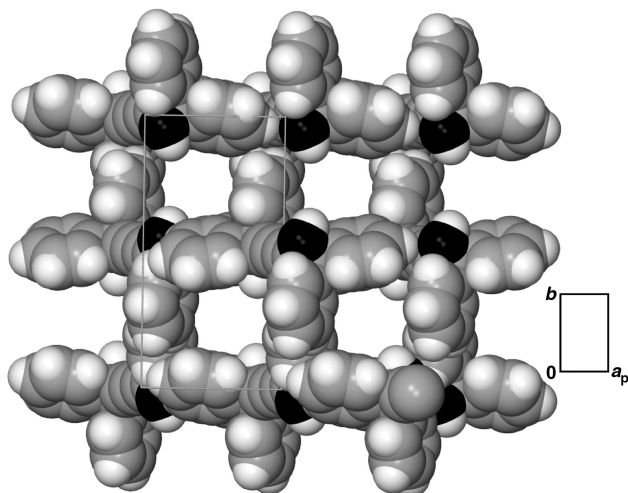


Fig. 3 Space-filling projection of **3** along [001] with guest molecules omitted, showing the open channels.

other two guests and thus explains the positional disorder of the sulfur atoms.

Lattice energy calculations

Lattice energy calculations were performed for **2**, **3** and **4** using the atom–atom potential method. We employed the program HEENY,¹⁴ using a force field of the type given in eqn. (1), where

$$V(r) = a \exp(-br) - c/r^6 \quad (1)$$

r is the interatomic distance and the coefficients a , b and c are those given by Gavezzotti.¹⁵ We incorporated a hydrogen bonding potential which is a simplified version of that given by Vedani and Dunitz¹⁶ and is formulated by eqn. (2), where R is

$$V(\text{H-bond}) = (A/R^{12} - C/R^{10})\cos^2 \theta \quad (2)$$

the distance between the hydroxy hydrogen and the acceptor atom A . θ is the Donor–H···A angle, and the $\cos^2 \theta$ term is the energy penalty paid by the bond to take non-linearity into account. We selected a representative host–guest pair and carried out appropriate summations of all host···host, host···guest and guest···guest interactions. The following values for the lattice energies were obtained: **2**, $-131.3 \text{ kcal mol}^{-1}$; **3**, $-125.1 \text{ kcal mol}^{-1}$ and **4**, $-134.3 \text{ kcal mol}^{-1}$.

Thermal analysis

Salient TG and DSC results are shown in Fig. 5.

H·½FUR decomposes in a single step in the mass loss curve [Fig. 5(a)], and the DSC shows a first endotherm, A, due to guest loss, followed by a sharp endotherm due to the melt of the host.

