Simultaneous electrophile–nucleophile Cl · · · π interactions stabilizing solid state inclusions: a new tool for supramolecular crystal engineering

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The crystalline inclusions of the host compound *trans*-11,12-bis[bis(*p*-chlorophenyl)hydroxymethyl]-9,10-ethanoanthracene, with guests such as pentan-2-ol [1·pentan-2-ol (1 : 1), 1a], 1,4-dioxane [1·1,4-dioxane (2 : 5), 1b] and *o*-xylene [1·*o*-xylene (1 : 2), 1c] were shown by X-ray analysis to have host matrices mainly determined by directional 'electrophile–nucleophile pairing' interactions, involving a chloro substituent and the adjacent aryl π electrons of a neighbouring molecule. The observed shorter Cl · · · centroid distances in 1a–c are between 3.33 and 3.75 Å. On the other hand, the versatility of host–guest interactions due to the different proton donor–acceptor abilities and polarities of the guests yielded various packing relations with different symmetries and conformations of the host hydroxy functions. Although compounds 1a and 1b contain H-bonded 1·pentanol and 1·dioxane aggregates, respectively, the realized packing arrangements seem to be a compromise between close packing on the one hand and hydrogen bonding on the other. Compound 1c is a lattice-type inclusion in which the *o*-xylene guests are trapped in tunnels formed by the bulky host molecules.

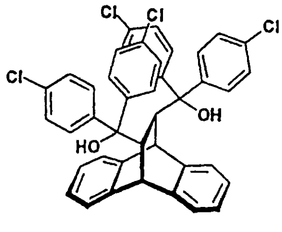
Crystal engineering[1] and solid state organic chemistry[2] including clathrate research[3] have emerged as challenging frontiers of potentially useful chemistry.[4] Understanding weak intermolecular interactions and widening the view on intermolecular aggregation patterns are critical points here. Use of hydrogen bonding[5] has been recognized as a useful tool, but there are also other potentially profitable specific intermolecular contacts. Halogen atoms covalently bonded to carbon are known to form short contacts to hydrogen, nitrogen, oxygen, sulfur and also to other halogens. All these contacts may control crystal packing to varying degrees.[1]

In the course of our studies of roof-shaped clathrands, a novel tetrachloro-substituted diol host **1** was prepared, and its clathrate forming ability was tested.[6] Host **1** has proven efficiency in crystalline inclusion formation involving organic guests of different compound classes.[6] A possibility of controlling the crystalline architecture lies in manipulating the type and orientation of the non-covalent interactions between the subunits (*i.e.* host and guest) by varying *e.g.* the proton donor–acceptor ability and polarity of the guest. Accordingly, we studied the crystalline inclusions of **1** with guests such as the protic compound pentan-2-ol [**1**·pentan-2-ol (1:1), **1a**], the aprotic polar 1,4-dioxane [**1**·1,4-dioxane (2:5), **1b**] and the apolar *o*-xylene [**1**·*o*-xylene (1:2), **1c**] in order to discover the mode of recognition and complexation of the different guests by **1** and to understand the crystal packing forces controlling the solid state inclusions.

Results and discussion

Crystallographic description of the structures 1a, 1b and 1c

Crystal data of compounds **1a–c** are given in Table 1. Figs. 1(*a*)–(*c*) are perspective views of the host–guest units. Stereopacking illustrations are shown in Figs. 2–4, and Figs. 5(*a*)–(*c*) present characteristic patterns of the arrangement of host matrices in compounds **1a–c**. Geometric parameters of selected intermolecular interactions are listed in Tables 2 and 3.



1

1a 1·pentan-2-ol (1:1)
1b 1·1,4 dioxane (2:5)
1c 1·*o*-xylene (1:2)

Molecular structures

The semi-rigid molecular skeleton of **1** has similar geometry in the inclusion compounds **1a–c**, and also resembles the one shown by the chlorine-free analogue host **2** in its cocrystals with nitroethane and benzene as guests.[6] Comparison of the selected torsion angles and also of the dihedral angles formed by the least-squares (LS) planes through the six phenyl rings of **1**, observed in compounds **1a–c**, suggests only limited flexibility for the host molecule. Accordingly, the tricyclic dihydroanthracene moiety has the usual 'roof' shape with a dihedral angle of about 60° between the two phenyl ring planes (the average angle for **1a–c**, with the root mean square deviation in square brackets, is 61[3]°), and the aryl ring planes within each diarylmethanol group are nearly perpendicular to each other (the dihedral angles in **1a–c** vary between 89 and 101° with the mean value 95[4]°). The three C–C bonds within the ethano bridge as well as those linking the diarylmethanol groups to the ethano bridge are elongated due to the strain caused by the bulky substituents (the lengths of these bonds in **1a–c** are between 1.568 and

