

Designing New Lattice Inclusion Hosts

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1 Introduction

Organic inclusion compounds may be classified, in the majority of cases, into two distinct categories. The more widespread group comprises unimolecular compounds where one host molecule interacts with one guest species.¹ Familiar examples include host types such as the cyclodextrins, crown ethers, cryptands, carcerands and their related derivatives. The synthesis of new materials of this type has become an extremely active and highly sophisticated branch of chemistry, partly because of their inherent 1:1 stoichiometry and because molecular modelling often permits reliable prediction.²

On the other hand, there are many other inclusion systems where the arrangement of molecules comprising the host lattice itself results in the observed host–guest properties.² Synthesis of new examples of these multimolecular or lattice inclusion compounds is problematical because lattice packing arrangements (even for simple organic molecules) cannot yet be predicted by computational methods – despite innovative approaches toward this end.³ How, therefore, can new lattice inclusion hosts be discovered? The traditional answer to this question used to be ‘by fortunate accident’,⁴ but in this article I shall describe how systematic approaches involving crystal engineering⁵ can now help us towards overcoming these formidable synthetic difficulties.

The black comedy *Cat’s Cradle* by Kurt Vonnegut⁶ relates how Dr Felix Hoenikker succeeds in synthesising the polymorph icenine. In the hands of his dysfunctional offspring, the existence of this close-packed and thermodynamically stable substance leads to an all-too-inevitable outcome – but how was this molecular lattice designed? This strikingly successful fictional example of crystal engineering was inspired by analysis of stacking arrangements of the cannon balls decorating court-house lawns and through modelling using the permutations of a cat’s cradle – techniques not so far removed, perhaps, from current methodology.

The concept of ionic close-packing is widely used to explain the structure of simple lattices such as that of sodium chloride. Similarly, one of the basic tenets of practical organic chemistry is that recrystallisation of a crude reaction product will yield crystalline material of high purity. Both these everyday illustrations presume that simple ions or molecules will pack together efficiently to yield high density structures, without void spaces which might contain guest species.⁷

In contrast, crystallisation of the extremely simple molecule H₂O results in formation of a rather open lattice structure accompanied by the remarkable density decrease from 0.9998 to 0.9168 g cm⁻³. This is caused, of course, by formation of the highly directional hydrogen-bonding network present in ice. Furthermore, a crystallographer would not be surprised if protein crystals for X-ray structural determination contained associated components such as water molecules, sodium ions, and the crystallisation solvent itself – sometimes in large quantities.

Hence, it is also possible that appropriate intermolecular forces combined with ‘awkward’ molecular shapes can lead to difficulties in close-packing, which might be alleviated by guest inclusion. Successful approaches to new lattice inclusion hosts, therefore, must take into account factors such as molecular size, shape and symmetry; and must also seek a fine balance between the intermolecular repulsive forces and attractive forces present. In supramolecular synthesis, specific types of intermolecular non-covalent attraction are akin to the synthons of conventional synthetic chemistry.⁸ We must learn to recognise these motifs, discover their influence on molecular packing, and develop the ability to use such arrangements to our advantage.⁹ The subtle interplay of these diverse factors is illustrated here for a selection of synthetic approaches to recently reported lattice inclusion systems.

2 Propeller Blades, Wheels and Axles

Since the initial report of the triphenylmethane–benzene compound by Kekulé in 1872 it has become recognised that inclusion properties are frequently associated with polyaryl systems that can adopt propeller-shaped arrangements. This is because the aryl–aryl interactions⁸ that predominate in such structures tend to result in formation of void spaces suitable for guest entrapment.

An interesting example is tris(5-acetyl-3-thienyl)methane **1**, reported to be a versatile host by bin Din and Meth-Cohn in 1977, but only now receiving proper structural attention.¹⁰ In the A-form of its 2:1 cyclohexane compound (Fig. 1) the near planar acetylthienyl groups are the propeller blades, which interact through two distinct offset face–face intermolecular mechanisms. One pair of blades overlaps thienyl⋯thienyl, while the other two pairs overlap carbonyl⋯thienyl. For all three the interplanar separation is about 3.6 Å – a characteristic value for this type of interaction. The heteroaromatic groups of **1** function just as effectively as the benzenoid rings traditionally associated with polyaryl propeller-shaped hosts, indicating considerable potential for further host design in this area.

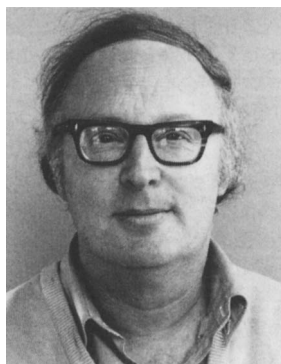
Direct connection of two polyaryl groups by a linear spacer leads to the wheel and axle compounds first recognised by Toda and since developed into a major class of inclusion hosts.¹¹ Hence, in structure **2**, the wheels are tris(*m*-tolyl)phosphine groups and the axle comprises a gold acetylide moiety. In the benzene compound of **2** the guest molecules occupy barrel-shaped cavities created by neighbouring *m*-tolyl rings (Fig. 2). Three *m*-tolyl groups describe the top, another three the bottom, and six others define the staves, of each barrel.¹²

Inclusion properties of both the above categories may be modified (and frequently enhanced) by incorporating hydrogen-bonding groups. Typical structures such as **3** and **4** suffer moderate crowding around their hydroxy groups, which can inhibit intermolecular hydrogen bonding. Consequently, polar guests able to act as bridging links between separate host molecules now tend to be included.¹¹

Inclusion systems stabilised by varying proportions of complexation and lattice dispersion forces have been termed coordinato-clathrates by Weber, and these often exhibit novel guest selectivity