H·2FUR decomposes in two distinct steps [Fig. 5(b)]. The

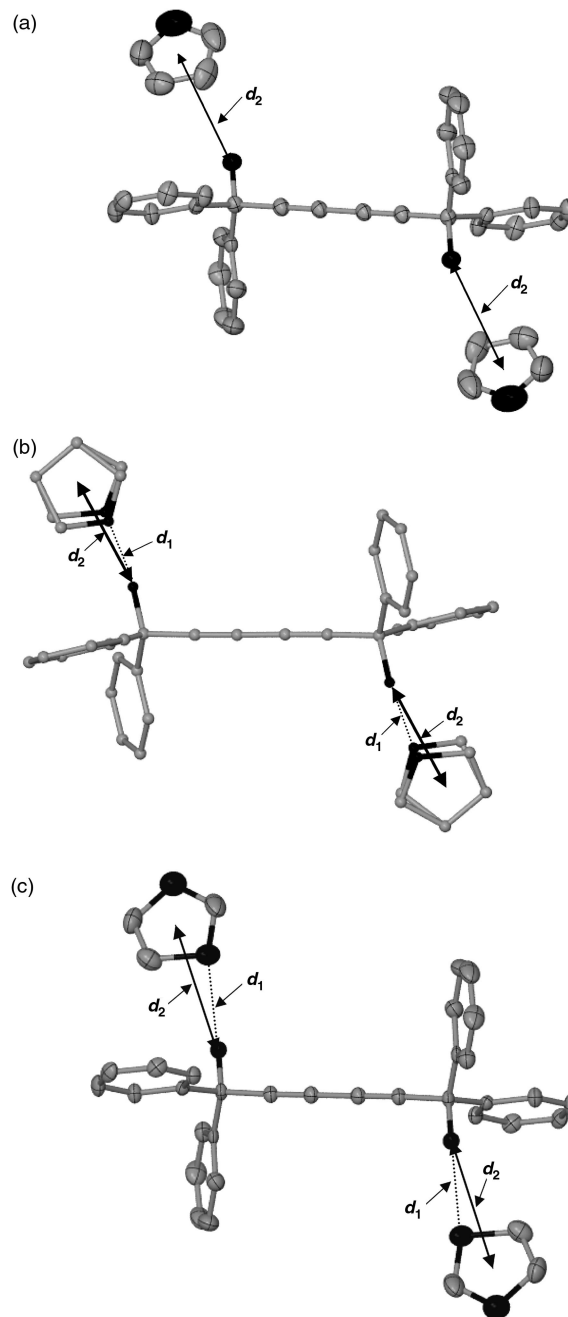


Fig. 4 The general position of the guest with respect to the hydroxy oxygen of the host [the guest centroid to hydroxy oxygen distance (d_2) and the hydrogen bonding distance (d_1)] for: (a) **2**, H·2FUR; (b) **3**, H·2THF; (c) **4**, H·2THIO.

TG curve clearly shows the stoichiometry of this decomposition reaction to be as given in eqns. (3) and (4). Each decomposition step shows corresponding endotherms, A and B, followed by the endotherm due to host melt.

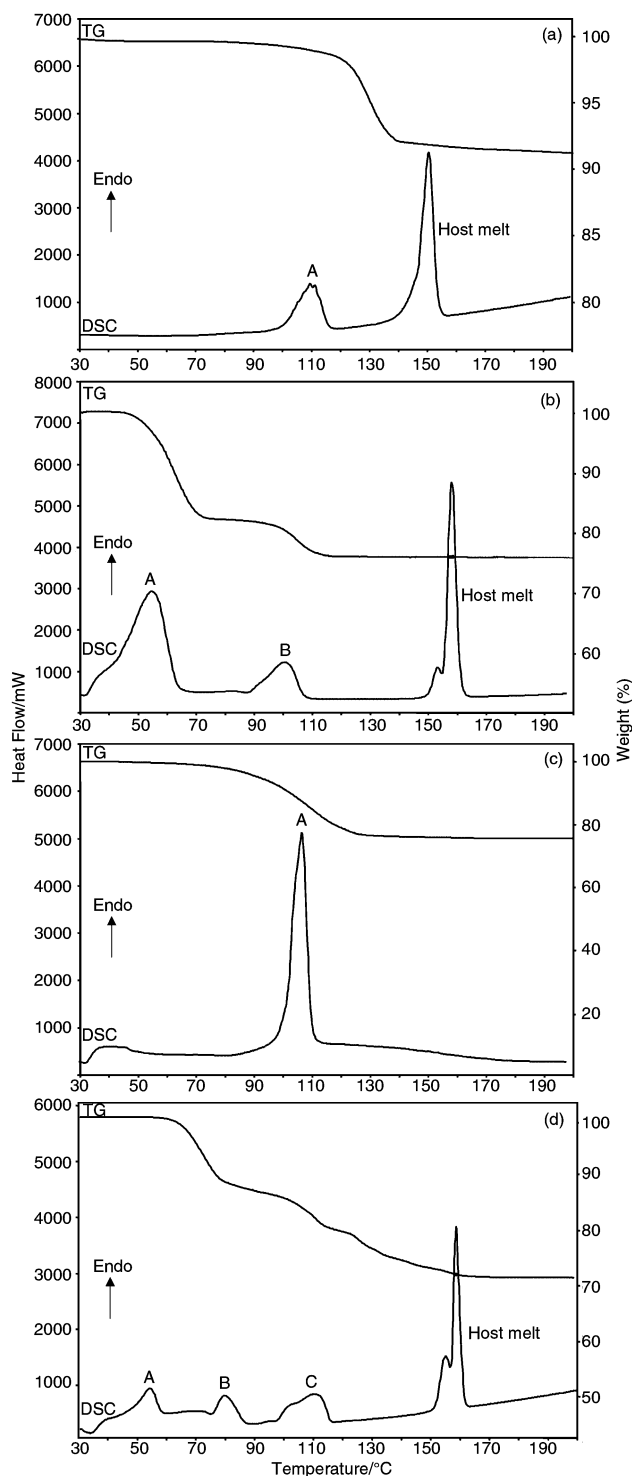
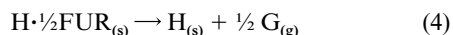


