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Molecular Recognition Based on Roof-shaped Diol Hosts. X-Ray Crystal Structures of Inclusion Compounds with Methanol, Pyridine and Toluene

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Abstract. Three crystalline inclusion compounds of roof-shaped *trans*-11,12-bis(diaryl-hydroxymethyl)-9,10-dihydro-9,10-ethanoanthracene host molecules [where aryl is 4-methyl-phenyl (**3**) or 4-*t*-butylphenyl (**4**)] have been studied by X-ray diffraction. The crystals of both the **3**·methanol (2 : 1) [a = 10.755(1), b = 11.571(1), c = 14.697(2) Å, α = 75.12(1), β = 89.67(1), γ = 87.13(1) °] and the **4**-pyridine (2 : 3) compounds [a = 14.045(3), b = 14.366(3), c = 15.607(3) Å, α = 91.62(1), β = 103.65(1) and γ =116.05(1)°] are triclinic (P–1), while the **3**·toluene (1 : 1) complex has orthorhombic (*Fddd*) symmetry [a = 16.041(1), b = 25.008(1), c = 40.440(4) Å]. The host–guest interactions in both triclinic crystals are characterised by hydrogen bonds, with different patterns however. The determined crystal structures indicate a compromise between the requirement of hydrogen bonding on the one hand and close packing on the other. The highly symmetrical host framework in the toluene (1 : 1) complex of **3** seems to be the result of shape recognition, although a tendency towards weak $(C_{methyl})H \cdots \pi_{aryl}$ interactions [$C_{methyl} \cdots \pi$ = 3.533(7) and 3.674(6) Å] between the hosts was observed. The present roof-shaped diol hosts give excellent examples of molecular recognition by exhibiting two significantly different conformations, mostly depending on the proton donor/acceptor ability of the guest component. (O)H ··· O intramolecular bonding between the two alcoholic groups characterises the so-called active form, whereas weaker (O)H ··· π and $\pi \cdots \pi$ interactions stabilise the 'inactive' conformation.

Key words: X-ray structure analysis, crystalline inclusion compounds, hydroxy hosts, methanol/pyridine/toluene guests, hydrogen bonding, isostructurality, 'chloro-methyl exchange rule'.

Supplementary Data relating to this article have been deposited with the British Library at Boston Spa, Wetherby, West Yorkshire, U.K., as Supplementary Publication No. SUP 82275 (102 pages).

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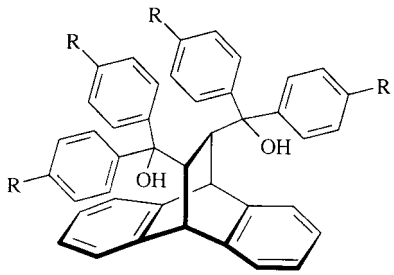
1. Introduction

Molecules containing bulky functional groups attached to a rigid framework have proved to be successful hosts, capable of forming crystalline inclusion compounds with a variety of molecular guests [1]. A most versatile structural design of this kind comprises a roof-shaped 9,10-dihydro-9,10-ethanoanthracene skeleton having two diarylmethanol clathratogenic groups appended in the 11,12-positions of the tetracyclic unit [2]. The clathrate formation ability of this new family of host compounds (Scheme 1) was tested with a broad variety of solvents resulting in a great number of crystalline complexes with guests of varying polarity and H-bonding ability [2]. The results indicated the present hosts to be substantial improvements compared with a basic roof-shaped host type previously studied by us [3]. X-ray studies of selected crystalline inclusion compounds of hosts **1** (R = H) and **2** (R = Cl) with different guests revealed two significantly different conformations of the host, most likely depending on the guest recognition modes [4]. In one of these forms, called the 'active' conformation, the two host OH groups form a rather strong intramolecular hydrogen bond as part of the H-bond system involving also the guest functionality, e.g., an alcoholic OH group, which yields a hydrogen bonded crystalline complex [2]. In the other, so-called 'inactive' conformation, the host OH groups are directed towards the nearest aryl rings of the roof-shaped moiety, thus forming weak intramolecular OH$\cdots\pi$ interactions giving rise to uncomplexed lattice type clathrates in the case of aprotic and apolar guests [2]. Nevertheless, the chloro-containing host compound **2** proved to be an exception, exhibiting the latter 'inactive' conformation independent of the proton donor/acceptor ability and polarity of the guest, but also suggesting that Cl$\cdots\pi$ contacts are structurally significant and important [5]. Intermolecular interactions involving the chloro substituents proved to play an important role also in the crystalline complexes of the mono-diarylmethanol substituted host analogues [6].



