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Pi–halogen dimer interactions and the inclusion chemistry of a new tetrahalo aryl host

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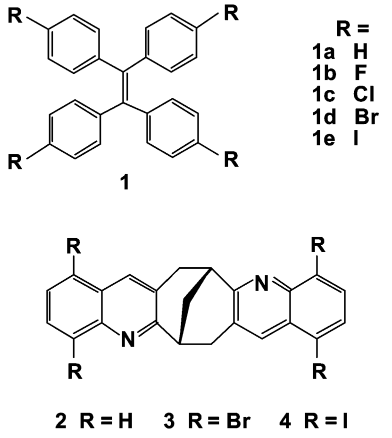
Received 4th September 2003, Accepted 28th October 2003
First published as an Advance Article on the web 21st November 2003

The preparation of 1,4,8,11-tetrabromo-5bα,6,12bα,13-tetrahydropentaleno[1,2-*b*:4,5-*b*′]diquinoline **6** is described. This is a further member of the tetrahalo aryl host family, and forms crystalline lattice inclusion compounds with many guests. The X-ray structures of the allyl cyanide, 1,2,3-trichloropropane, chlorobenzene, toluene, benzene–water, methyl chloroform and carbon tetrachloride inclusion compounds are described, and compared with that of the solvent-free apohost. Although several different structural types are produced, the recently reported pi–halogen dimer (PHD) interaction plays an important role in all of these, except for that of pure **6** (where the packing energy is the least favourable of the series).

Introduction

Recently we have identified a new group of host molecules termed the tetrahalo aryl family.[1] These compounds contain both inclined aromatic planes and four halogen atoms at the extremities of their molecular structures. On crystallisation they show a strong tendency to form lattice inclusion (clathrate) compounds,[2,3] whereas their parent hydrocarbon analogues do not. Thus, the propeller-shaped compounds **1b–e** described by Tanaka and Toda[4–6] and the V-shaped diquinoline derivatives **3**,**4** prepared by ourselves[1,7] show host properties, unlike their corresponding hydrocarbons **1a** and **2** (Scheme 1).



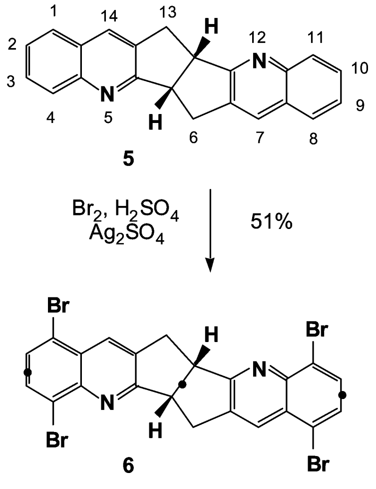
Scheme 1 The structures of the first six tetrahalo aryl hosts, and those of their parent hydrocarbon non-host molecules.

We anticipate that a wide range of tetrahalo aryl host compounds will be obtained in due course, but there is no expectation that their supramolecular behaviour and crystal packing should be similar. In this area (see, for example[8,9]) small changes in molecular structure often cause major changes in supramolecular behaviour. This will be seen also in this paper where the properties of the tetrabromide **6** are compared to those of its earlier homologue **3**.

Results and discussion

Preparation of the tetrabromo diquinoline host 6

The diquinoline derivative **5**[9] was brominated using the protocol of de la Mare *et al.* for dibromination of quinoline.[10,11] Thus, reaction of **5** with bromine in the presence of silver sulfate and concentrated sulfuric acid yielded the new tetrabromide **6** in 51% yield (Scheme 2). Samples of **6** crystallised from a number of solvents were shown to be inclusion compounds by ^{1}H NMR and IR spectroscopy. Therefore, as predicted, compound **6** is a new member of the family of tetrahalo aryl hosts. X-Ray quality inclusion crystals are obtained far more readily for **6** than for its homologue **3**. In this paper, the structures of the allyl cyanide, 1,2,3-trichloropropane, chlorobenzene, toluene, benzene–water, methyl chloroform and carbon tetrachloride inclusion compounds are discussed, as well as that of the solvent-free (apohost) material. Numerical details of the solution of seven of these X-ray structures are presented in Table 1.



Scheme 2 Preparation of the tetrabromo diquinoline host molecule **6**. The black circles added to the molecular structure designate the bond centroids used for measuring the fold-angles (see Table 2) of **6** present in its various crystal structures.

Staircase inclusion structures

Crystallisation of **6** from allyl cyanide yielded the compound $(\mathbf{6})_2\cdot$(allyl cyanide) in the triclinic space group $P\bar{1}$. This material has a staircase inclusion structure related to those found earlier involving the tetrahalo aryl host **3**.[1,7] A further staircase inclusion compound is produced when **6** is recrystallised from 1,2,3-trichloropropane.[12] As with the compounds of **3**, the basic building block is the pi–halogen dimer (PHD) interaction,[13] wherein two molecules of **6** of opposite chirality associate by

DOI: 10.1039/b310638a

Table 1 Numerical details of the solution and refinement of the crystal structures formed by **6**