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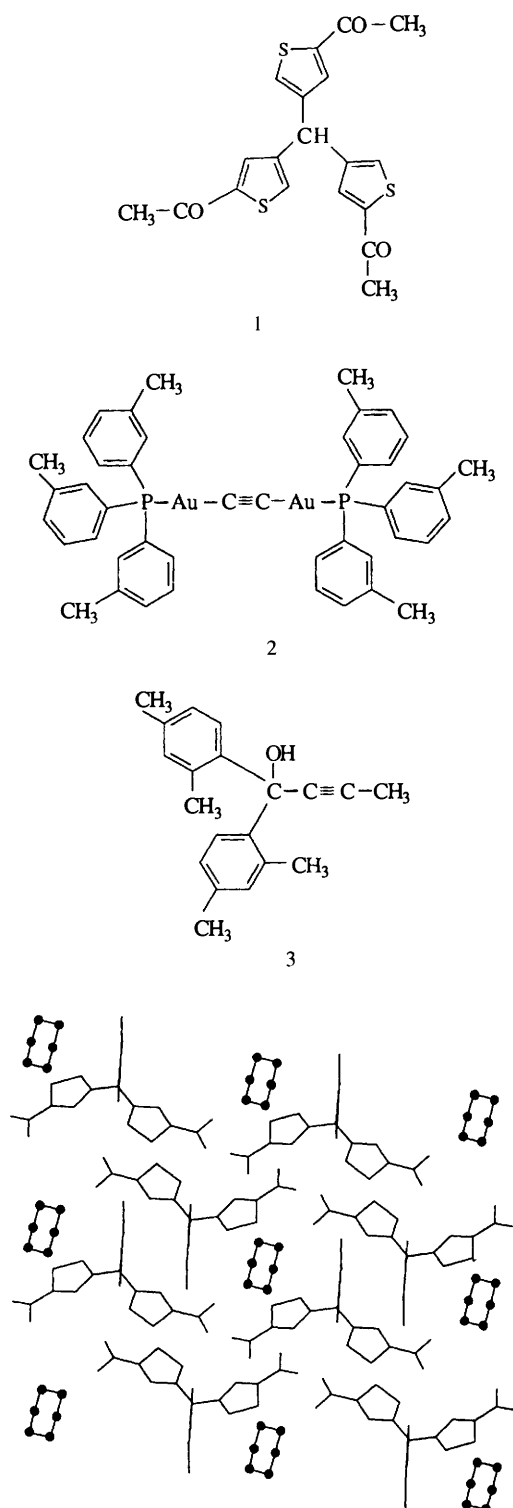


Figure 1 Crystal packing in 1_2 (cyclohexane) viewed along a . For clarity the tris(5 acetyl 3 thienyl)methane hosts are drawn as molecular frameworks, cyclohexane carbons are shown as filled spheres, and all hydrogen atoms are omitted. Thienyl-thienyl interactions are edge on, and the carbonyl-thienyl interactions are inclined, in this view. The cyclohexane guests occupy channels along a .

arising from the balance between these factors.¹³ For example, the acetylenic alcohol **3** is able to remove ethanol from aqueous solutions through formation of the complex **3** (ethanol). Heating of this solid liberates the pure guest, thereby providing an unusual and valuable isolation procedure.¹⁴

The crystal structure of **3** (ethanol) (Fig. 3) reveals that two molecules of each type are hydrogen bonded together through the cyclic

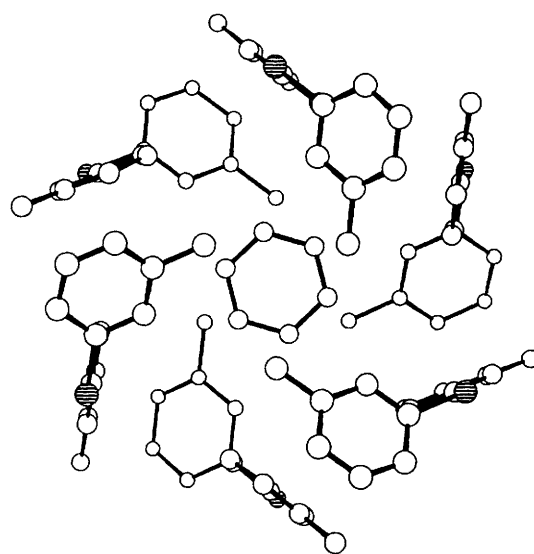
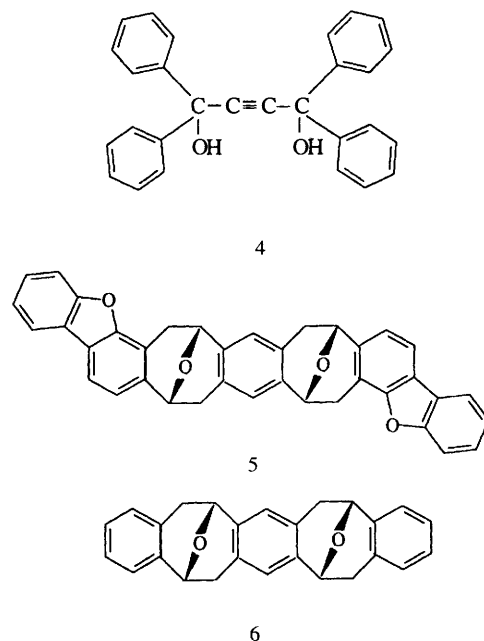


Figure 2 Benzene in a barrel. For clarity only the $P(m\text{-tolyl})_2$ partial structure of compound **2**, which is directly involved in the host-guest construction, is drawn here. Hydrogen atoms are omitted and phosphorus atoms are hatched. The six peripheral edge on m -tolyl groups define the walls, while the other six define the ends, of the barrel-shaped cavity present in **2** (benzene).



array $(-O-H)_4$, which is a well-known supramolecular motif amongst alcohols.¹⁵ In this instance, this is the dominant interaction present. The parallel aryl groups visible in Fig. 3 are actually about 5.5 Å apart and do not interact, but inter-complex stabilisation is provided through $\equiv C-CH_3$ aryl interactions.

3 Inclined Planes and Rigid Spacers

Another key strategy is the targeting of molecules the structures of which involve inclined planar sub-structures. For example, two planar units may be joined edge-edge to give scissor-shaped molecules, or edge-face to give either T-shaped or roof-shaped molecules. As demonstrated most convincingly by Weber,¹⁶ significant numbers of such compounds exhibit inclusion properties. These characteristics often persist in the extended structures obtained through addition of further planar sub-structures and/or rigid spacer groups as shown here.