Fig. 5 Thermal analysis results for: (a) 1, H·½FUR; (b) 2, H·2FUR; (c) 3, H·2THF; (d) 4, H·2THIO.



H·2THF decomposes in a single step in the TG curve, but the DSC shows a single endotherm due to the host dissolution in the THF [Fig. 5(c)].

Fig. 5(d) shows that the decomposition of H·2THIO is more complex than that of H·2THF. The TG curve has three distinct steps but the mass losses do not correspond to a simple stoichiometry. However, the DSC shows three distinct endotherms for the guest loss, as well as the endotherm for the host melt. Details of the thermal analyses are given in Table 3.

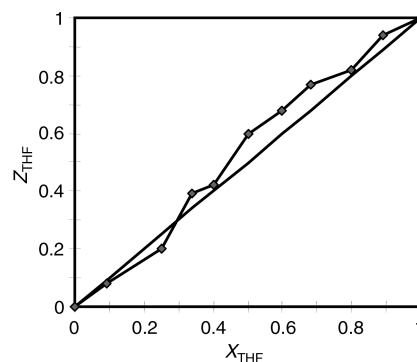


Fig. 6 Competition experiment result for thiophene vs. THF (X is the mole fraction of THF in the liquid mixture and Z is the mole fraction of THF in the crystalline compound).

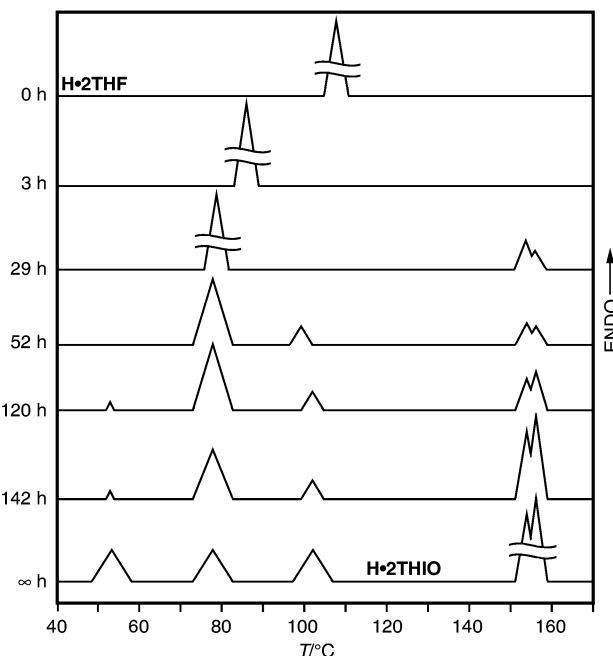


Fig. 7 Schematic representation of guest exchange as a function time $\text{H}\cdot 2\text{THF}_{(s)} + \text{thiophene}_{(g)} \rightarrow \text{H}\cdot 2\text{THIO}_{(s)} + \text{THF}_{(g)}$.

Selectivity and guest exchange

We have carried out a competition experiment between THF and thiophene for the host compound. The results are shown in Fig. 6 and we note that the host shows no selectivity. We surmise that this is due to the fact that the compounds are virtually isostructural, both having their guests located in channels, and their lattice energies are similar. We therefore carried out guest exchange experiments as follows.

A powder of H·2THF was exposed to thiophene vapour at 25 °C in a closed vessel. The resultant product was analysed periodically by DSC, and the results are given schematically in Fig. 7. We note that the starting compound shows the single dissolution endotherm of the THF release, with $T_{\text{peak}} = 102$ °C. As guest exchange proceeds, this endotherm occurs at progressively lower temperatures and additional peaks due to thiophene emission appear. The host melt endotherm begins to appear after 29 h and the guest exchange is practically complete after 142 h. At this point the DSC trace is virtually identical to that of the pure H·2THIO compound.