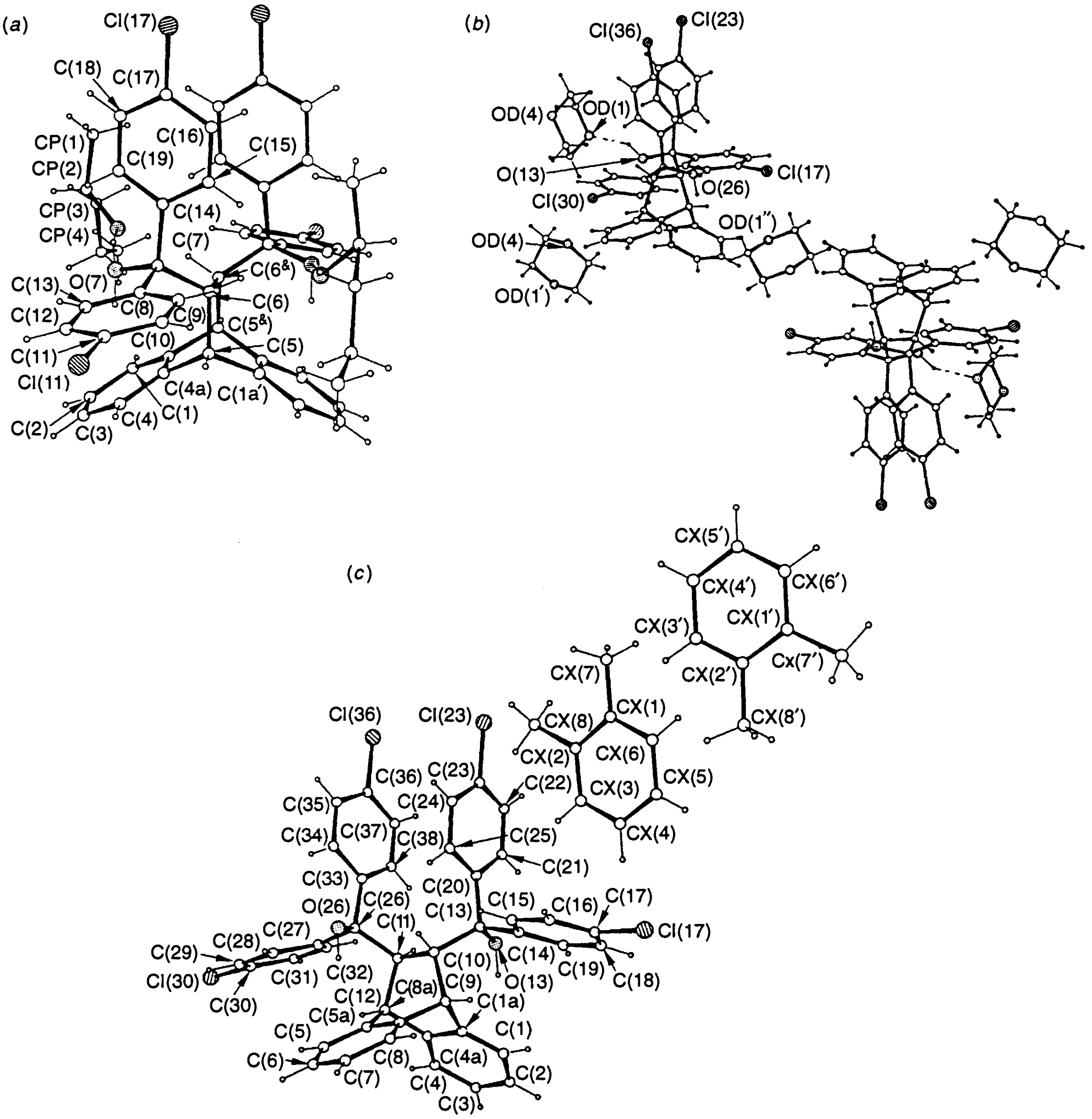


Fig. 1 Perspective views of the stoichiometric units of the inclusion compounds **1a** [**1**·pentan-2-ol (1 : 1)] (*a*), **1b** [**1**·1,4-dioxane (2 : 5)] (*b*) and **1c** [**1**·*o*-xylene (1 : 2)] (*c*). The crystallographic atomic labelling is shown in (*a*) and (*c*), whereas in (*b*) only selected atoms of the host are labelled for clarity. Host **1**, however, has the same labelling in **1b** as in **1c**. Solid and dashed lines mean covalent and hydrogen bonds, respectively. Heteroatoms are shaded. The pentan-2-ol guest in **1a** (*a*) occupies two disorder sites, each with 50% occupancy.

1.581 Å with a mean value of 1.575[4] Å). The remaining bond distances and bond angles generally conform to expected values, and are also in accordance with those observed for the related chlorine-free analogue **2**. The mean C–Cl covalent bond length in **1** is 1.748[5] Å, and the average deviation of the Cl atoms from the corresponding phenyl ring planes is as low as 0.05[4] Å.