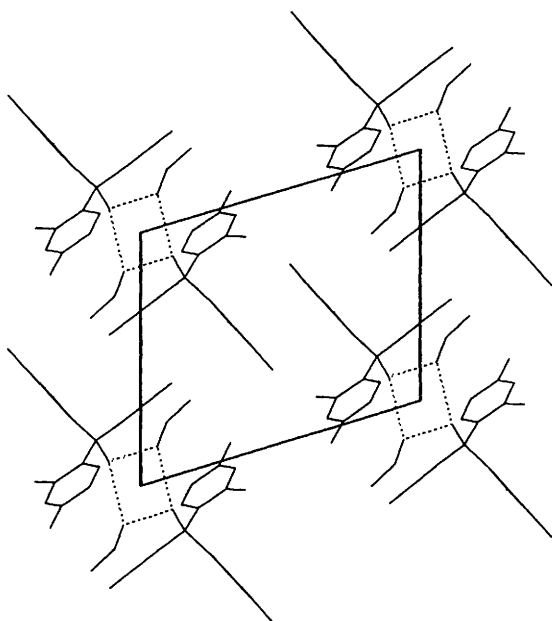


Figure 3 The unit cell of **3** (ethanol) viewed along a and with the host-guest hydrogen bonded cycles ($-\text{O}-\text{H}$)_n represented by dashed lines. For simplicity all molecules are reproduced as framework drawings and all hydrogens are omitted. The hydrogen bonded units are linked through $\equiv\text{C}-\text{CH}_3 \cdots$ aryl interactions.

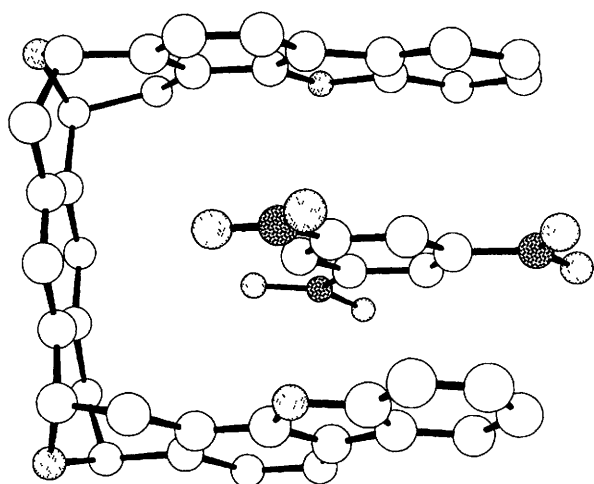


Figure 4 The filled molecular cleft compound **5** (1,3,5-trinitrobenzene). Oxygen atoms are lightly stippled, nitrogens are heavily stippled, and hydrogen atoms are omitted.

Three planar units joined edge-face-edge as a U-shaped cleft can result in a unimolecular compound, as illustrated in Fig. 4 for the combination of **5** and 1,3,5-trinitrobenzene. In this structure the separation between the dibenzofuran units and the aromatic guest is about 3.3 Å. However, if the depth of the cleft is insufficient, as in the related molecule **6**, then multimolecular inclusion compounds result instead.¹⁷

The inclusion properties of tetraarylporphyrin derivatives have been developed extensively by Strouse and his colleagues. Indeed, these porphyrin sponges arguably now constitute the most comprehensive family of lattice clathrate hosts.¹⁸ The peripheral aryl groups of these hosts are attached in edge-on fashion to the central planar ring and, consequently, these molecules pack as corrugated sheets, which stack to produce parallel guest-containing channels. This is illustrated in Fig. 5 by the host zinc tetraphenylporphyrin **7** as its inclusion compound **7**·(naphthacenequinone).

Extension of the wheel and axle concept by replacing the central linear spacer by a rigid planar group is typified by the polythiophene derivatives **8** and **9** reported by Kobayashi.¹⁹ Both compounds form

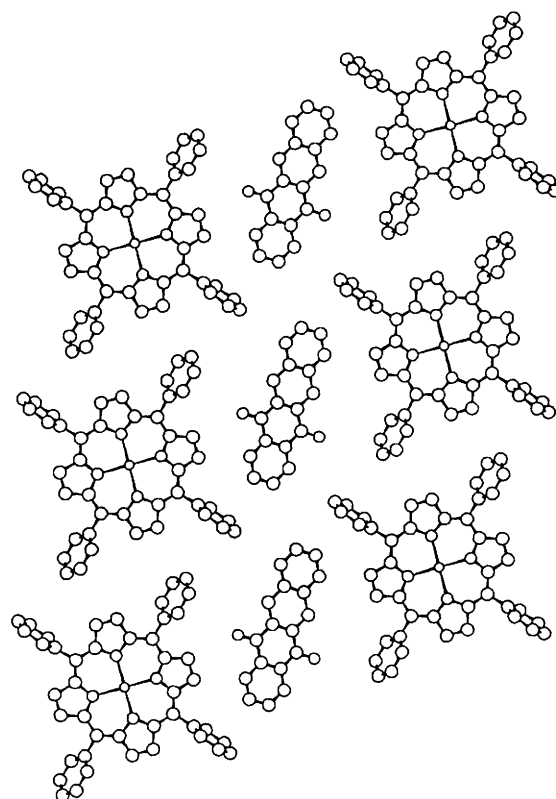
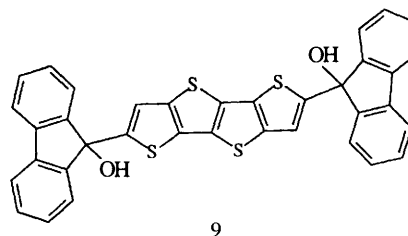
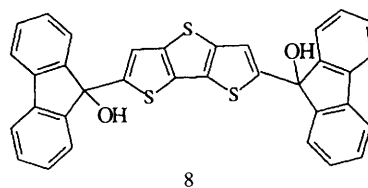
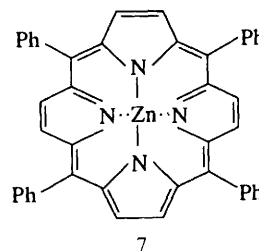


Figure 5 A typical porphyrin sponge inclusion structure (zinc tetraphenylporphyrin **7**·(naphthacenequinone)), showing the characteristic guest-filled channel arrangement. Hydrogen atoms are omitted for clarity.



hydrogen-bonded complexes with Me_2SO , but the stoichiometry and structural type alternate with the number of fused thiophene units in the central planar group. When this is odd then hydrogen-bonded host dimer formation is possible resulting in a compound such as **8**₂·(Me_2SO)₂, but if even then materials like **9**·(Me_2SO)₂ are produced. The crystal structures of these closely related compounds are compared in Fig. 6.

Further implications of this particular design concept are explored later in Sections 5 and 6.