Similar experiments were carried out for the guest exchange in all possible combinations of G_1 and G_2 and the reverse reaction. The overall reaction may be represented by eqn. (5), where G_1 , $G_2 = \text{furan, THF, thiophene}$.

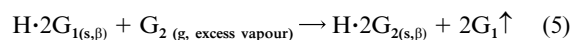
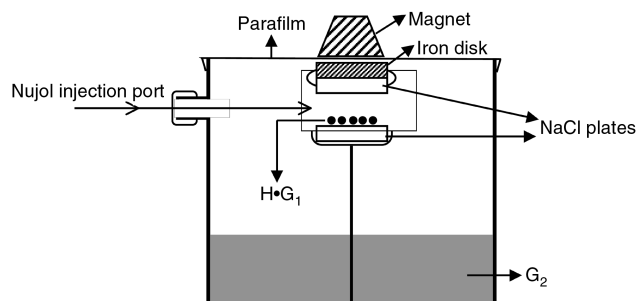
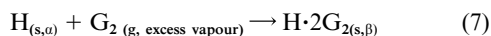
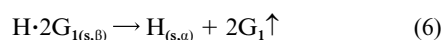


Table 3 Thermal analysis data

Inclusion compound		1	2	3	4
H : G ratio		2 : 1	1 : 2	1 : 2	1 : 2
TG results	Calc. %mass loss	7.57	23.70	25.76	28.82
	Exp. %mass loss	7.68	23.85	25.35	28.87
DSC results	Peak A $T_{on}/^{\circ}\text{C}$	101.18	44.66	102.53	47.61
	Peak B $T_{on}/^{\circ}\text{C}$	—	91.28	—	75.11
	Peak C $T_{on}/^{\circ}\text{C}$	—	—	—	97.27

**Fig. 8** Apparatus for controlled guest exchange and subsequent IR measurements.

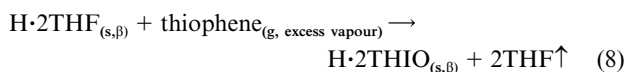
There are two possible mechanisms for the guest exchange. 1. The host–guest system retains its structure throughout the exchange, and so behaves like a zeolite, with the channels remaining open to accommodate incoming and outgoing guest molecules. This process is represented by eqn. (5). 2. The host–guest system desorbs to yield the apohost, which in turn absorbs the incoming guest and forms the new structure. This may be represented by eqns. (6) and (7) where G_1 , G_2 = furan, THF, thiophene.



Here the apohost is in its α , non-porous phase, and the inclusion compound is shown as the β , clathrate phase.

In the latter mechanism, there would be a small but detectable amount of the apohost (α -phase) present throughout the time of guest exchange. Since the stretching frequencies $\nu(\text{OH})$ for complexed and uncomplexed host compound are different, IR spectroscopy was considered a suitable probe. In order to investigate this possibility we set up a series of experiments in which we exposed a small quantity of the $\text{H}\cdot 2\text{G}_{1(s,\beta)}$, placed on a sodium chloride IR plate, to G_2 vapour. The apparatus was sealed by Parafilm tightly stretched across the neck of the container. A second NaCl plate, attached to an iron disc, was suspended 8 mm above the lower plate and held by a magnet (Fig. 8). After a suitable time interval a few drops of Nujol were injected on to the exposed compound. The magnet was removed and the upper plate was allowed to fall and seal the lower plate. The Parafilm was then removed, the NaCl plates extracted and IR spectra immediately recorded. This method ensured that at no time was the inclusion compound exposed to the air during guest exchange.

For the overall exchange in eqn. (8), we monitored the IR



spectra after 48, 72, 96 and 120 h. The IR spectra clearly showed an absorption band at 3530.7 cm^{-1} corresponding to the $\nu(\text{OH})$ stretch of the apohost as well as absorption bands at 3279.9 cm^{-1} and 3349.3 cm^{-1} corresponding to the hydrogen-bonded $\nu(\text{OH})$ for the $\text{H}\cdot 2\text{THF}_{(s,\beta)}$ and $\text{H}\cdot 2\text{THIO}_{(s,\beta)}$, respect-

ively. Similar values of IR shifts have been obtained by Toda *et al.* for inclusion compounds of this host, H, with xylidines.¹⁷ This clearly establishes the mechanism shown in eqns. (6) and (7).