Properties/Compound	(**6**)$_2$·(allyl cyanide)	(**6**)$_3$·(chlorobenzene)$_2$	(**6**)$_3$·(toluene)$_2$	(**6**)$_3$·(benzene)$_{2.5}$(water)$_{0.5}$	(**6**)·(methyl chloroform)	(**6**)·(carbon tetrachloride)	**6**
Molecular formula	$(C_{22}H_{12}Br_4N_2)_2\cdot(C_4H_5N)$	$(C_{22}H_{12}Br_4N_2)_3\cdot(C_6H_5Cl)_2$	$(C_{22}H_{12}Br_4N_2)_3\cdot(C_7H_8)_2$	$(C_{22}H_{12}Br_4N_2)_3\cdot(C_6H_6)_{2.5}\cdot(H_2O)_{0.5}$	$(C_{22}H_{12}Br_4N_2)\cdot(C_2H_3Cl_3)$	$(C_{22}H_{12}Br_4N_2)\cdot(CCl_4)$	$C_{22}H_{12}Br_4N_2$
M	1315.0	2097.0	2056.2	2076.2	757.4	777.8	624.0
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$Fdd2$
a/Å	11.946(5)	13.179(5)	13.164(3)	13.144(7)	10.455(3)	10.440(5)	27.579(7)
b/Å	14.524(7)	13.971(7)	13.998(4)	13.939(6)	10.733(3)	10.691(5)	32.870(8)
c/Å	15.121(7)	20.762(9)	20.750(6)	20.671(9)	12.049(4)	11.984(5)	4.447(1)
α/°	117.54(3)	78.60(3)	79.08(2)	79.67(3)	81.24(2)	81.73(3)	90
β/°	105.10(3)	79.29(3)	79.91(2)	81.27(2)	83.93(2)	84.05(2)	90
γ/°	91.66(3)	80.08(3)	80.14(2)	80.10(2)	73.22(2)	73.97(2)	90
V/Å^3	2211(2)	3645(3)	3658(2)	3642(3)	1276.7(7)	1269(1)	4031(2)
D_c/g cm^{-3}	1.97	1.91	1.87	1.89	1.97	2.03	2.06
Z	2	2	2	2	2	2	8
μ_{Mo}/mm^{-1}	7.224	6.651	6.554	6.585	6.577	6.721	7.919
$2\theta_{max.}$	46	46	46	44	50	50	50
Crystal decay	None	None	None	None	None	33%	None
Min., max. trans. factor	0.36, 0.47	0.24, 0.47	0.25, 0.46	0.19, 0.53	0.25, 0.39	—	0.56, 0.64
Unique refl.	6126	10131	10149	8889	4487	4457	1011
Observed reflections	4290	5187	5200	4159	3201	2513	811
R_{merge}	0.019	0.036	0.026	0.040	0.017	0.057	—
R	0.041	0.047	0.052	0.049	0.051	0.085	0.039
R_w	0.048	0.054	0.057	0.053	0.084	0.108	0.048
CCDC supp. publ. no. (and reference)	190558[13]	219112	195710[19]	219113	219111	190557[13]	195711[19]

means of one *endo*-facial aromatic offset face–face (OFF)[14,15] and four aromatic pi–halogen[16] interactions. In this motif, two of the electron rich bromine atoms position themselves over the electron deficient π-systems of the host pyridine rings. Thus, there are two Br to staircase-step interactions, and two Br to staircase-surround interactions (as illustrated in Fig. 1). Geometrical parameters for the PHD units present in the various crystal structures of **6** are listed later in Table 2.

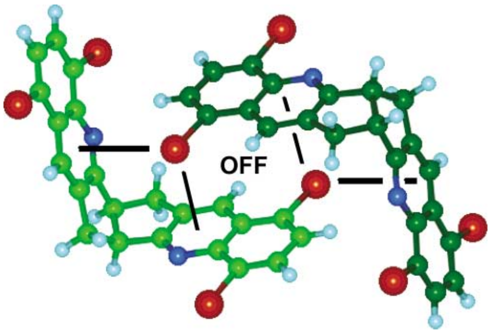


Fig. 1 A pi–halogen dimer (PHD) interaction present in the structure $(\mathbf{6})_2$·(allyl cyanide). The *endo*-faces of opposite enantiomers of the host associate as an aromatic offset face–face (OFF) interaction. This is supplemented by four pi–halogen associations (indicated by the solid lines) to create the compact centrosymmetric building block. Colour code: host C green (opposite enantiomers coloured light or dark), H pale blue, N blue, Br brown.

In the structure $(\mathbf{6})_2$·(allyl cyanide)[17] there are two crystallographically independent host molecules A and B (designated by brown or ochre bromine atoms, respectively, in Figs. 2 and 3). These form centrosymmetric pi–halogen dimers, A–A* and B–B*, where the asterisk indicates the **6** molecule of opposite handedness. These opposite enantiomers are designated by light or dark green carbon atoms in a number of the Figures in this paper.

The compact PHD units stack alternately along *b*, by means of aromatic OFF interactions, to produce parallel staircase

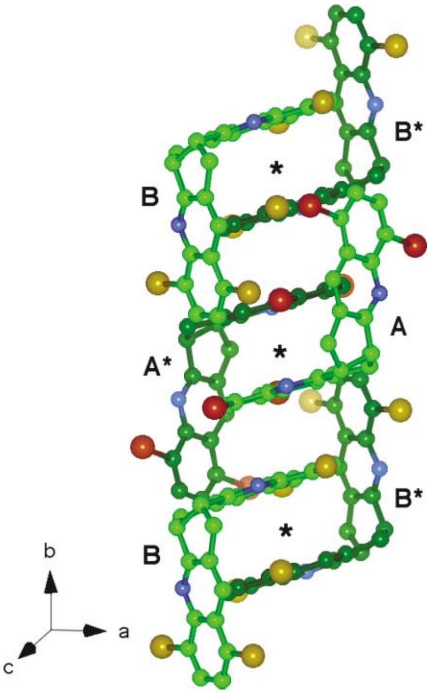


Fig. 2 Part of a staircase assembly of host molecules in $(\mathbf{6})_2$·(allyl cyanide) with the opposite host enantiomers coloured light or dark green. The A–A* (brown Br) and B–B* (ochre Br) PHD units stack alternately along *b*, but have a mutual rotation about *b* of close to 90° giving rise to a rhomboid cross-section for the staircase. The inversion centres of the PHD units are indicated by asterisks, and the host hydrogen atoms are omitted for clarity.