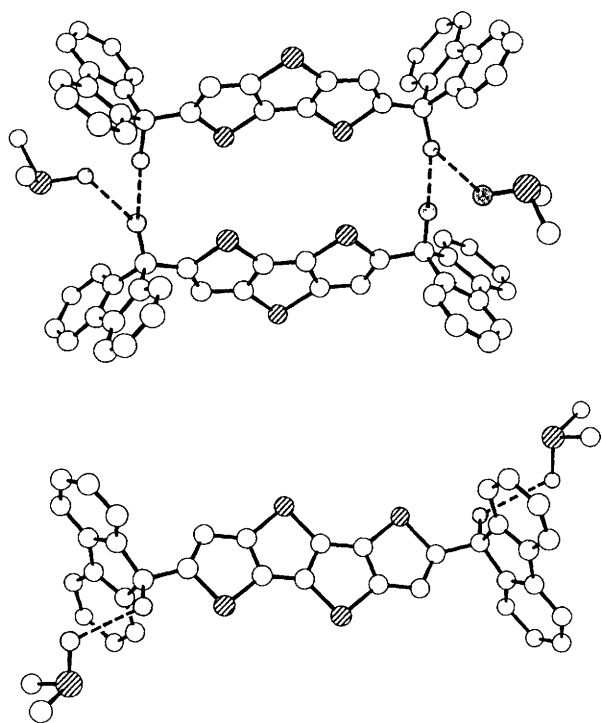


Figure 6 Variation of inclusion structure with the number of fused thiophene rings in the central planar spacer group. Top: odd number of units yielding **8₂** (Me_2SO)₂. Bottom: even number of units giving **9** (Me_2SO)₂.

4 Hydrogen Bonded Lattices Inspired by Hydroquinone

Hydroquinone **10** is such a small and highly symmetrical molecule that one would expect it to pack in a trivial lattice arrangement. Surprisingly, therefore, its most stable crystal form at room temperature (α hydroquinone) has a highly convoluted structure containing an amazing 54 molecules per unit cell.²⁰ As for the case of ice, the demands imposed by intermolecular hydrogen bonding and symmetry dominate other contributing factors such as molecular size and shape. Hence, hydroquinone **10** exhibits molecular simplicity but supramolecular complexity. Because of these remarkable properties it has played a central role in the development of inclusion chemistry.

Packing difficulties can be overcome, in part, by adopting the β -hydroquinone lattice (Fig 7) and by including small guest molecules. Such materials were first noted by Wohler in 1849 but their exact nature was not proved till nearly a hundred years later through the work of Powell who largely founded the modern era of structure-based inclusion chemistry. The β -hydroquinone structure is a superlattice constructed from two identical interpenetrating (but unconnected) simple cubic sublattices. Small voids between these sublattices imprison the guest molecules within the superlattice.²¹ The design of new organic superlattices built up from two or more equivalent interpenetrating sublattices is a fascinating current aspect of crystal engineering and is frequently associated with guest inclusion. Readers are directed to the excellent account in this Journal by Zaworotko.²²

MacNicol noted the characteristic hydrogen-bonding pattern present in β hydroquinone and realised that it was also present in inclusion compounds formed by Dianin's compound **11** and related

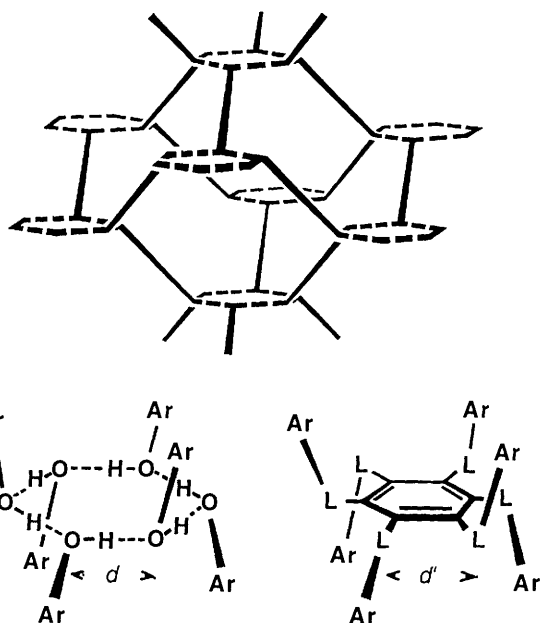
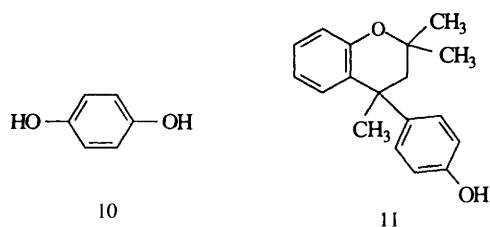


Figure 7 Top: Diagrammatic representation of one β hydroquinone sublattice emphasising the network characteristics of this part structure. The solid tapering rods represent hydroquinone molecules **10**, and the dashed lines indicate hydrogen bond cycles ($-\text{O}-\text{H}$)₆. Bottom left: Representation of one hydrogen bonded hexamer motif which is the supramolecular core of the above structure. Bottom right: Diagrammatic representation of the hexa host principle, showing aryl (Ar) and linking (L) groups, and comparing the interatomic separation (d') with that present (d) in the ($-\text{O}-\text{H}$)₆ core of β hydroquinone.

derivatives. In a brilliant piece of thinking he realised that the 'arms' of a hexa-substituted benzene would adopt a closely related geometry, which also would be favourable for guest inclusion (Fig 7). Hence, for the first time an entire family of new lattice inclusion hexa hosts such as **12**, without a direct molecular relationship to previously known compounds, were successfully designed and synthesised.²³ This striking outcome represents the first direct application of what we would now describe as the supramolecular synthesis of new inclusion hosts.

A more recent strategy by the MacNicol group affords novel inclusion hosts termed Piedfort assemblies²⁴ where the central aromatic core is doubled in thickness (Fig 8). This is achieved by assembly of two stacked tri-substituted aromatic units, which replace the previous hexa-substituted molecule but retain its three-fold symmetry. Hence, for example, 2,4,6-tris[4-(2-phenylpropan-2-yl)phenoxy]-1,3,5 triazine **13** forms the highly crystalline 1:2 adduct with dioxane illustrated in Fig 9.