1 R = H
2 R = Cl
3 R = CH_3
4 R = $C(CH_3)$

Scheme 1.

Now the question arises whether the methyl and *t*-butyl substituted derivatives **3** and **4** follow the outlined trends of the basic unsubstituted host (**1**) or of its chloro compound (**2**) or possibly neither, but represent a new recognition pattern induced by the steric requirements of the substituents. This would throw light on the robustness relating to the supramolecular interaction mode of this general host

design, which is a deciding factor in crystal engineering [7]. Hence, cocrystals of **3** (R = CH_3) and **4** (R = *t*-butyl) with guests of various characteristics, namely **3**·methanol (2 : 1), **3**·toluene (1 : 1) and **4**·pyridine (2 : 3) (containing a polar protic, non-polar non-protic and polar non-protic guest, respectively), were studied by X-ray diffraction. This work is a part of our investigations [2, 5] of the inclusion behaviour of the bulky roof-shaped diarylmethanol-substituted hosts **1–4**.

2. Experimental

2.1. PREPARATION OF THE CRYSTALLINE INCLUSION COMPOUNDS

The host compounds **3** and **4**, synthesised as described earlier [2], were dissolved under heating in a minimum amount of the respective guest solvent, and the solutions were allowed to cool slowly. Crystals taken out of the mother liquor for X-ray studies were immediately covered by epoxy glue in order to prevent solvent evaporation.

2.2. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT

The intensity data, collected with a STOE/AED2 diffractometer (graphite monochromator) and using the ω–2θ scan mode, were corrected for background, deterioration, Lorentz and polarisation effects, but not for the relatively modest absorption effects (Table I). The starting structure models, derived by application of direct methods (SHELXS [8]) and usually comprising the host molecule and probably fragments of the guests, were completed and refined using the SHELXL-93 [9] program package. The alcoholic hydrogen positions/disorder sites were derived from difference electron density ($\Delta\rho$) calculations and were held riding on their parent oxygens during the subsequent calculations, whereas those of the carbon-bonded H atoms were derived from geometric evidence after each refinement cycle [9]. The CH_3 groups were treated as rigid and freely rotating [9]. The non-hydrogen positions with full site occupancy were refined together with their anisotropic displacement parameters. Isotropic vibrational parameters were refined for the non-hydrogen disorder sites and also for most of the hydrogen positions, whereas fixed isotropic displacement parameters (1.2 times the U_{eq} of the parent non-H atom) were given for some H disorder sites [i.e., those of methanol in **3**·methanol (2 : 1), and those of the *t*-Bu groups and of one of the pyridine guests in **4**·pyridine (2:3)].

Although the mode of complexation of the guests varies in these compounds (Figures 1–4), the X-ray studies show guest molecules exhibiting both static and dynamic disorder in all three crystal structures. As a consequence, distance constraints had to be used in the refinements of the guest components. In the **3**·methanol (2 : 1) structure (Figures 1a and 2), the disorder skeleton of methanol comprises a carbon position at the origin and two centrosymmetrically related oxygen disorder sites with equal probability due to the requirement of the inversion

Table I. Crystal data, experimental parameters and selected details of the refinement calculations for **3**·methanol (2 : 1), **4**·pyridine (2 : 3), and **3**·toluene (1 : 1).