Table 2 Molecular parameters for the tetrabromide molecule **6** in its eight crystal structures

Properties/Guest	C_4H_5N	$C_3H_5Cl_3$	C_6H_5Cl	C_7H_8	C_6H_6–H_2O	$C_2H_3Cl_3$	CCl_4	No guest
Host fold angle(s)/°	106.2, 100.3	105.8, 98.8	109.9, 114.9, 108.9	110.4, 114.8, 108.8	108.9, 113.0, 107.3	98.4	99.6	109.7
Packing coefficient (%)	69.7	N/a.	67.5	67.3	68.0	68.7	68.7	69.9
Type of PHD unit	A–A* B–B*	A–A* B–B*	A*–B[a]	A*–B[a]	A*–B[a]	A–A*	A–A*	None
Br · · · pyridine ring centroid (step) distance/Å	3.45 3.43	3.45 3.41	3.64, 3.62	3.65, 3.61	3.58, 3.56	3.52	3.51	None
Br · · · pyridine ring centroid (surround) distance/Å	3.71 3.74	3.61 3.61	3.66, 3.57	3.69, 3.61	3.76, 3.60	3.70	3.71	None

[a] Plus the enantiomeric (but dimensionally identical) PHD unit A–B*.

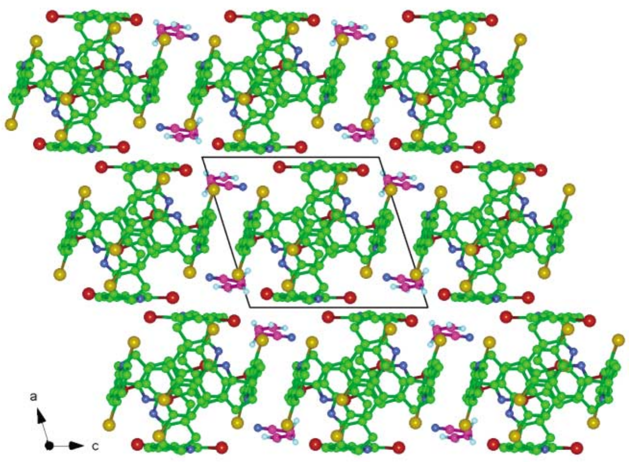


Fig. 3 Projection view in the *ac* plane of nine neighbouring staircases in the structure $(\mathbf{6})_2$·(allyl cyanide) showing the rhomboid staircase cross-section. The B-type PHD units (ochre Br) associate as rows along *c* by means of aromatic OFF interactions. Adjacent rows have their A-type PHD units (brown Br) offset. Colour code: allyl cyanide guest C purple.

assemblies (Fig. 2). Thus, a staircase is constructed by using one of the aromatic wings of each V-shaped host molecule as a staircase-step. The second aromatic wing of the host contributes to the staircase-surround along *b*. The surrounds point upwards on one side of the staircase, and downwards on the other. The A–A* and B–B* dimers stack in the staircases almost orthogonally and there is no symmetry relationship between these dimeric units. Adjacent PHD units are, however, linked by Br ··· Br contacts[18] of 3.72 Å (step–step) and 3.91 Å (step–surround).

The principal difference between the A–A* and B–B* dimers present in $(\mathbf{6})_2$·(allyl cyanide) results from their inter-staircase associations. Projection of the staircases in the *ac* plane reveals that each has a rhomboid cross-section (Fig. 3). B-Type dimers in adjacent staircases associate as rows along *c* by means of aromatic OFF interactions, but the A-type dimers do not pack in this manner and adjacent rows are mutually offset. Inter-row Br ··· Br interactions (3.59 and 3.86 Å) are present between A and B dimers. The hydrocarbon part of each allyl cyanide molecule is positioned near an acute apex of the rhomboid, and these guests are translated along *b* in small channels between the parallel staircases. There are also host–guest Br ··· N interactions of 3.73 and 4.07 Å that assist in stabilising the structure.

Inclusion of aromatic guests

Crystallisation of **6** from chlorobenzene yielded the compound $(\mathbf{6})_3$·(chlorobenzene)$_2$. The alteration in stoichiometry is associated with a major change in lattice structure, even though the triclinic space group $P\bar{1}$ is retained. This new structure involves layers of host molecules, rather than staircase assemblies, and is quite complex. It involves three crystallographically independent host **6** molecules (A–C; distinguished by brown, ochre or yellow coloured Br atoms in Fig. 4 and subsequent Figures) and two independent chlorobenzene guests (purple or dark blue heavy atoms). Furthermore, the latter guest is disordered.

Host molecules stack on top of each other in a face to face manner to generate parallel layers in the *ab* plane. The chlorobenzene guests are accommodated between these host layers, and are orientated orthogonally (edge-on in Fig. 4) to the host molecules.

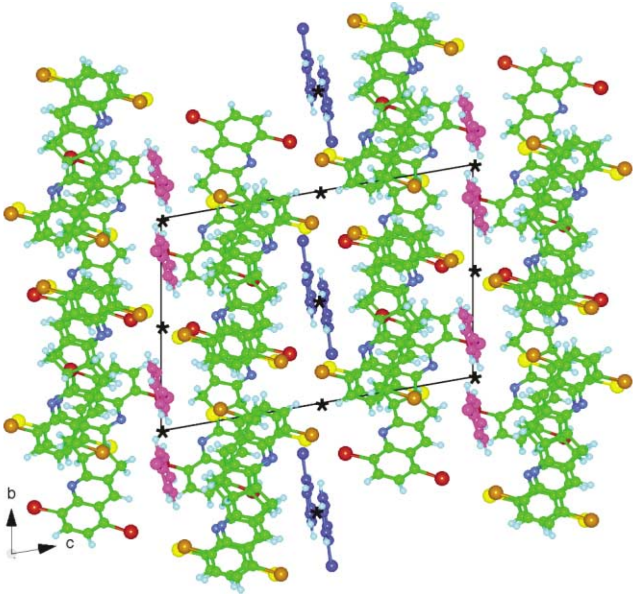


Fig. 4 The structure $(\mathbf{6})_3$·(chlorobenzene)$_2$ projected in the *bc* plane, showing face-on views of the parallel stacked host layers in the *ab* plane and edge-on views of the guest molecules between these. There are different alternating host inter-layer regions (at *z* = 0, 1 and *z* = ½), occupied in turn by the two crystallographically independent guests (purple or dark blue heavy atoms).