More recently, inspection of the β -hydroquinone superlattice suggested to Ermer²⁵ that the dimensions of [60]fullerene closely matched those of a single sublattice unit. Furthermore, he reasoned that aryl-aryl interactions between the electron-acceptor fullerene and the electron-donor hydroquinone rings should provide considerable stabilisation if a host-guest compound were produced. On testing this outstanding idea it was indeed found that crystallisation of a mixture of the two components afforded black crystals of composition **10**₃·(C₆₀) where the fullerene was embedded within just one β -hydroquinone sublattice as illustrated in Fig 10.

5 Other Hydrogen-bonded Network Structures

Of course, hydroquinone is by no means the only molecule capable of providing a strong hydrogen bonded host network containing guests. Indeed, allusions to interpenetrating lattice structures²² and Dianin's compound **11**²³ have already been made. Hydrogen bonding is usually stronger, and often more directional, than the other intermolecular attractions present in a lattice inclusion structure. Therefore, the requirement here is for the host to exert a

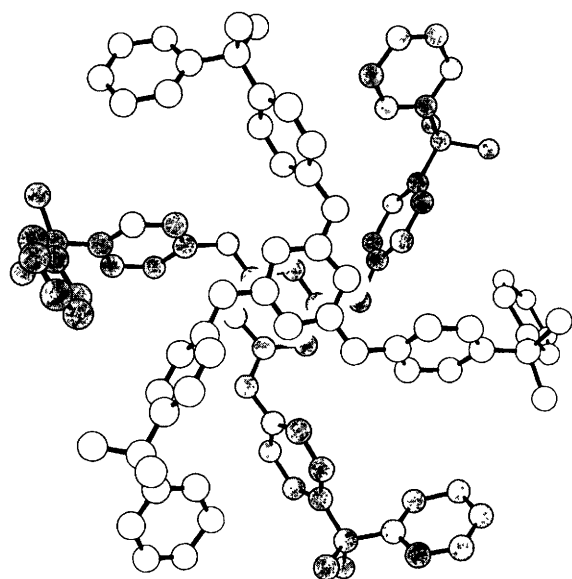
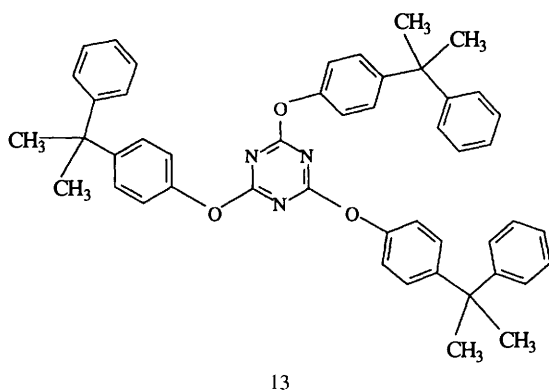
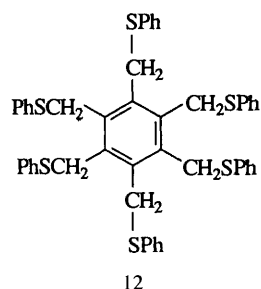


Figure 8 The Piedfort unit of 2,4,6-tris[4-(2-phenylpropan-2-yl)phenoxy]-1,3,5-triazine molecules **13** in its inclusion compound $13 \cdot (\text{dioxane})_2$, emphasising its symmetry, the double thickness aromatic core, and the six pendant arms. Non-hydrogen atoms of one molecule of **13** are represented by open spheres, and those of the other by shading. The inter-triazine aryl-aryl separation is *ca.* 3.5 Å.



dominant effect on the molecular combination by providing a strong intermolecular network of low density. Three quite different cases of this phenomenon are described here.

The steroidal bile acids are an important family of compounds involving a flexible side chain with a terminal carboxylic acid group, attached to a rigid fused-ring steroidal skeleton whose β -face is hydrophobic and α -face hydrophilic owing to the presence of hydroxy substituents. These materials frequently self-associate by means of convergent intermolecular hydrogen bonding, thereby producing head-tail bilayers. Crystal packing results in flexible parallel hydrophobic channels, which frequently enclose less polar guest molecules.²⁶

An illustration of how this behaviour can be modified and controlled is provided by cholamide, the amide derivative **14** of the natural product cholic acid. In its inclusion compounds one amide hydrogen atom participates in the host-host hydrogen-bonding

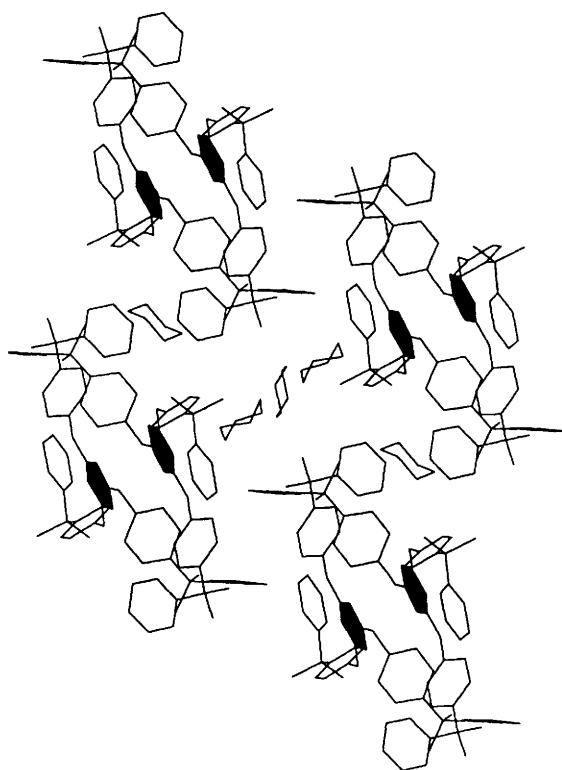


Figure 9 Lattice packing in $13 \cdot (\text{dioxane})_2$ showing four Piedfort units and their associated guest molecules. For clarity, all molecules are shown in framework representation, all hydrogens are omitted, and no distinctions are made between carbon and heteroatoms. Each triazine core is shown as a solid hexagon to emphasise the Piedfort units in this structure.