Compound	**3**·methanol (2 : 1)	**4**·pyridine (2 : 3)	**3**·toluene (1 : 1)
Empirical formula	C_{93} H_{88} O_5	$C_{131}H_{147}$ N_3 O_4	C_{53} H_{50} O_2
host	C_{46} H_{42} O_2	C_{58} H_{66} O_2	C_{46} H_{42} O_2
guest	C H_4 O	C_5 H_5 N	C_7 H_8
host:guest stoichiometry	2 : 1	2 : 3	1 : 1
Formula weight	1285.64	1827.52	718.94
Temperature /K	173(2)	253(2)	293(2)
Wavelength/Å	0.71073	0.71073	1.54184
Crystal system	Triclinic	Triclinic	Orthorhombic
Space group	P-1 (No. 2)	P-1 (No. 2)	Fddd (No. 70)
Unit cell dimensions			
a /Å	10.775(1)	14.045(3)	16.041(1)
b/Å	11.571(1)	14.366(3)	25.008(1)
c/Å	14.697(2)	15.607(3)	40.440(4)
α/deg	75.12(1)	91.62(1)	90
β /deg	89.67(1)	103.65(1)	90
γ/deg	87.13(1)	116.05(1)	90
Cell volume/Å^3	1768.7(3)	2717.7(10)	16223(2)
Refinement of the cell parameters			
Number of θ values used	50	64	30
θ_{min}–θ_{max}/deg	5.1–11.7	9.3–13.4	8.5–22.7
Z	1	1	16
$D_{c,X-ray}$ /g cm^{-3}	1.207	1.117	1.177
μ/mm^{-1}	0.073	0.066	0.533
F(000)	686	986	6144
Crystal size /mm	0.30 × 0.20 × 0.45	0.45 × 0.55 × 0.49	0.22 × 0.09 × 0.38
θ range for data collection/deg	1.82 to 25.04	1.60 to 25.01	3.45 to 69.37
Index ranges: min/max h, k, l	−12/9, −13/13, 0/17	−16/16, −17/17, 0/18	0/18, 0/30, 0/48
No. of reflections collected	5895	9561	3769
No. of unique reflections	5811	9561	3389
R(int)	0.0964	–	0.3010
Refinement method	Full-matrix least-squares on F^2		
No. of data used in the final refinement[a]	5806	9561	3377
No. of restraints	1	15	6
No. of parameters refined	513	695	248
Final R indices R (F) [$I > 2\sigma(I)$]	0.038	0.050	0.066
No. of reflections with $I > 2\sigma(I)$	3366	6234	1239
wR (F^2)[b]	0.108	0.153	0.253
Goodness-of-fit on F^2	1.021	1.019	0.991
Extinction coefficient[c]	0.0105(10)	0.0097(9)	0.00012(2)
Largest diff. peak and hole/e$^-$ Å^{-3}	0.38 and −0.34	0.39 and −0.41	0.55 and −0.27

[a] A few reflections [8 for **3**·MeOH (2 : 1) and 12 for **3**·toluene (1 : 1)] have been excluded from the final refinement calculations due to potential systematic errors.
[b] The weights of the F^2 values were calculated as $[\sigma^2(F^2) + (\mathbf{c}_1 \cdot P)^2 + \mathbf{c}_2 \cdot P]^{-1}$ where $P = (F_\mathbf{o}^2 + 2F_c^2)/3$, and the constants $\mathbf{c}_1$ and $\mathbf{c}_2$ had the values 0.0425 and 0.0 for **3**·MeOH (2 : 1), 0.0660 and 1.28 for **4**·pyridine (2 : 3), and 0.1290 and 0.0 for **3**·toluene (1 : 1), respectively.
[c] Fc is multiplied by $k[1 + 0.001\mathbf{x}F_c^2\lambda^3/\sin(2\theta)]^{-1/4}$, where **x** is an extinction coefficient, refined by least-squares, and k is the overall scale factor.

symmetry. The relatively high atomic displacement parameters of the methanol C and O disorder sites (mean $U_{eq} \approx 0.16$ Å^2) and also some residual electron density (a few peaks with $0.38 > \Delta\rho > 0.19$ eÅ^{-3}) in the vicinity of the methanol guest indicate the approximate character of the derived disorder model (Figure 5a). Moreover, the host hydroxyl and methyl hydrogens were also found to be disordered. The final structure model contains two disorder sites for each of these H atoms.

In the **4**·pyridine (2 : 3) compound (Figures 1b and 3), each host is hydrogen bonded to a guest, but there are additional guest molecules in the crystal without H-bond interaction, located on the centre of symmetry. The pyridine ring is not centrosymmetric, and therefore, two nearly overlapping disorder models, with equal probability and with the N atom at opposite locations (Figure 5b), had to be assumed for this latter pyridine guest in order to retain the $P\bar{1}$ crystal symmetry. Furthermore, relatively high $\Delta\rho$ peaks ($\Delta\rho_{max} \approx 0.9$ eÅ^{-3}) at correct positions near to the *t*-butyl groups indicated rotational disorder for these groups. The site occupation factor (sof) of the methyl carbons in three *t*-butyl groups refined to values significantly below 0.90 [i.e., 0.827(5), 0.867(6) and 0.786(5) for the trimethyl groups linked to C(39), C(43) and C(51), respectively], which prompted us to include three minor disorder sites of methyl carbons (without H atoms) for each of these three –C(CH$_3$)$_3$ groups. However, no disorder positions were taken into account for the fourth *t*-Bu substituent [at C(30)] of host **4** (Figure 1b), with the refined sof = 0.956(5).