Nevertheless, the orientation of the hydroxy functions of **1** seems to be a soft parameter, which may be seriously affected by the host–guest interactions and/or by the crystal packing forces. In the absence of stronger intermolecular interactions involving the alcoholic H atom, the OH group is directed into the face of the nearest aromatic ring of the dihydroanthracene moiety of the same molecule. Such an 'inactive' conformation was exhibited by host **2** in its inclusion compounds with nitroethane and benzene guests,[6] and was also observed for **1** in compounds **1a–c** [*cf.* Figs. 1(*a*)–(*c*)]. This 'inactive' orientation of the host hydroxy functions is probably supported by a weak electrostatic attraction between the OH group and the π electron cloud of the involved aryl ring, although the O · · · centroid and H · · · centroid distances, observed for **1** in **1a** and **1b** (Table 2) and also for **2** in **2**·nitroethane (1 : 1) and **2**·benzene (2 : 1),[6] are slightly longer than those previously reported for such a bond.[7–11] A similar 'inactive' host conformation can also be seen in **1c**, but the O · · · centroid/H · · · centroid distances [3.528(5)/2.66 and 3.521(6)/2.57 Å for O(13)H and O(26)H, respectively] are in this latter case significantly longer than those cited above.[7–11] Yet, because the (O)H · · · π contact is assumed to have electrostatic character and electrostatic forces fall off much more slowly with distance than for example van der Waals' forces,[12] the possibility that the O(H) · · · centroid approach should contribute to the stabilization of the molecular conformation of **1** also in **1c** cannot be completely ruled out. Moreover, the observed intramolecular centroid · · · centroid distances (Table 3) between two of the aryl substituents indicate possible π · · · π stacking interactions between them, which may contribute to further stabilization of the molecular conformation of host **1** in these structures (*cf.* below). Nevertheless, the O(13)-H group in **1b** has a different orientation due to the hydrogen bond connection to one of the dioxane guests [Table 2, Fig. 1(*b*)].

Table 1 Crystal data, experimental parameters and selected refinement details of compounds **1a**, **1b** and **1c**[a]

	1a	**1b**	**1c**
Formula			
Host	$C_{42}H_{30}O_2Cl_4$	$C_{42}H_{30}O_2Cl_4$	$C_{42}H_{30}O_2Cl_4$
Guest	$C_5H_{12}O$	$C_4H_8O_2$	C_8H_{10}
Host : guest stoichiometry	1 : 1	2 : 5	1 : 2
Formula mass	796.66	1857.55	920.84
T/K	193 ± 1	173 ± 1	173 ± 1
Radiation used	Mo-Kα	Mo-Kα	Mo-Kα
Crystal system	Orthorhombic	Monoclinic	Orthorhombic
Space group	$Fddd$ (No. 70)	$P2_1/n$ (No. 14)	$Pc2_1n$ (No. 33)[b]
Unit cell dimensions			
a/Å	16.112(2)	9.796(1)	9.978(5)
b/Å	24.667(2)	13.466(1)	18.026(2)
c/Å	40.254(2)	34.851(2)	26.060(4)
α/°	90.0	90.0	90.0
β/°	90.0	97.10(1)	90.0
γ/°	90.0	90.0	90.0
V_c/Å^3	15 998(3)	4562.5(6)	4687(3)
Z	16	2	4
F(000)	6656	1944	1928
D_c/g cm^{-3}	1.323	1.352	1.305
μ/mm^{-1}	0.336	0.311	0.296
Crystal size/mm	0.30 × 0.20 × 0.17	0.45 × 0.27 × 0.11	0.53 × 0.56 × 0.11
Refinement of the unit cell dimensions			
No. of reflections used	40	52	40
Range of θ/°	5.3–11.7	5.0–12.6	5.2–11.4
Data collection			
No. of collected reflections	3822	7993	8552
Range of θ/°	1.5–25.0	1.9–25.0	1.9–27.5
No. of standard reflections	4	5	5
Time interval between the standards/min	90	90	90
Intensity instability/%	< 2.6	< 3.1	< 10.2
Data processing and structure refinement			
No. of unique reflections	3537	7993	5508
R_{int}	0.0	0.0	0.096
No. of variables refined	257	617	645
$wR(F^2)$[c]	0.149	0.126	0.097
No. of F^2 values used[d]	3522	7976	5496
S (goodness of fit on F^2)	0.970	0.961	0.918
$R(F)$	0.053	0.046	0.041
No. of F values [$I > 2\sigma(I)$] used	1523	3877	1462
Final $\Delta\rho_{max}/\Delta\rho_{min}$/e Å^{-3}	0.62/−0.52	0.41/−0.36	0.38/−0.37

[a] Esds, where given, are in parentheses. [b] $Pc2_1n$ has the same symmetry as the tabulated $Pna2_1$, but has another, non-standard setting of the unit cell (*bca*). [c] The weights of the F^2 values were assumed as $w = [\sigma^2(F_o^2) + (cP)^2]^{-1}$ where $P = (F_o^2 = 2F_c^2)/3$ and the constant, c, had the values 0.0708 for **1a**, 0.0617 for **1b** and 0.0442 for **1c**. [d] A few reflections (15 for **1a**, 17 for **1b** and 12 for **1c**) have been excluded from the final refinement calculations due to potential systematic erors.