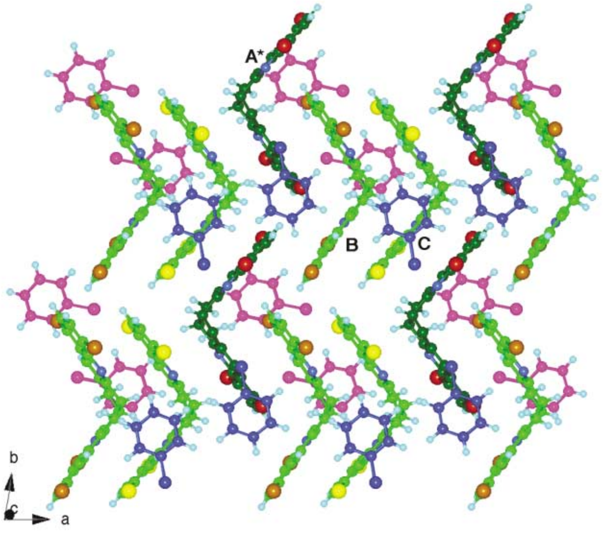


Fig. 5 Projection view in the *ab* plane of the structure $(\mathbf{6})_3$·(chlorobenzene)$_2$. The opposite host enantiomers in the partial layer shown are coloured light or dark green. Host molecules associate into A*–B PHD units that are linked through C host molecules by means of OFF interactions. The crystallographically independent chlorobenzene guests lie below and above the layer. Their heavy atoms are coloured purple (below) or dark blue (above). Opposite enantiomers of the host are coloured light or dark green.

The overlapped nature of the host stacks can be seen when part of a layer is projected in the *ab* plane (Fig. 5). Opposite enantiomers of the independent host molecules A* and B associate to form a pi–halogen dimer motif, while the third type (C) links the *exo*-surfaces of three identical adjacent PHD units by means of two *exo,endo* and two *exo,exo* OFF interactions. This group of three **6** molecules is repeated by translation to generate the layer. There are inversion centres between alternate layers of $(\mathbf{6})_3$·(chlorobenzene)$_2$, and therefore the adjacent layers involve A–B* PHD units linked by C* host molecules.

As usual, the PHD units are constructed from opposite enantiomers of the host. However, $(\mathbf{6})_3$·(chlorobenzene)$_2$ is unusual in employing different independent host molecules, so this version of the pi–halogen dimer is not centrosymmetric (Table 2).

The crystal structure is further stabilised by multiple host–host inter-layer Br ··· Br interactions of 3.70, 3.87, 3.97 Å (ordered guest space at *z* = 0, 1), 3.56, 3.64, 3.71 Å (disordered guest space at $z = ½$), and poorer intra-layer values of 4.17, 4.19 Å. In addition, there are host–guest Br ··· Cl interactions[18] of 3.50, 3.78, 3.81 and 3.86 Å.

Crystallisation of **6** from toluene[19,20] yielded a compound $(\mathbf{6})_3$·(toluene)$_2$ in space group $P\bar{1}$ that was isostructural with the chlorobenzene case. In this structure, both of the independent guest molecules were ordered. The volumes of a methyl group and a chlorine atom are close (23.5 and 19.9 Å^3),[21] and it is frequently found that chloro- and methyl-aromatic analogues pack in a similar manner.[18]

Bromine–bromine interactions are also important in this structure. Here, the inter-layer interactions are 3.49, 3.53, 3.66, 3.73, 3.77, 3.79, 3.81 and 3.98 Å, but only poor Br ··· Br intra-layer contacts of 4.16 and 4.19 Å are present.

Crystallisation of **6** from benzene gave the inclusion compound $(\mathbf{6})_3$·(benzene)$_{2.5}$(water)$_{0.5}$ in space group $P\bar{1}$. The host lattice of this compound is isostructural with the chlorobenzene and toluene compounds, but the guest arrangement differs in two respects. This structure now contains water as a second guest, and a third independent aromatic molecule is present. All three types of benzene guest are ordered.

Projection of the structure of $(\mathbf{6})_3$·(benzene)$_{2.5}$(water)$_{0.5}$ in the *bc* plane (Fig. 6) reveals its close relationship with that of the chlorobenzene compound (Fig. 4). As before, the host molecules (A–C) are arranged in parallel layers with independent benzene molecules (purple and dark blue) between these. The additional benzene guests (red) are positioned on a centre of symmetry and lie at an angle in the dark blue benzene inter-layer region. The water molecules (represented by black spheres) are disordered around a centre of symmetry in the purple benzene inter-layer region. Projection of the structure onto the *ab* plane (Fig. 7) further emphasises the close relationship of the $(\mathbf{6})_3$·(benzene)$_{2.5}$(water)$_{0.5}$ and $(\mathbf{6})_3$·(chlorobenzene)$_2$ compounds (Fig. 5).