It is worth mentioning that, although the distribution of observed intensities suggested the presence of a centre of symmetry for both triclinic crystals, trials have been made to refine the structures without assuming inversion symmetry in order to find a better solution for the problems depending on the static disorder of the guests and of certain groups of the hosts. The calculations in $P1$, however, confirmed the centric space group symmetry in both cases.

It proved hard to find a good-quality single-crystal of the **3**·toluene (1 : 1) compound, though several were tested on the diffractometer. Finally, a rather thin crystal, with modest scattering ability but with the comparatively best reflection profiles, was selected for data collection with Cu$K\alpha$ radiation. The **3**·toluene (1 : 1) compound (Figures 1c and 4) exhibits orthorhombic *Fddd* (No. 70) space group symmetry, the same relatively high symmetry as that of the related pentan-2-ol containing co-crystals of **2** (R = Cl) [5], suggesting homeostructurality [10] for these two inclusion compounds. The molecular symmetry (C_2) of the hosts perfectly coincides with a crystallographic two-fold rotor in both cases, whereas neither the pentan-2-ol, nor the toluene guest has such symmetry. Thus, the toluene molecule in **3**·toluene (1 : 1) occupies two symmetry-related disorder positions (Figure 5c) with equal probability, just as the alcoholic guest did in the **2**·pentan-2-ol (1 : 1) compound [5]. The approximate disorder skeleton of the loosely bound toluene guest (the mean value of the U_{iso}'s is 0.23 Å^2) was treated isotropically, and no toluene hydrogens were taken into account in the final structure-factor calculation.

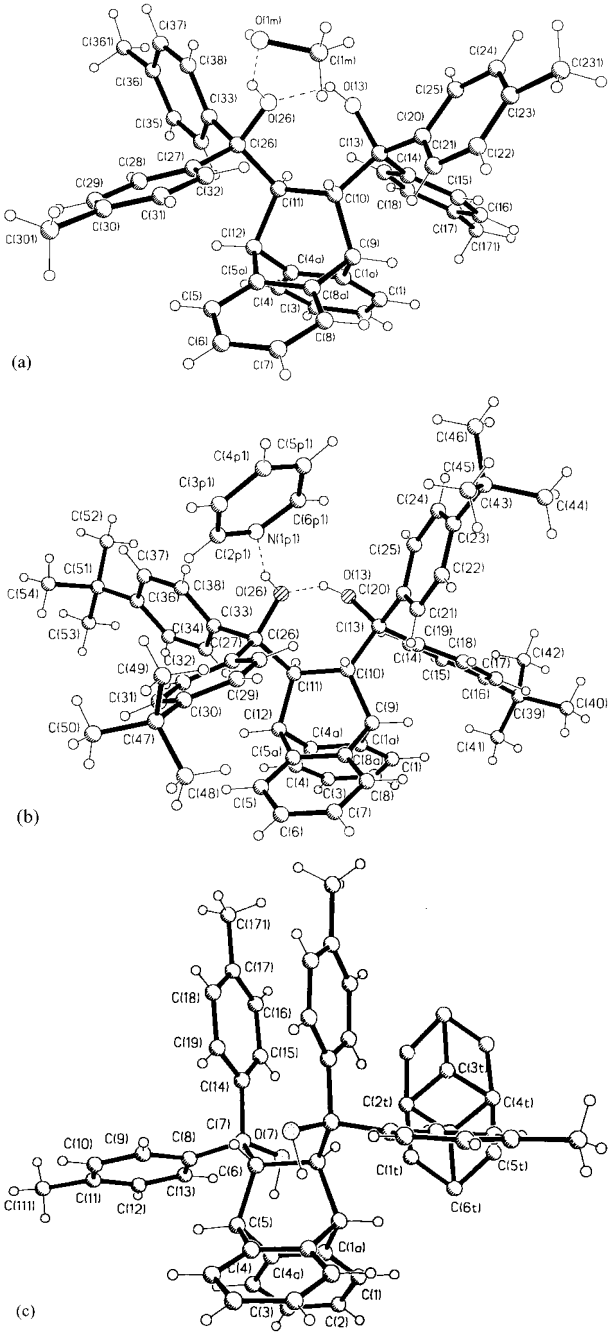


Figure 1. Perspective views of the 1 : 1 host–guest units observed in **3**·methanol (2 : 1) (a), **4**·pyridine (2 : 3) (b) and **3**·toluene (1 : 1) (c), with crystallographic labelling of the unique non-hydrogen positions. For the disordered atoms in **3**·methanol (2 : 1) (a) and **4**·pyridine (2 : 3) (b), having two disorder sites each, only one position is included, for clarity.