The small guest molecules show the expected geometries. Accordingly, the dioxane guests in **1b** occur in the usual 'chair' form and the *o*-xylene molecules in **1c** are flat, indicating that these guests are held firmly. The xylene phenyl ring atoms are coplanar within 0.022 and 0.009 Å, and the deviation of the C(X7)/C(X8) atoms [Fig. 1(*c*)] from these planes are 0.070(6)/0.042(7) and 0.013(5)/0.014(7) Å in the unprimed and primed molecules, respectively. The pentan-2-ol guest in **1a** proved to be disordered. The half-occupied disorder models, which partly overlap each other [*cf.* experimental part below and Fig. 2(*b*)], could not be refined properly. Thus, the pentanol positions are relatively uncertain, as indicated also by the atomic displacement parameters refined for them [U_{iso} of the C(P) atoms range between 0.10 and 0.18 Å^2, and U_{eq} of the O(P) atom is 0.111(3) Å^2].

Host–guest interactions and packing relations

The inclusion compounds **1a–c** are different with respect to the polarity and proton donor–acceptor ability of the guest.

In **1a**, both the host and the guest contain alcoholic OH groups, thus having the potential of forming a coupled system of hydrogen bonds with full H-bond saturation. Such a system of closed rings, involving the host and guest OH functions, has been detected in the related **2**·EtOH (1:2) complex,[6] and also in four alcoholic inclusions of different single-bridged triarylmethanol hosts.[13] Moreover, inclusion of EtOH by host **2**[6] and MeOH by an analogous, tetra-*p*-methyl (instead of *p*-Cl) substituted host[14] led to a conformational change of the biscarbinol host, so that the two OH groups form a relatively strong intramolecular hydrogen bond as a part of the hydrogen bond pattern.[6,13] On the contrary, the host OH functions in **1a** exhibit the 'inactive' conformation (*cf.* above), and only a single O–H···O bond is observed from the pentanol guest to the host (Table 2). Moreover, the O···O distance of about 3 Å suggests only a moderate strength for this bond, allowing the guest alcohol to be disordered in the crystal. Thus, neither the requirement of maximum saturation of hydrogen bonds, nor the maximum acceptor rule[15–17] is fulfilled in the present alcoholic inclusion. A similar anomaly was noticed earlier in the 9-phenyl-2,7-dibromofluoren-9-ol·propan-2-ol (2:1) complex.[13] A possible reason for the deviation from the expected behaviour is the simultaneous requirement of close packing, which in certain cases can be achieved only by packing of smaller units of host–guest associates using weaker forces. The packing arrangement in the dibromofluorenol·propanol (2:1) complex[13] is probably supported by Br···Br contacts [Br···Br = 3.526(1) Å], whereas weaker interactions involving the halogen atoms (Table 3) seem to be directing the packing of the H-bonded aggregates in **1a**. Accordingly, intermolecular Cl···π approaches link the hosts [Fig. 5(*a*)] in the direction of the *bc* diagonal, and relatively short Cl···Cl contacts are

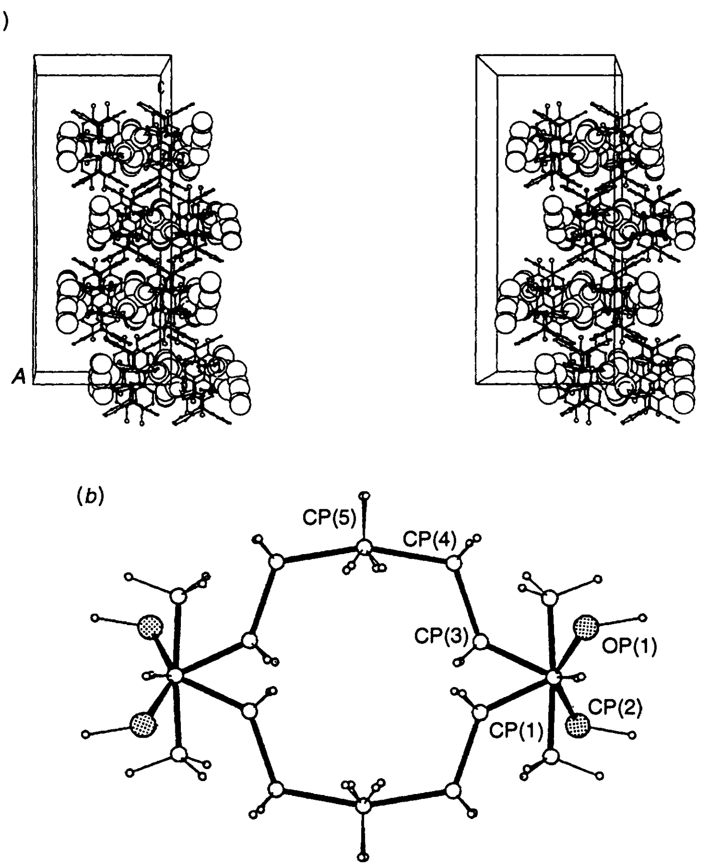


Fig. 2 (*a*) Packing illustration showing the crystal structure of **1a** [**1**·pentan-2-ol (1 : 1)]. The hosts are shown in ball-and-stick style; the guests are drawn as space-filling models. The C-bonded H atoms of the host are excluded for clarity. (*b*) Perspective view of the unit of four pentanol disorder sites, occupied by two guest molecules, as occurring in each cavity of the host matrix. O atoms are shaded.