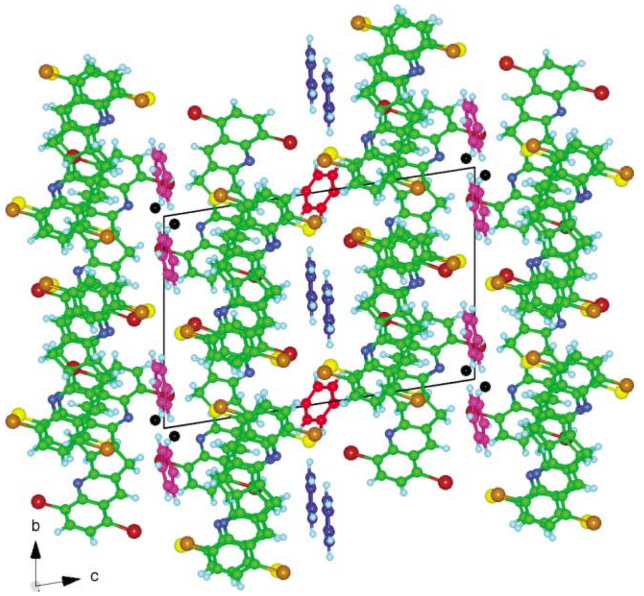


Fig. 6 The structure of $(\mathbf{6})_3$·(benzene)$_{2.5}$(water)$_{0.5}$ projected onto the *bc* plane should be compared with that of $(\mathbf{6})_3$·(chlorobenzene)$_2$ in Fig. 4. The three independent host molecules **6** are indicated by brown, ochre or yellow bromine atoms; the three independent benzene guests by purple, dark blue or red carbon atoms; and the water molecules by black spheres.

There are Br ··· Br interactions of 4.11 Å (intra-layer), 3.48, 3.60, 3.65, 3.94 Å (between molecules across one inter-layer region), and 3.60, 3.66, 3.73, 3.74 Å (between molecules across the second inter-layer region). In addition, all three benzene molecules exhibit a guest pi ··· Br interaction of about 3.7 Å to the edge of the guest. The water molecules are hydrogen bonded to the host nitrogen atoms (*O*–H ··· *N* 2.99 Å), to the purple benzene molecules (*O* ··· *H*–C 2.55 Å), and to neighbouring host molecules (*O* ··· *H*–C 2.79 and 2.81 Å).

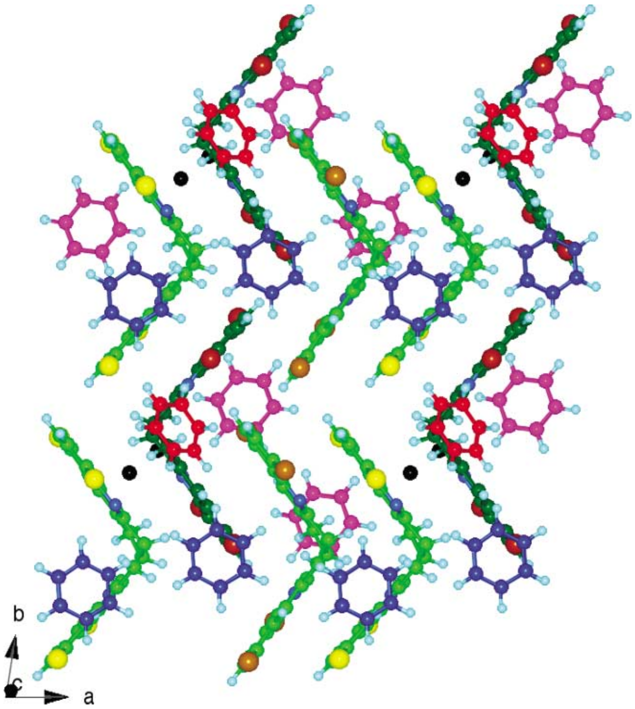


Fig. 7 This projection of the $(\mathbf{6})_3$·(benzene)$_{2.5}$(water)$_{0.5}$ structure in the *ab* plane is similar to the comparable view of $(\mathbf{6})_3$·(chlorobenzene)$_2$ in Fig. 5. Opposite enantiomers of the host are coloured light or dark green. One type of benzene (purple C atoms) and the water are below the layer, while the other two types of benzene (blue or red C atoms) are above the layer.

It is not clear why the packing arrangement in $(\mathbf{6})_3$·(benzene)$_{2.5}$(water)$_{0.5}$ is preferred over the original 3 : 2 host–guest stoichiometry (or, conversely, why the earlier compounds did not adopt the 3 : 2.5 : 0.5 stoichiometry). This outcome is probably related to the slightly smaller size of benzene and its greater affinity for water.

Inclusion of haloalkane guests

Crystallisation of **6** from 1,1,1-trichloroethane yielded an inclusion compound with the different stoichiometry (**6**)·(methyl chloroform) in space group $P\bar{1}$. This structure contains zigzag layers of hosts that trap guests within channels of rectangular cross-section along *c* as illustrated in Fig. 8. The guest molecules in this compound are disordered over three positions (occupancies 0.49, 0.31 and 0.20), and associate within the parallel channels by means of Cl ··· Cl interactions. There are also Br ··· Cl (3.5 Å upwards) and π ··· Cl (3.3 Å upwards) interactions between hosts and guests.

The arrangement of host molecules within a layer of (**6**)·(methyl chloroform) is illustrated in Fig. 9. Molecules of **6** with the same chirality are linked into chains by means of aromatic edge–face EF interactions.[22] These chains then pack parallel to each other, with adjacent chains being of opposite handedness.