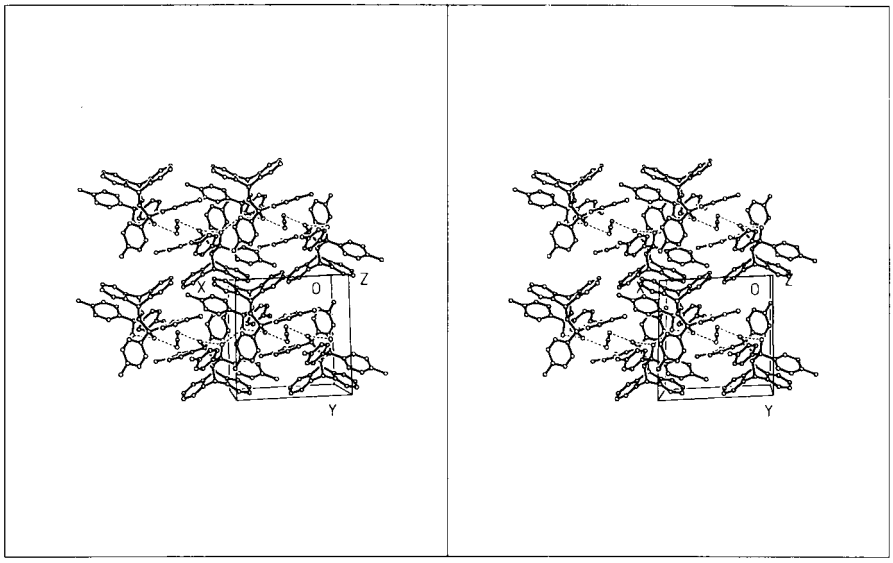


Figure 2. Stereo packing diagram of the **3**·methanol (2 : 1) compound. The hydrogens are omitted for clarity.

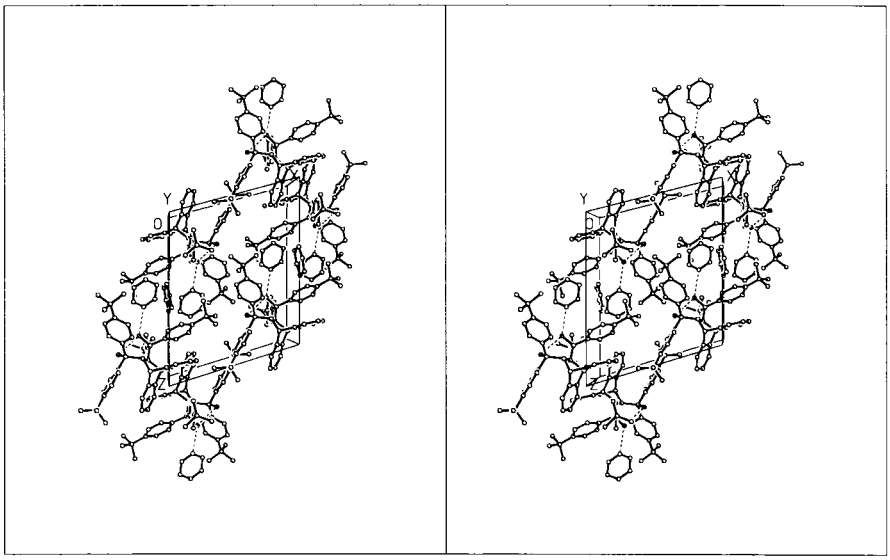


Figure 3. Stereo packing illustration of the **4**·pyridine (2 : 3) compound. The hydrogens in general, and one position of each pair of disorder sites (observed, e.g., in the host *t*-butyl groups and in the space-filling pyridine guest) are omitted for clarity.