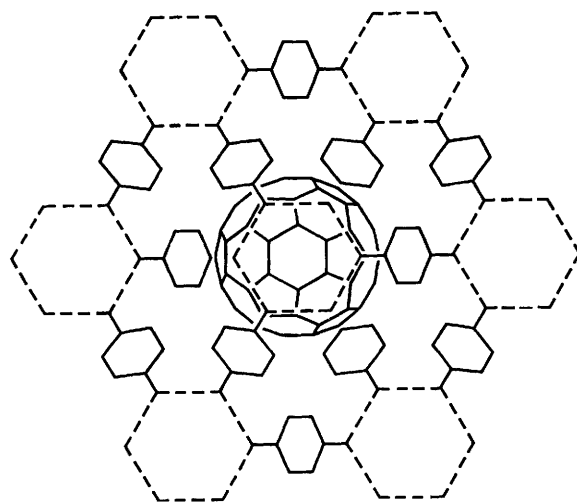


Figure 10 Diagrammatic representation of $(\text{hydroquinone})_3 \cdot (\text{C}_{60})$ viewed along *c*. The small solid hexagons represent the aryl rings, and the large dashed hexagons the $(-\text{O}-\text{H})_6$ cycles.

network. However, the other hydrogen protrudes from the channel wall and is now available as a molecular hook for polar hydrogen-bond acceptor groups like alcohols and ethers, as shown in Fig. 11 for **14** · (dioxane).²⁶

Our own work has uncovered a remarkable family of inclusion hosts related to the simple diol **15** where the hydroxy groups assemble around a threefold screw axis producing a hydrogen-bonded 'spine'. The alicyclic framework functions as a rigid spacer group and results in these diols crystallising as lattices containing large parallel canals (Fig. 12) in which guests are trapped on a size and shape basis. This spine motif is another example of a supramolecular synthon⁸ and

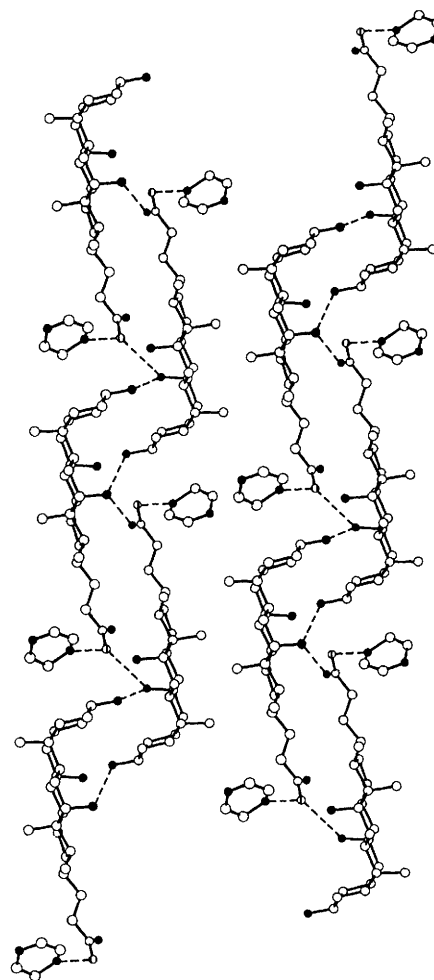
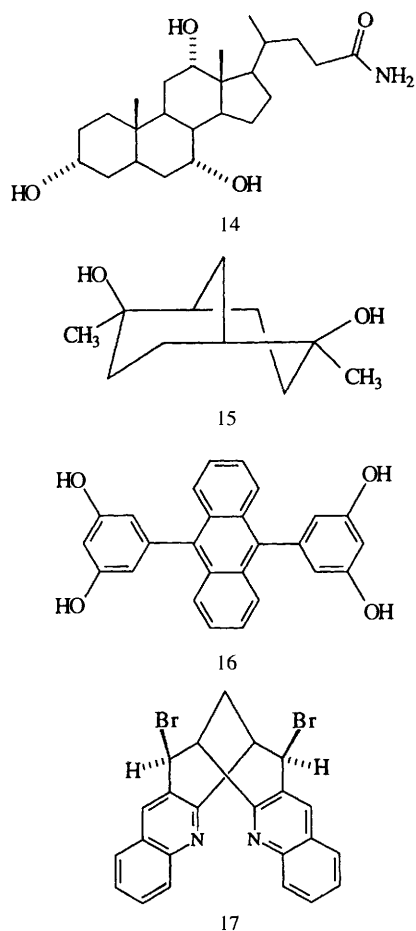


Figure 11 Structure of (cholanamide **14**)-(dioxane) viewed along the *b* axis. Oxygens are shown as solid spheres, nitrogen atoms are striped, and hydrogen bonds are indicated by dashed lines. All hydrogen atoms are omitted.

can be transplanted into other alicyclic systems thereby providing a family of hosts termed the helical tubulands. These have exactly the same crystal packing but differ considerably in their canal dimensions and resulting inclusion properties.²⁷ The cutaway view of **15**₃·(chlorobenzene) shown in Fig. 13 reveals the head–tail guest packing arrangement along one such canal of this helical tubulate compound.

The third example illustrating network hydrogen-bonding hosts is Aoyama's phenol **16**,²⁸ which combines this property with those of the inclined plane systems discussed in Section 3. In the inclusion compound **16**·(benzophenone)₂, the four phenol groups of **16** hydrogen bond to their neighbours creating a rather open layer structure in which the protruding anthracene groups are orthogonal to the phenolic rings. This results in the construction of a series of open cages with two benzophenone guest molecules occupying each cage. Each guest is stabilised by its carbonyl oxygen accepting a phenolic hydrogen bond and through aryl...aryl interaction with the anthracene groups (Fig. 14).

Offset stacking of these layers affords a series of tubes formed by placing the open cages on top of each other. These tubes can be envisioned by imagining an infinite number of Fig. 14 units directly stacked on top of each other in a fully eclipsed manner. Consequently, the benzophenone guests occupy parallel tubes running through the crystal lattice.

It is particularly noteworthy that, despite the considerable differences in molecular structure between the building blocks **15** and **16** and also in the construction of their inclusion networks, both compounds behave rather similarly. Both include guests in parallel tubes, their networks can survive as apohosts on removal of guest species, and their inclusion structures can be regenerated on exposure to guest vapour. These properties are remarkably similar to some of those exhibited by inorganic zeolitic structures.