Inter-chain association occurs through two types of supramolecular synthon. Adjacent pairs of chains are alternately linked by centrosymmetric pi–halogen dimer interactions, and centrosymmetric aryl edge–edge C–H ··· N dimers (C–*H* ··· *N* 2.73 Å, *C*–H ··· *N* 3.48 Å). The latter motif is notable for utilising one of the two benzylic bicyclo[3.3.0]octane C–H bridgehead hydrogen atoms, rather than an aryl hydrogen as is usually the case.[9,23,24]

Crystallisation of **6** from CCl_4 yielded the isostructural compound (**6**)·(carbon tetrachloride). The guest molecules in this compound again are disordered over three positions (occupancies 0.42, 0.38 and 0.20). The guests within the parallel

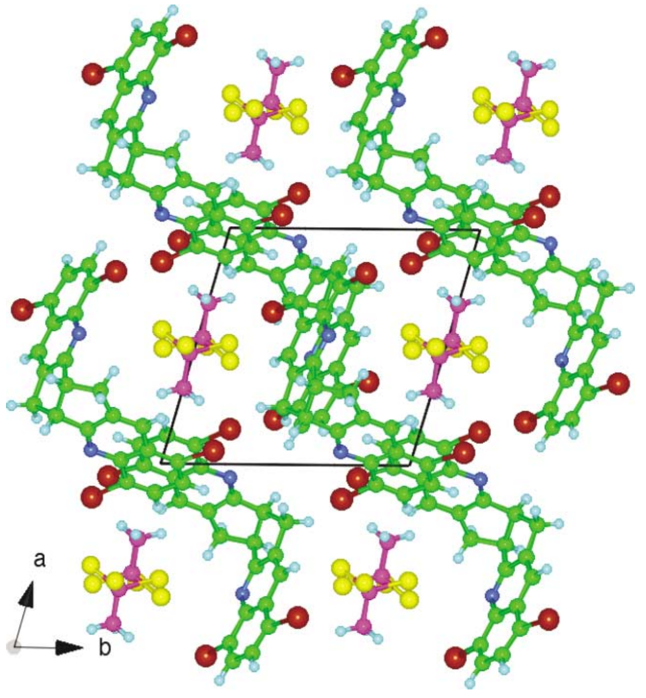


Fig. 8 The structure of (**6**)·(methyl chloroform) projected in the *ab* plane, showing the zigzag layers of host molecules and the guests enclosed in rectangular-shaped channels running along *c*. Only one disorder component of the guest is shown. Colour code: guest C purple, and Cl yellow.

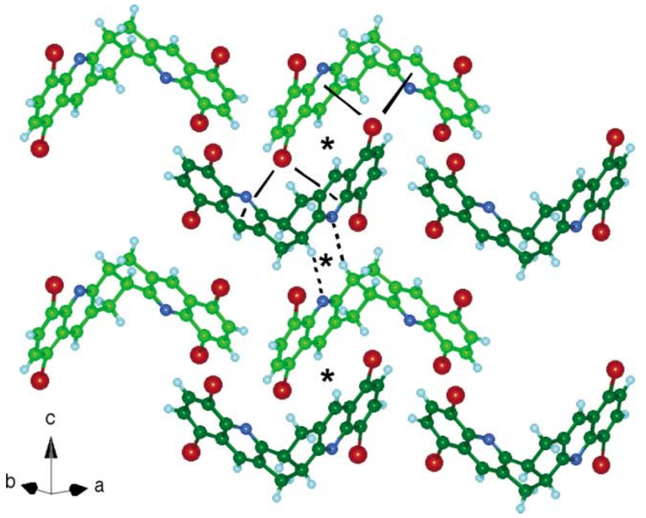


Fig. 9 The arrangement of molecules within a host layer in the (**6**)·(methyl chloroform) structure. Opposite enantiomers of **6** are colour coded light or dark green. Asterisks indicate the inversion centres present within the PHD motif and the edge–edge C–H ··· N dimer interactions.

channels along the *c* axis associate through Cl ··· Cl interactions of 3.66 Å.[17] There are also Br ··· Cl (3.4 Å upwards) and π ··· Cl (3.3 Å upwards) interactions between hosts and guests. The inter-host aryl edge–edge C–H ··· N dimer in (**6**)·(carbon tetrachloride) has values of C–*H* ··· *N* 2.77 Å and *C*–H ··· *N* 3.55 Å.

Crystal structure of the apohost 6

Crystallisation of **6** from α,α,α-trifluorotoluene, or from ethyl acetate, afforded the solvent-free apohost in the orthorhombic space group *Fdd*2.[19,20] This crystal structure is very different from those of its inclusion compounds, and is the only one of the series not to involve the PHD interaction. The structure is simpler, with molecules of **6** arranged as homochiral stacks running along the *c* axis. There is a herringbone packing relationship between these stacks, as seen clearly in Fig. 10.

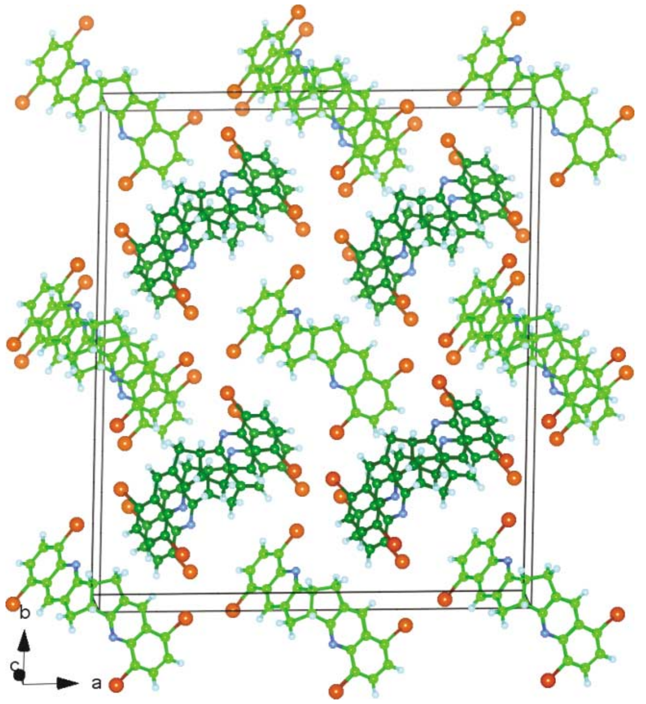


Fig. 10 The crystal structure of the apohost **6** projected close to the *ab* plane. Opposite enantiomers are designated by light or dark green carbon atoms. The molecular stacks along *c* pack in a herringbone manner. Each row of stacks in the *bc* plane is homochiral, but the handedness of these rows alternates along *a*.