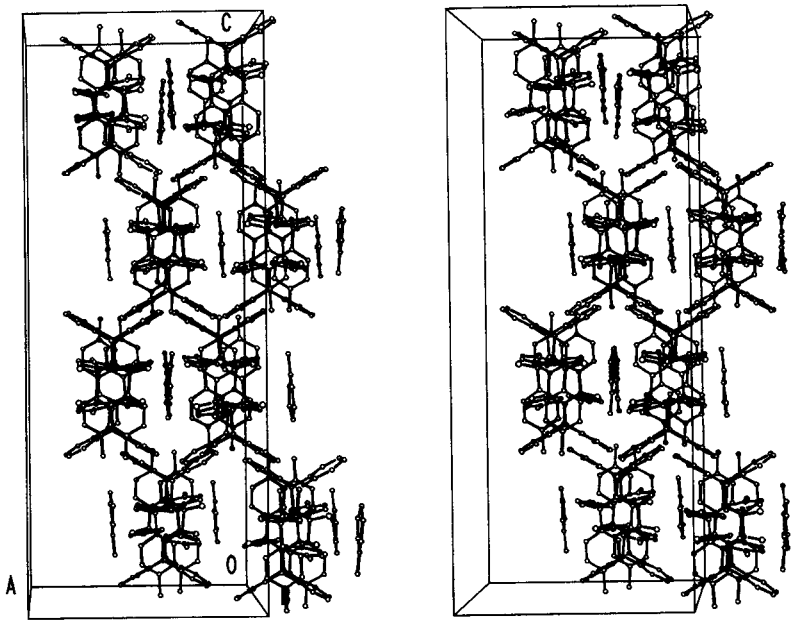


Figure 4. Stereo packing diagram of the **3**·toluene (1 : 1) compound. The hydrogens are omitted for clarity.

Crystal data and further details of the refinement calculations are summarised in Table I.

3. Results and Discussion

3.1. MOLECULAR STRUCTURES

The X-ray studies revealed that the present semi-rigid roof-shaped diol hosts may have two significantly different conformations, specified earlier as the 'active' and 'inactive' forms (see the Introduction), mostly depending on the characteristics of the guest component.

In the so-called 'active' conformation [2, 4] the two OH groups form a rather strong intramolecular hydrogen bond as a part of the H-bonding system, which involves also the guest functionalities. Hosts **3** and **4** exhibit this conformation when including methanol and pyridine, respectively (Figures 1a, b, Table II), and compound **1** was also found to have this conformation in its ethanol (1 : 2) inclusion crystal [2].

In the other, so called 'inactive' form [2, 4], the diarylmethanol substituent groups are rotated so that the OH groups end up above the periphery of the 9,10-dihydro-9,10-ethanoanthracene phenylene rings, and simultaneously two of the phenyl substituents [the C(14)···C(19) ring and its intramolecular symmetry-related equivalent] arrive at approximately parallel positions near to each other

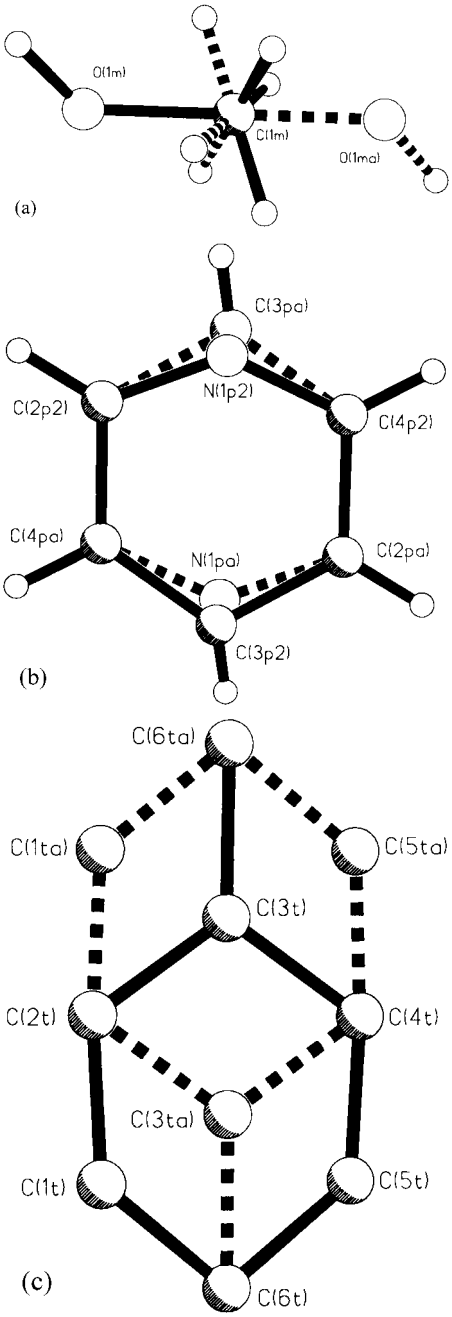


Figure 5. Structure models of the disordered guest molecules, such as methanol in **3**·methanol (2 : 1) (a), one of the pyridines in **4**·pyridine (2 : 3) (b) and toluene in **3**·toluene (1 : 1) (c). Atom labels with an 'a' in the last position indicate symmetry-generated positions.