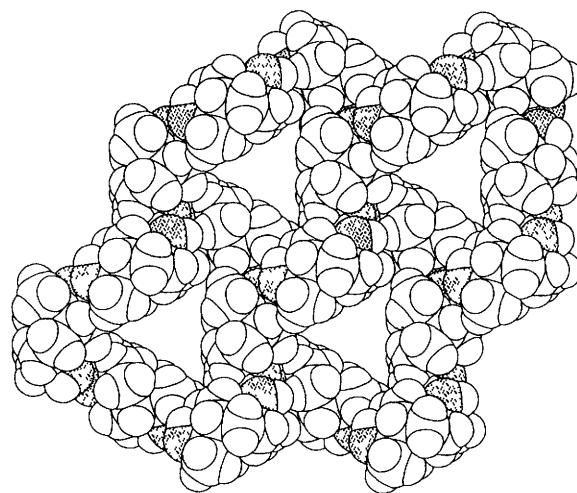


Figure 12 Projection in the *ab* plane of a section through the helical tubuland lattice of diol **15** showing the parallel canals of triangular cross-section. The helical characteristics of each canal are largely masked in this representation. Oxygen atoms of the helical hydrogen bonded spine motifs are stippled.

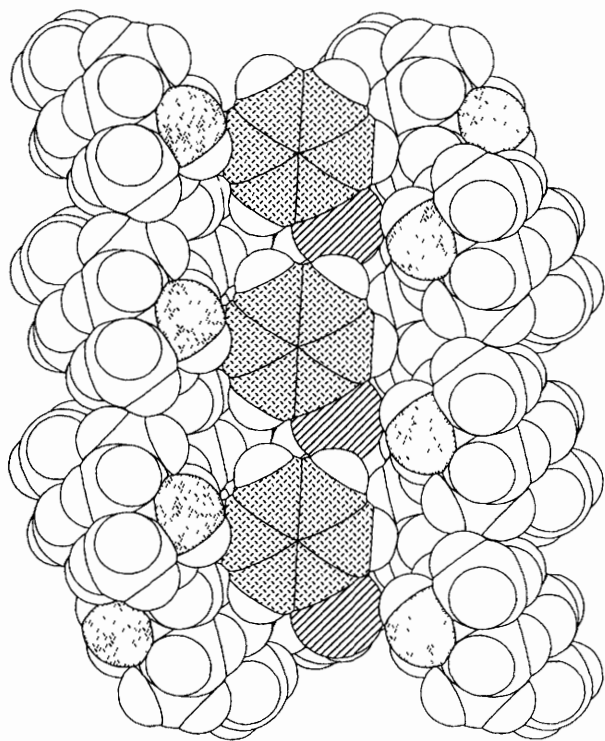


Figure 13 View of one canal of 15_3 ·(chlorobenzene) with one column of canal wall diol molecules removed to show the guest arrangement. In this instance head-tail packing is adopted through utilisation of a 2.4 Å Ar-H···Cl interaction between neighbouring guests.

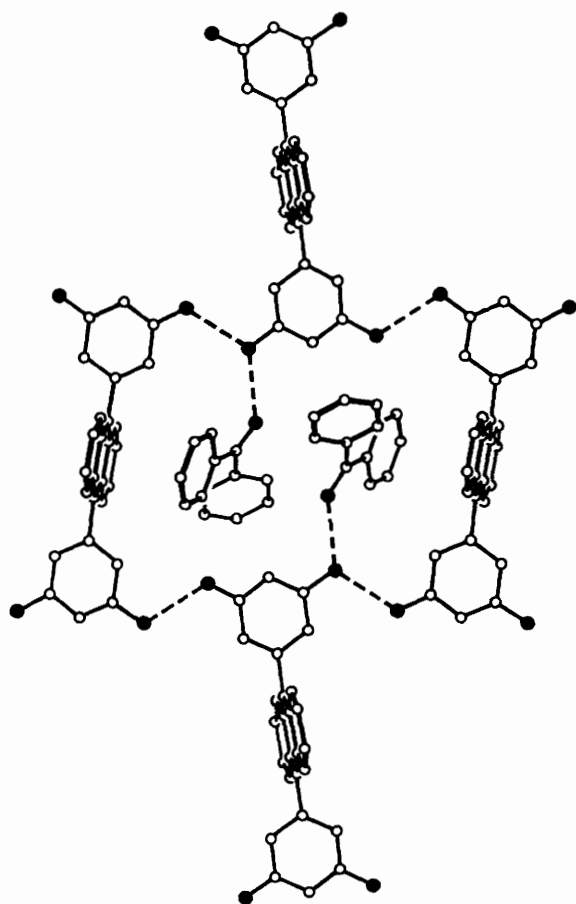


Figure 14 The hydrogen bonding network present in a molecular sheet of **16**·(benzophenone)₂, showing incorporation of two guests in the supramolecular cavity. Repeated eclipsed stacking of this unit affords an example of the guest-filled zeolite-like tubes which run parallel throughout this structure.

6 Selective and Stereoselective Inclusion Properties

A particularly important area of inclusion chemistry is the design of hosts capable of highly selective inclusion properties, and the following three very different cases illustrate this aspect. The roof-shaped host **17** bears *exo*-bromo substituents which reduce efficient aryl-aryl packing and encourage neighbouring molecules to associate in other ways. This results in **17** being a selective host for small polyhalogenated guests that help create a network of halogen···halogen⁵ interactions, as illustrated in Fig. 15 for **17**·(CHCl₃). Non-halogenated molecules of comparable size and shape are excluded.²⁹

Chirally pure materials are assuming ever-growing importance in organic chemistry, and hence there is considerable interest in devising chiral host systems capable of controlling stereoselective separations or reactions. Inclusion hosts are especially valuable for such processes since, subject to mechanical losses, the active agent is fully recoverable. These areas have been pioneered especially by Toda and his colleagues who have developed highly original applications of new chiral hosts.³⁰ An illustration is provided here by (*S,S*)-(-)-**18**, which can be used to resolve racemic 2-methylpiperidine **19** through two distinct procedures.

First, if host and racemic guest are crystallised from toluene then a 1:1 complex of (*S,S*)-(-)-**18** and (*R*)-(-)-**19** is produced. Distillation under reduced pressure then affords a 67% yield of (*R*)-(-)-**19** in 71% ee. In this inclusion structure one hydroxy group of **18** is hydrogen bonded to both the piperidine and a second molecule of **18**.