The packing of **6** molecules results in a unit cell with a short *c* axis of only 4.45 Å. This is not related to the short axis structures studied by Schmidt and which led to his introduction of the term crystal engineering.[25,26] The cinnamic acid compounds used in his work interacted by means of steering Cl ··· Cl interactions of around 4.0 Å. In the present case, neighbouring molecules in each stack are translated by the *c* cell value. Therefore, the bromine atoms are separated by 4.45 Å and too far apart to play a significant supramolecular role in the structure. Instead, stacking of **6** involves aromatic OFF interactions of around 3.6 Å. There are, however, groups of effective interstack Br ··· Br interactions (3.67, 3.71 and 3.85 Å) in this structure.

Comparison of the crystal structures

Our previous tetrahalo aryl host **3** invariably forms staircase inclusion compounds.[1,7] Despite many attempts we have been unable to obtain other types of inclusion compound, or crystals of the apohost. The new compound **6** differs in both these respects. Although **6** can form staircase structures, other types of inclusion structure are accessible when the guest molecules are changed. Hence, the supramolecular properties of **3** and **6** are quite distinct, despite their molecular structures differing by only one methylene unit.

Molecule **6** has a slightly twisted V-shaped structure with the potential for conformational adaptation to different circumstances of host packing or guest inclusion. One means of comparison is the fold-angle (values listed in Table 2) present in the various compounds. The fold-angle is defined by the three bond centroids marked on the molecular structure of **6** in Scheme 2. The values here are unremarkable. They lie between 98.4 and 114.9°, despite much greater or smaller values being possible for the flexible diquinoline framework.

Packing coefficients (Table 2) are also consistent (67.3–69.9%) across the series of seven refined compounds. The allyl

Table 3 Energy (kcal mol^{-1}) and molecular packing calculations for the tetrabromide **6** and its inclusion compounds

Properties/Guest	C_4H_5N	C_6H_5Cl	C_7H_8	C_6H_6–H_2O	$C_2H_3Cl_3$	CCl_4	None
Van der Waals energy	−203	−328	−326	−309	−109	−83	−373
Coulombic energy (QEq)	−129	−91	−147	−152	−80	−132	+40
Total energy[a]	−332	−419	−473	−461	−189	−214	−333
Unit cell volume/Å^3	2212	3645	3658	3642	1277	1269	4031
Relative packing energy[b]	−150	−115	−129	−127	−148	−169	−83

[a] Calculated crystal packing energy (kcal mol^{-1} of unit cells). [b] Total energy ÷ unit cell volume/1000. (Packing energy per 1000 Å^3 of the crystals).

cyanide compound value is relatively high (69.7%), but it is the apohost structure that has the highest value (69.9%).

Calculated density values (Table 1) for five of the inclusion crystals range between 1.87 and 1.97 g cm^{-3}, but the carbon tetrachloride compound is higher (2.03 g cm^{-3}). Comparison of these values is problematical due to the differences in host–guest stoichiometry and also in the types of elements present. It is noteworthy, however, that the highest density is that of the apohost **6** (2.06 g cm^{-3}).[27]

It is significant that all the inclusion compounds investigated here utilised the pi–halogen dimer (PHD) interaction as part of their solid state structure, but that this was not the case for the apohost. The bromine to pyridine ring centroid distances for the various PHD interactions are listed in Table 2.

Each PHD unit is formed between opposite enantiomers of the host **6** so, in its simplest centrosymmetric case (methyl chloroform or carbon tetrachloride), there is just one Br-step and one Br-surround value. The allyl cyanide compound contains two crystallographically independent **6** molecules and forms two centrosymmetric PHD units (A–A* and B–B*) with slightly different geometries. In contrast, the three compounds that include aromatic guests form non-centrosymmetric PHD units A–B* (plus the dimensionally identical enantiomorph A*–B). The latter examples have slightly longer Br-step distances (3.56–3.64 Å) than for the centrosymmetric cases (3.43–3.52 Å).

Crystal lattice energy calculations were performed on the seven refined crystal structures using the Cerius^2 ® package[28] which gave the lattice packing energy per mole of unit cells (Table 3). Since the bigger the volume considered, the larger the energy value obtained, correction to a common standard volume is necessary for a meaningful comparison. Here, the total energy was divided by the unit cell volume/1000, which is equivalent to normalising all five structures at a common volume of 1000 Å^3.

Pure **6** has the highest energy (−83 kcal mol^{-1}); the chlorobenzene, benzene–water, and toluene compounds have significantly lower, but comparable, energies (−115, −127, −129 kcal mol^{-1}); the methyl chloroform and allyl cyanide compound values are also comparable (−148 and −150 kcal mol^{-1}); while the carbon tetrachloride compound has the lowest energy (−169 kcal mol^{-1}) of the series.

These data indicate that although the apohost has the best packing coefficient and highest density, it also has the least favourable packing energy. There are energetic difficulties with its apparently simple crystal structure that can be reduced by the formation of lattice inclusion compounds. In all of the inclusion structures reported here, this guest inclusion took place concomitant with the host adopting the pi–halogen dimer (PHD) interaction as part of its packing strategy.

Experimental

NMR data were recorded using a Bruker ACF300 instrument at 25 °C and carbon substitution information was determined using the DEPT procedure. MS data (EI) were recorded by Dr J. J. Brophy using a VG Quattro triple quadrupole instrument. The microanalytical results were determined at the Australian National University, Canberra.