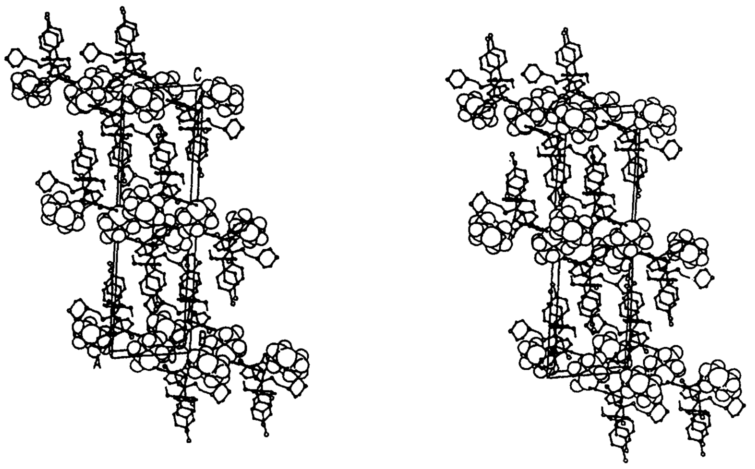


Fig. 3 Packing diagram of compound **1b** [**1**·1,4-dioxane (2:5)]. The H-bonded host–guest 1 : 1 associates are drawn in ball-and-stick style without the C-bonded H atoms, whereas additional guests, trapped in the crystal mainly by lattice forces, are represented by space-filling models. The hydrogen bond is drawn as a thin line.

assumed to steer the packing in the *ac* and *abc* directions (Table 3). In this way, highly symmetrically arranged hosts create uniform cavities, and each cavity is occupied by two pentanol guests distributed on four partly overlapping disorder sites [Fig. 2(*b*)].

The organization of the **1**·1,4-dioxane (2:5) crystal resembles those of the dioxane inclusions of single-bridged triarylmethanols.[18] However, host **1** has two hydroxy functions but uses only one of them to bind a guest *via* an H-bond, whereas the other OH group exhibits the 'inactive' conformation (*cf.* above), in spite of the fact that the crystallographic asymmetric unit contains one and a half additional dioxane molecules. This latter guest type is included in the crystal by weak lattice forces supported by possible electrostatic C–H···O interactions [Table 2, Fig. 1(*b*)].

Inclusion of the aprotic apolar *o*-xylene guest by **1** resulted in a lattice-type inclusion, **1c** [Fig. 1(*c*)], as expected. The host molecules form tunnels in the crystallographic *c* direction, which are filled with the *o*-xylene guests. Even though the host alcohols have the potential to form hydrogen bonds with each other, the host lattice of **1c** is governed again by weaker Cl···π interactions [Fig. 5(*c*)]. Noteworthy, however, is the fact that since Cl···π connections involving molecules with ideal C_2 molecular and crystallographic symmetry give rise

Table 2 Distances and angles in possible hydrogen bonds in crystals of **1a**, **1b** and **1c**[a]

		Distance/Å			Angle/°
Atoms involved	Symmetry	Donor···Acceptor	D–H	H···A	∠D–H···A
1a [**1**·pentan-2-ol (1 : 1)]					
O(P1)–H(P10)···O(7)	x, y, z	3.027(8)	1.02	2.02	173
0(7)–H(7)···centroid(1)[b]	x, y, z	3.283(3)	0.97	2.34	164
C(6)–H(6)···O(P1)	$-x + 0.25, -y + 0.25, z$	3.426(11)	1.00	2.46	162
1b [**1**·1,4-dioxane (2 : 5)]					
O(13)–H(13)···O(D1)	x, y, z	2.841(3)	1.05	1.90	147
O(26)–H(26)···centroid(2)[b]	x, y, z	3.308(3)	1.04	2.29	168
C(4)–H(4)···O(D4′)	x, y, z	3.354(5)	0.95	2.47	154
C(8)–H(8)···O(D1″)	x, y, z	3.338(4)	0.95	2.44	157
C(25)–H(25)···O(D4)	$x-1, y, z$	3.274(4)	0.95	2.44	146
C(15)–H(15)···O(D4)	$x-1, y, z$	3.336(4)	0.95	2.40	168
1c [**1**·*o*-xylene (1 : 2)]					
C(X3′)–H(X3′)···O(26)	$-x + 1.5, y, z + 0.5$	3.405(6)	0.95	2.63	139

[a] Esds, where given, are in parentheses. The hydrogen positions were not refined. [b] Centroid means the centre of the respective aromatic ring. Accordingly, in **1a**: ring 1 : C(1a)···C(4a); in **1b**: ring 2 : C(5a)···C(8a).