In contrast, if the materials are crystallised from methanol solution then the quite different 1:1:1 complex of (*S,S*)-(-)-**18**, methanol, and (*S*)-(+)-**19** is obtained. This time distillation produces a 67% yield of (*S*)-(+)-**19** in 62% ee. This crystal structure differs in having the methanol acting as a hydrogen-bonded link between the two molecules of **18**, and creates an environment suited to the alternative enantiomer of **19**. In these, and other similar resolution experiments, repetition of the procedure generates products of extremely high optical purity.

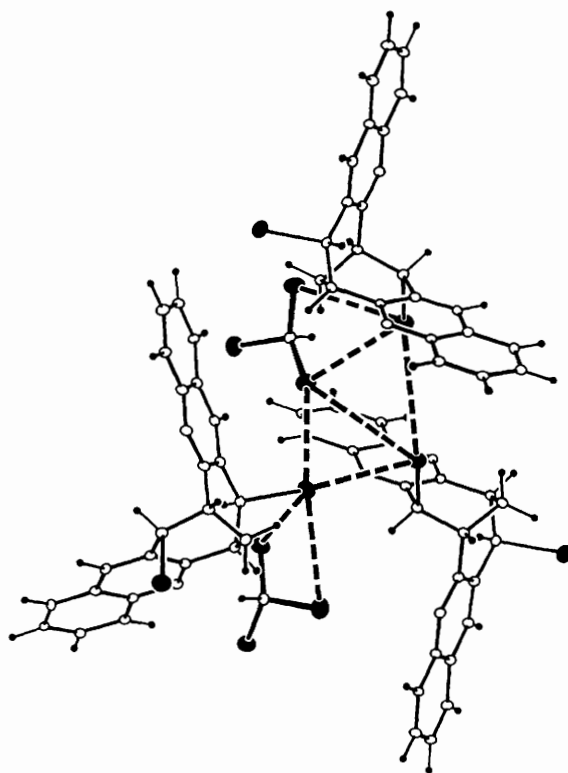
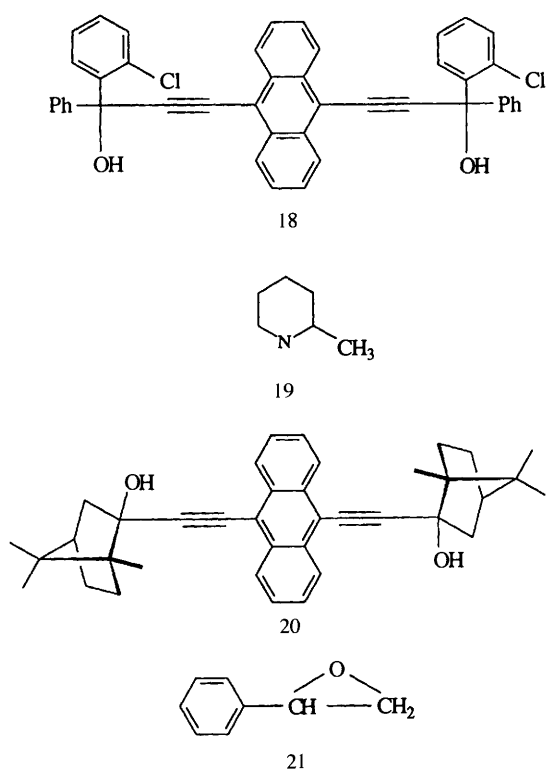


Figure 15 The different intermolecular halogen-halogen attractions (3.46–4.10 Å) present in the structure **17**·(CHCl₃) indicated by heavy dashed lines. These form a network allowing specific trapping of small polyhalogenated guests. Bromo and chloro atoms are shown as large filled spheres, and hydrogens as small filled spheres.



The structure of host **18** represents further development of the wheel and axle and inclined plane design strategies (see Sections 2 and 3), as does its interesting cousin **20** developed by Weber.³¹ In this case, use of bulky camphor groups as the wheels allows facile introduction of chirality from natural sources without any need for resolution. This host includes the aromatic epoxide (*S*)-(+)-**21** as a 1:1 compound, but totally excludes the (–)-enantiomer, on crystallisation from solution. Design features readily discernible in this inclusion structure (Fig. 16) involve both host–host and host–guest hydrogen-bonding, aryl–aryl interactions, and coordination-lattice attractions.

7 Conclusions

The design of new lattice inclusion compounds has now left traditional serendipity far behind. Synthetic approaches using analogy with known examples, or based on design elements such as planes and spacers, are well-established and frequently successful.

With our rapidly advancing understanding of intermolecular attractive forces, opportunities for synthesis are entering an exciting new phase. Lattice inclusion compounds are an excellent choice for developing applications of these supramolecular synthons, since the formation of poorly packed host lattices must depend on important factors, which are capable of our recognition and exploitation. Such knowledge, backed up by strong chemical intuition, eventually will allow design to order of entirely new lattice inclusion systems. Materials capable of specific inclusion behaviour will be especially important targets.

Acknowledgements I thank Dr Marcia Scudder for data retrieval from the Cambridge Structural Database³² and for generation of the figures illustrating this article. Additional artwork was kindly carried out by Martin Dudman. We thank the Australian Research Council for financial support of our own research into inclusion chemistry.

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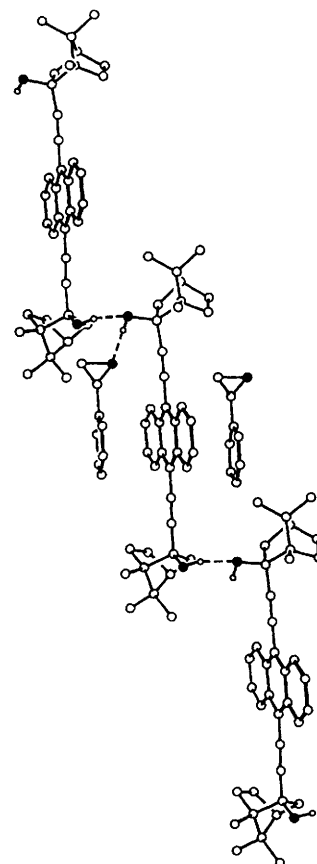


Figure 16 The molecular arrangement in **20**·[(*S*)-(+)-**21**] with hydrogen bonding represented by dashed lines. Oxygen atoms are indicated by solid spheres and only hydroxy hydrogens are drawn. The stabilising aryl–aryl interactions between the guest molecules and the planar naphthyl spacer group are clearly apparent.

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