All reactions went essentially to completion, with lifetimes varying between 2 and 144 h. We are aware that the kinetics of such reactions will depend upon a number of factors which include the particle size distribution of $\text{H}\cdot 2\text{G}_1$ solid, the vapour pressure of the incoming guest, G_2 , and the strength of the host–guest interactions of both the reactant and product.

We surmise that the relative ease of the guest exchange is, firstly, because of the presence of a small quantity of the apohost during the exchange and, secondly, due to the fact that the new structure formed is very similar to that at the start.

We have measured the size of the channels by mapping the structures with the host compound drawn with van der Waals radii and have noted that there is a loose fit for the various guest molecules in the channels. This indicates that guest movement within the channels is not hindered, aiding guest exchange.

Conclusions

We have demonstrated the possibility of carrying out guest exchange in organic inclusion compounds. The process is favoured by structures which are isomorphous with respect to the host and which yield host–guest compounds having similar lattice energies. The mechanism of the exchange requires the presence of a small quantity of the apohost and is aided by the channel topology of the inclusion compounds.

Experimental

The inclusion compounds **1**, **3** and **4** were obtained by dissolving the host compound (H) in the minimum amount of guest. Suitable quality crystals appeared by slow evaporation overnight. The inclusion compound **2** was obtained by placing a 10 ml beaker containing host powder into a 100 ml jar that contained 20 ml of furan. The system was kept closed at room temperature and the crystals were obtained after 12–24 h. Crystals of compound **4** could be prepared in the same way. Cell dimensions were obtained from the intensity data measurements on a Nonius Kappa CCD diffractometer using graphite-monochromated Mo-K α radiation. The strategy for the data collection was evaluated using the COLLECT¹⁸ software. For all four structures data were collected by the standard ϕ scan and ω scan techniques. For each structure all sets of data were scaled and reduced using DENZO-SMN.¹⁹ The structures were solved by direct methods using SHELX-86²⁰ and refined employing full-matrix least-squares with the program SHELX-97²¹ refining on F^2 . Program X-Seed²² was used as a graphical interface for structure solution and refinement using SHELX. ‡

Thermal analysis

Thermogravimetry (TG) and differential scanning calorimetry (DSC) were carried out on a Perkin Elmer PC7-Series system. These experiments were performed over the temperature range 30–300 °C at a heating rate of 20 °C min⁻¹ with a purge of dry nitrogen flowing at 30 ml min⁻¹. The samples were crushed, blotted dry and placed in open platinum pans for TG experiments and in crimped but vented aluminium pans for DSC.

Competition experiment

A competition experiment was carried out between thiophene and tetrahydrofuran as follows. A series of 11 vials were made

‡ CCDC reference numbers 166351–166354. See <http://www.rsc.org/suppdata/p2/b1/b105248a/> for crystallographic files in .cif or other electronic format.

up with mixtures of two guests such that the mole fraction of a given guest varied from 0 to 1. Host compound was added to each mixture, keeping the ratio of host to total guest at 1 : 105. The vials were closed, sealed with Parafilm and refrigerated to prevent guest evaporation which would affect H : G ratios in the vials. The resulting crystalline inclusion compounds were filtered, dried and placed in vials with silicone seals. The crystals were heated to release the guest mixtures, which were then analysed by gas chromatography.

Guest exchange

The inclusion compounds **2**, **3** and **4** were prepared by placing 10 ml beakers containing host powder into a 100 ml jar that contained about 20 ml of furan, THF and thiophene, respectively. The systems were kept closed at 25 °C and the inclusion compounds were obtained after 12–24 h. The formation of complexes was confirmed by TG and DSC analysis. The 10 ml beakers now containing complexes were then placed in new 100 ml jars containing one of the other two liquid guests and exposed to their vapours. For the observation of guest exchange, samples were taken after suitable time intervals and analysed using DSC.

Acknowledgements

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