1,4,8,11-Tetrabromo-5bα,6,12bα,13-tetrahydropentaleno-[1,2-*b*:4,5-*b*′]diquinoline (6)

Diquinoline **5**[9] (0.81 g, 0.58 mmol), Ag_2SO_4 (0.49 g, 1.57 mmol), and sulfuric acid (98%; 2.0 mL) were placed in a round-bottom flask fitted with a reflux condenser and drying tube, and then the suspension was warmed to give a solution. After cooling to room temperature, the flask was wrapped in foil to exclude light and the mixture was stirred magnetically. Bromine (1.0 mL) was added dropwise, and the mixture stirred at room temperature for 3 h. The reaction mixture was poured into aqueous NaOH (2.0 M; 50 mL). Solid sodium sulfite was added until all excess bromine had been reduced. The resulting suspension was extracted several times using dichloromethane and the combined organic extracts dried (Na_2SO_4). Solvent was evaporated from the filtrate to give a white solid which was crystallised from dichloromethane–methanol to yield the tetrabromide **6** (0.18 g, 51%), mp 270–271 °C; IR (paraffin mull) 1580w, 1290m, 1255w, 1180m, 1090s, 1030w, 955m, 905s, and 805s cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.78 and 3.82 (two m, 2H, *A*BX), 3.98 and 4.04 (d, 2H, J_{AB} = 17.3 Hz, A*B*X), 4.40–4.43 (m, 2H, AB*X*), 7.54 (d, 2H, *J* = 8.3 Hz), 7.79 (d, 2H, *J* = 8.3 Hz), 8.28 (s, 2H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 35.3 (CH_2), 47.8 (CH), 121.3 (C), 124.3 (C), 128.2 (C), 129.8 (CH), 131.4 (CH), 132.1 (CH), 136.8 (C), 145.9 (C), and 169.7 (C); *m*/*z* (EI$^+$; M$^+$ and > 15%): 628 (M$^+$, four ^{81}Br, 3%), 626 (M$^+$, three ^{81}Br/one ^{79}Br, 15), 624 (M$^+$, two ^{81}Br/two ^{79}Br, 22), 622 (M$^+$, one ^{81}Br/three ^{79}Br, 14), 620 (M$^+$, four ^{79}Br, 3), 220 (16), 218 (18), 165 (44), 164 (100), 140 (27), 139 (65), 138 (58), 137 (22), 114 (20), 113 (64), 112 (27), 100 (16), 99 (21), 88 (30), 87 (50), 86 (37), 75 (29), 74 (30), 63 (53), 62 (29), 51 (23), 50 (24); Anal. Calcd. for $C_{22}H_{12}Br_4N_2$ (FW = 623.9): C, 42.35; H, 1.94; N, 4.49. Found: C, 42.26; H, 1.92; N, 4.51%. Crystals of the inclusion compounds were grown by slow evaporation of solutions of **6** in the specific solvent under test.

Structure determinations

For all structures, reflection data were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromated molybdenum radiation (λ = 0.7107 Å). Data for all structures (except the CCl_4 compound, for which an irregular fragment sealed in a tube to lessen decomposition was used) were corrected for absorption.[29] Reflections with $I > 2\sigma(I)$ were considered observed. The structures were determined by direct phasing (SIR92)[30] and Fourier methods. Hydrogen atoms for each structure were included in calculated positions. Atoms of each host molecule were refined with independent positional parameters; individual anisotropic temperature parameters were assigned to the bromine atoms, and a 15-parameter TLX rigid-body thermal parameter (where T is the translation tensor, L is the libration tensor and X is the origin of libration) described the thermal motion of the remaining atoms.[31] In the allyl cyanide compound, the guest molecule was refined as individual atoms, while for all other host–guest compounds, the guests were modelled as rigid groups with the thermal motion of each defined by TLX parameters. Guest disorder occurred in the chlorobenzene compound (for one of the two independent molecules, with occupancies 0.53 and 0.47), and for the CH_3CCl_3 and CCl_4 compounds where the solvent was disordered over three approximately coincident sites with occupancies (0.49, 0.31 and 0.20) and (0.42, 0.38 and 0.20) respectively. Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{½}$. The weighted residual was defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{½}$. Atomic scattering factors and anomalous dispersion parameters were from *International Tables for X-ray Crystallography*.[32] The CCDC supplementary publication numbers for the structures are listed in Table 1.†

Energy calculations

Intermolecular potential for atoms i, j with charges q_i, q_j separated by d_{ij} is given by eqn. (1), and comprises the van der Waals and coulombic energies. The atom parameters e^a (kcal mol^{-1}), r^a (Å), are: C, 0.095, 1.95; N, 0.077, 1.83; H, 0.015, 1.60; Br, 0.370, 1.98; Cl, 0.283, 1.98. The combination rules are given in eqns. (2) and (3). The permittivity ε in eqn. (1) = 1.

$$E_{ij} = e^a{}_{ij}\,[(d_{ij}/d^a{}_{ij})^{-12} - 2(d_{ij}/d^a{}_{ij})^{-6}] + (q_i \cdot q_j)/(\varepsilon \cdot d_{ij}) \quad (1)$$

$$d^a{}_{ij} = r^a{}_i + r^a{}_j \quad (2)$$

$$e^a{}_{ij} = (e^a{}_i \cdot e^a{}_j)^{0.5} \quad (3)$$

Atom partial charges q were calculated using the QEq procedure of Rappe and Goddard,[33] as implemented in the MSI Cerius^2 ® software.[28] This method of equalisation of chemical potential is responsive to geometry. The lattice energy computed was normalised to allow for variation in cell volume: the values quoted are energy per 1000 Å^3. Since the crystal densities are similar, this compensates for the fact that the energy calculations for the different structures incorporated different numbers of atoms.

Acknowledgements

We thank the Australian Research Council for financial support of this work.

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