Table II. Distances (Å) and angles (deg) in O(H)···O/N hydrogen bonds and in possible C(H)···O intermolecular interactions in compounds **3**·methanol (2 : 1) and **4**·pyridine (2 : 3). Esd's, where given,[a] are in parentheses

Atoms involved	Symmetry	Distances			Angle
		Donor···Acceptor	D-H	H···A	<D-H···A
3·methanol (2 : 1)					
O(13)–H(13)···O(26)	x, y, z	2.594(2)	0.92	1.84	137
O(26)–H(26)···O(1M)	x, y, z	2.586(5)	0.89	1.78	148
O(26)–H(26′)···O(13)	x, y, z	2.594(2)	0.93	1.73	153
O(13)–H(13′)···O(13)	$-x, 1-y, 1-z$	2.773(2)	0.90	1.88	177
C(1M)–H(3M)···O(26)	$1-x, 1-y, 1-z$	3.128(2)	0.98	2.20	156
4·pyridine (2 : 3)					
O(13)–H(13)···O(26)	x, y, z	2.646(9)	0.99	1.71	155
O(26)–H(26)···N(1P1)	x, y, z	2.736(14)	0.97	1.80	161
C(46)–H(461)···O(13)	$1-x, 1-y, 1-z$	3.464(5)	0.96	2.75	132

[a]The hydrogen positions/disorder sites were not refined (see the text).

(Figure 1c). In the case of host **3** in its **3**·toluene (1 : 1) inclusion compound, the hydroxy O(7) atom is located 2.932(3) Å above the C(1a)···C(4a) phenylene ring plane and 2.952(6) Å from C(4a). The distance between O(7) and the centre of the ring [O(7)···π] is 3.327(4) Å. Furthermore, the observed dihedral angle between the planes of the C(14)···C(19) ring and its symmetry-related intramolecular equivalent is 4.5(2)°, and the distance between the ring centres is 3.562(3) Å. These observations suggest the presence of weak intramolecular interactions of both (O)H···π and π···π type, which may contribute to the stabilisation of this 'inactive' form. A similar conformation has been observed earlier in the nitroethane (1 : 1) and benzene (2 : 1) cocrystals of host **1** [2], and also in three inclusion compounds of the chloro-containing host **2** [5].

The roof-shaped ethanoanthracene moieties of hosts **3** and **4** show the expected geometry, in agreement also with our earlier observations on the closely related host molecules **1** and **2** [2, 5]. Accordingly, the dihedral angle between the 9,10-dihydro-9,10-ethanoanthracene phenylene rings that form the roof are 121.62(7) [**3**·methanol (2 : 1)], 121.50(9) [**4**·pyridine (2 : 3)] and 117.5(2)° [**3**·toluene (1 : 1)], and the C–C bonds forming the ethano bridge and also those linking the diarylmethanol groups to the ethano bridge are somewhat elongated. The mean values of these elongated C–C distances (with the root mean square deviation from the arithmetic average given in brackets) are 1.573{8} in **3**·methanol (2 : 1), 1.571{12} in **4**·pyridine (2 : 3) and 1.574{5} Å in **3**·toluene (1 : 1), while the remaining bond lengths and bond angles generally conform to commonly accepted values. The two phenyl rings within each diarylmethanol group are roughly perpendicular to each

Table III. Distances (Å) and angles (deg) in selected intra- and intermolecular connections involving the host molecules in the homeostructural crystal structures of **3**·toluene (1 : 1) and **2**·pentan-2-ol (1 : 1).[a] The esd's, where given,[b], are in parentheses