Table 3 Possbile Cl···π, π···π and Cl···Cl interactions, observed in three solid inclusion compounds of host **1**

		Distance/Å	Angle/(°)
Atoms	Symmetry	Cl/π···π/Cl	∠C–Cl···π or C–Cl···Cl
1a [**1**·pentan-2-ol (1 : 1)]			
Cl(11)···centroid(2)[a]	$x, -y - 0.25, -z + 0.75$	3.534(2)	91.4(1)
Cl(11)···centroid(3)[a]	$x, -y - 0.25, -z + 0.75$	3.438(2)	163.9(2)
Centroid(3)···centroid(3)[a,b]	$-x + 0.25, -y + 0.25, z$	3.552(3)	
Cl(11)···Cl(17)	$-x + 0.5, y - 0.25, z + 0.25$	3.517(2)	103.7(2)
Cl(17)···Cl(11)	$-x + 0.5, y + 0.25, z - 0.25$	3.517(2)	148.7(2)
Cl(17)···Cl(17)	$-x + 0.5, -y, -z + 0.5$	3.708(2)	90.8(2)
1b [**1**·1,4-dioxane (2 : 5)]			
Cl(30)···centroid(3)[a]	$x, y - 1, z$	3.385(2)	105.6(1)
Cl(30)···centroid(4)[a]	$x, y - 1, z$	3.743(2)	159.1(1)
Centroid(4)···centroid(6)[a]	x, y, z	3.758(2)	
1c [**1**·*o*-xylene (1 : 2)]			
Cl(30)···centroid(3)[a]	$-x + 2.5, y, z - 0.5$	3.381(3)	103.9(2)
Cl(30)···centroid(4)[a]	$-x + 2.5, y, z - 0.5$	3.356(2)	164.7(2)
Centroid(4)···centroid(6)[a]	x, y, z	3.529(3)	

[a] Centroid means the centre of the respective aromatic ring. **1a**: ring 2: C(8)···C(13); ring 3: C(14)···C(19). **1b** and **1c**: ring 3: C(14)···C(19); ring 4: C(20)···C(25); ring 6:C(33)···C(38). [b] The π···π interaction is intramolecular in all three compounds. In **1a**, however, the crystallographic asymmetric unit contains only one half of the host.

to broad bands in **1a**, this arrangement is disrupted into chains in **1b** and **1c** by the slightly dissymmetric hosts [Figs. 5(*a*)–(*c*)].

Comments on the intermolecular interactions

Although the three crystalline inclusions of the chloro-containing host **1** show different crystallographic symmetries and stoichiometric ratios, they have a special structural feature in common with reference to the host matrix. This feature is that the shortest host–host approach is between a Cl atom and the π electron systems of neighbouring aryl rings forming a novel type of supramolecular synthon[19,20] involving one chlorine and two aromatic rings [Table 3, Figs. 5(*a*)–(*c*)]. A previous analysis of the crystallographic environment around the carbon–halogen bond[21] has shown that electrophiles in general tend to approach halogens at an angle of *ca.* 100° and nucleophiles at *ca.* 165°. This angle characteristics is a consequence of the nonsphericity of the charge distribution of the halogen atoms.[1,21,22] In many (C–)Cl···Cl(–C) interactions the two C–Cl···Cl angles are different. One is *ca.* 90° and the other near 180°, suggesting that Cl atoms can act both as electrophiles and nucleophiles, forming an 'electrophile–nucleophile pairing' interaction.[21,23] Halogen···π(aryl) approaches occur frequently in compounds containing both covalently bonded halogen atoms and aromatic rings.[20,24,25] It is worth noting, however, that the chlorines taking part in Cl···π interactions in compounds **1a**–**c** have two approaches each, with C–Cl···π angles near to 100 and 165° (Table 3). These chlorines thus seem to be involved in 'electrophile–nucleophile pairing' interactions. The angular properties of the Cl···π interactions, recorded both in the literature[24,25] and in Table 3, are similar to those of Cl···Cl contacts,[1,20–23] suggesting a close relationship between them. Accordingly, both probably have the same specific directional effects, which manifest themselves as a pattern in crystals.[1] In the Cl···π interactions in **1a**–**c**, one aryl ring acts as an electrophile and the other as a nucleophile. The different behaviour of the aromatic rings is possibly due to their different crystallographic environments: the nucleophilic ring is simultaneously involved in a π···π stacking interaction from its opposite face with the nearest aryl moiety in the same molecule (*cf.* above), whereas the electrophilic one has no such contact. The observed shorter Cl···π and π···π contact distances involving the same ring (Table 2) seem to support this view. On the other hand, the Cl···π distances of 3.33–3.75 Å might suggest only weak attraction forces between the chlorine atom and the aryl ring, though such a contact can be an effective steering device in organic crystal structures in competition with other weak interactions such as the Cl···Cl contact. In

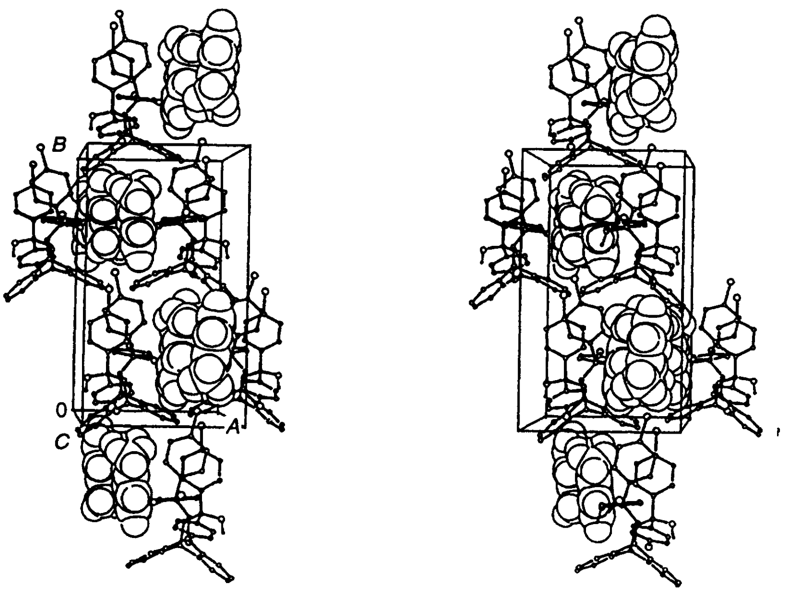


Fig. 4 Packing illustration of compound **1c** [**1**·*o*-xylene (1 : 2)] with the host in ball-and-stick style and the guests as space-filling models. The host (C–)H atoms are omitted for clarity.

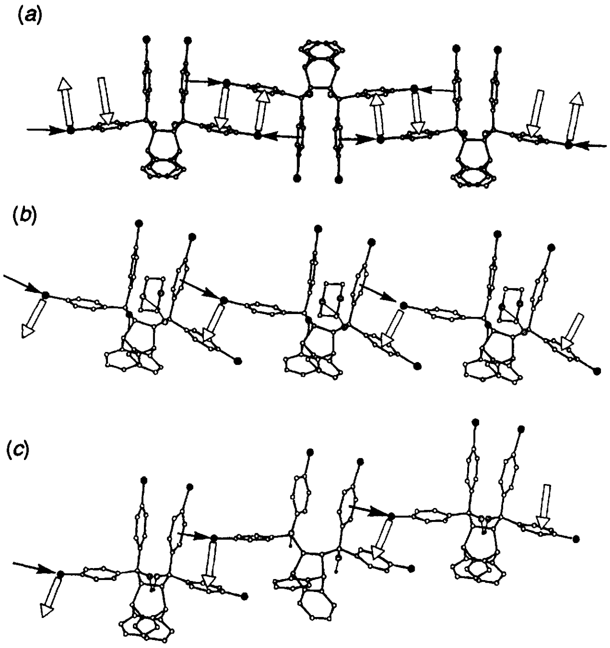


Fig. 5 Characteristic packing patterns in the inclusion compounds of host **1** with pentan-2-ol [**1**·pentan-2-ol (1 : 1)], (*a*), 1,4-dioxane [**1**·1,4-dioxane (2 : 5)] (*b*) and *o*-xylene [**1**·*o*-xylene (1 : 2)] (*c*) as guest. The (C–)H atoms as well as the guests, except the H-bonded dioxane guest in (*b*), are omitted for clarity. The $\pi \longrightarrow \mathrm{Cl}$ interactions are represented by open and shaded arrows for electrophilic and nucleophilic approaches, respectively, showing the direction of the potential electron transfer. Heteroatoms are shaded.

the pentanol inclusion of **1**, the $\mathrm{Cl}\cdots\pi$ connections seem to act in conjunction with the shorter $\mathrm{Cl}\cdots\mathrm{Cl}$ contacts (Table 3), giving rise to a crystalline architecture with a remarkably high (*Fddd*) symmetry. Moreover, host **1** in **1a** exhibits molecular as well as crystallographic symmetry. As a consequence, both aryl rings joined by the intramolecular $\pi\cdots\pi$ stacking interaction (Table 3) are acting simultaneously as nucleophiles in their respective $\mathrm{Cl}\cdots\pi$ interaction, and the host molecules in **1a** striving to satisfy both close packing and the weak electronic effects form a ribbon-like structure [*cf.* Fig. 5(*a*)]. In contrast to this, in **1b** and **1c** where the intermolecular $\mathrm{Cl}\cdots\mathrm{Cl}$ distances are all longer than 4.28 Å and π–π stacking appears less effective, displacement of host molecules is presumably directed rather by the requirements of the $\mathrm{Cl}\cdots\pi$ approaches. Correspondingly, here a chain-like alignment of host molecules will be observed instead of ribbons [*cf.* Figs. 5(*b*) and (*c*)].

Summary and conclusion

The X-ray diffraction study of three inclusions of the tetrachloro-substituted new diol host **1** revealed the presence of relatively short $\mathrm{Cl}\cdots\pi$ contacts between the host molecules. The repeated appearance of the same $\mathrm{Cl}\cdots\pi$ interaction pattern (*i.e.* identical supramolecular synthons[19,20]), manifested as bands or chains in three crystals with various symmetries, host–guest interactions and packing relations, suggest that these connections are structurally significant and important. The angular properties and the possible electrophile–nucleophile pairing characteristics of the observed $\mathrm{Cl}\cdots\pi$ contacts indicate an analogous relationship to the well-documented $\mathrm{Cl}\cdots\mathrm{Cl}$ interactions.[1,19–23] Accordingly, the directional nature of the $\mathrm{Cl}\cdots\pi$ contacts makes these relatively weak interactions capable of influencing the packing of organic molecular crystals decisively, thus providing a new tool for crystal engineering of both homomolecular and supramolecular organic solids.

Experimental

Preparation of the crystalline inclusion compounds

The host compound, obtained as described earlier,[6] was dissolved under heating in a minimum amount of the respective guest solvent. The solution was allowed to cool slowly. Crystals, taken out of the mother liquor for X-ray studies, were immediately covered with epoxy glue in order to prevent solvent evaporation.

X-Ray data collection and processing

Intensity data were measured on a STOE/AED2 diffractometer, using graphite monochromatized Mo-Kα radiation ($\lambda = 0.710\,69$ Å) and the ω–2θ scan method. The derived F^2 values were corrected for background, crystal deterioration, Lorentz and polarization effects. Crystal data are presented in Table 1.

Structure model and refinement

Preliminary structure models were derived by applications of direct methods (SHELXS),[26] and were refined by full-matrix least-squares (LS) calculation based on F^2 for all reflections (SHELXL-93).[27] The (C–)H positions were recalculated before each refinement cycle using geometric evidence,[26] whereas the (O–)H atoms were located from difference electron density ($\Delta\rho$) maps and were held riding on the parent oxygens during the subsequent calculations. Isotropic vibrational parameters were refined for the hydrogen positions and for the partially occupied carbon positions of the disordered pentan-2-ol guest in **1a** (*cf.* below), while the non-hydrogen atoms with full site occupancy as well as the pentanol oxygen in **1a** were treated anisotropically. A few reflections (15 for **1a**, 17 for **1b** and 12 for **1c**), have been omitted from the final refinement calculation due to potential systematic errors. The weights of the F^2 values were assumed[26] as $w = [\sigma^2(F^2) + (cP)^2]^{-1}$ where $P = (F_o{}^2 + 2F_c{}^2)/3$ and the constant c had the values 0.0708 for **1a**, 0.0617 for **1b** and 0.0442 for **1c**. Further details of the refinement calculations together with the final crystallographic R values are shown in Table 1.

Compound **1a** exhibits an unusually high symmetry for a molecular crystal, *Fddd*, where the C_2 molecular symmetry of host **1** perfectly coincides with a crystallographic twofold rotor. The pentan-2-ol guest, on the other hand, has no such symmetry. The $\Delta\rho$ calculation revealed 32 disorder sites for the 16 pentanol molecules in the unit cell, each with 50% site occupancy due to the crystal symmetry requirements. Two of the pentanol carbon atoms [C(P2) and C(P5), *cf.* Figs. 1(*a*) and 2(*b*)] occur in special positions ($\frac{1}{8}$,y,$\frac{1}{8}$ and $\frac{1}{8}$,$\frac{1}{8}$,z, respectively), resulting in partially overlapping pentanol disorder sites. As a consequence, the pentanol model has been subjected to constrained refinement in order to yield an acceptable molecular geometry.

The crystallographic asymmetric unit of compound **1b** contains one host and two and a half guest molecules. Thus, the stoichiometric unit consists of two hydrogen-bonded host–dioxane (1:1) associates and two space-filling guests occupying general positions, and one additional space-filling dioxane, located around the crystallographic inversion centre [*cf.* Fig. 1(*b*)].

The systematic absences observed in the diffraction pattern of compound **1c** were consistent with the centric *Pcmn* (No. 62) and acentric $Pc2_1n$ (No. 33), space group symmetries. The intensity statistics[26] as well as the supposed unit cell content suggested the acentric space group for **1c**, which was then confirmed by the successful solution and refinement of the structure. In the course of the refinement procedure[27] the Flack x parameter was calculated, yielding the final value 0.01(6), thus providing evidence that the handedness of the studied crystal has been assigned correctly.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for authors', *J. Chem. Soc., Perkin Trans. 2*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 188/29. Lists of the anisotropic displacement parameters and the $F_{obs} - F_{calc}$ values are available directly from one of the authors (I. C.).

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