Connections	Symmetry	**3**·toluene (1 : 1)	**2**·pentan–2–ol (1 : 1)
O–H$\cdots\pi$			
O(7)$\cdots\pi_{(1)}$[c]	*x, y, z*	3.327(4)	3.283(3)
O(7)–H(7)	*x, y, z*	1.01	0.97
H(7)$\cdots\pi_{(1)}$[c]	*x, y, z*	2.42	2.34
<O(7)–H(7)$\cdots\pi_{(1)}$[c]	*x, y, z*	148	164
C(H)$\cdots\pi$/Cl$\cdots\pi$			
C(111)/Cl(11)$\cdots\pi_{(2)}$[c]	*x, −y−0.25, −z + 0.75*	3.533(7)	3.534(2)
<C(11)–Cl(11)$\cdots\pi_{(2)}$[c]	*x, −y−0.25, −z + 0.75*		91.4(1)
C(111)–H(112)[d]	*x, y, z*	0.96	
H(112)$\cdots\pi_{(2)}$[c]	*x, −y−0.25, −z + 0.75*	2.75	
< *C*(111)–H(112)$\cdots\pi_{(2)}$[c]	*x, −y−0.25, −z + 0.75*	139	
C(111)/Cl(11)$\cdots\pi_{(3)}$[c]	*x, −y−0.25, −z + 0.75*	3.674(6)	3.438(2)
<C(11)–Cl(11)$\cdots\pi_{(3)}$[c]	*x, −y−0.25, −z + 0.75*		163.9(2)
C(111)–H(113)[d]	*x, y, z*	0.96	
H(113)$\cdots\pi_{(3)}$[c]	*x, −y−0.25, −z + 0.75*	3.28	
<C(111)–H(113)$\cdots\pi_{(3)}$[c]	*x, −y−0.25, −z + 0.75*	107	
$C_{methyl}\cdots C_{methyl}$/Cl$\cdots$Cl			
C(17l)/Cl(17)$\cdots$C(171)/Cl(17)	*−x + 0.25, −y + 0.25, z*	3.62(1)	3.703(2)
C(111)/Cl(11)$\cdots$C(l71)/Cl(17)	*−x + 0.5, y − 0.25, z + 0.25*	3.93(1)	3.517(2)
C(171)/Cl(17)$\cdots$C(171)/Cl(17)	*−x + 0.5, −y, −z + 0.5*	3.91(1)	3.708(2)
$\pi_{(3)}$[c]$\cdots\pi_{(3)}$[c]	*−x + 0.25, −y + 0.25, z*	3.562(3)	3.552(3)

[a] From [5].
[b] The hydrogen positions were not refined (see the text).
[c] π means the centre of the corresponding aryl ring, such as (1): C(1a)$\cdots$C(4a) ring; (2): C(8)$\cdots$C(13) ring, (3): C(14)$\cdots$C(19) ring.
[d] Fixed C_{methyl}-H distance (see the text and SHELXL-93) [9].

other. The observed dihedral angles range from 72.9 to 98.2° with an average value of 91{11}°.

The geometries deduced for the present guest components, on the other hand, are rather uncertain due to the disorder (Figures 5a–c) and the relatively high mobility of the atoms forming the guests molecules (see the experimental section).

3.2. PACKING RELATIONS

The mode of complexation of the methanol and pyridine guests by the diol hosts **3** and **4**, respectively, is characterised by hydrogen bonds (Table II), as expected. The hosts in their 'active' forms are involved in both intra- and intermolecular H-bonds in both structures, but the created H-bond patterns are different. Using the graph-set assignment suggested by Etter [11] and further developed by Bernstein *et al.*

[12], the hydrogen-bonding pattern in **3**·methanol (2 : 1) has the notation $\mathbf{D}_{\mathbf{5}}^{\mathbf{5}}(\mathbf{10})$, whereas that in the **4**·pyridine (2 : 3) compound is designated $\mathbf{D}_{\mathbf{3}}^{\mathbf{2}}(\mathbf{5})$.

In the methanol inclusion crystal of **3** (Figure 2) the hosts are linked together two by two *via* an (O)H···O bond (Table II). Although the host dimers formed have two OH functions each available for hydrogen bond interaction with the alcoholic guest, the crystal contains only one guest per each host dimer. The excess of host OH functions together with the size of the cavity allotted to the relatively small guest alcohol molecules makes disorder of the methanol molecules possible. Hence, each methanol has two centrosymmetrically related positions for its OH group (Figure 5a), accepting a hydrogen bond either from one or the other of the neighbouring, centro-symmetrically related host dimers. Although the diol host and methanol guest both have eminent proton donor and acceptor abilities, host **3** was found to act only as a proton donor and the guest alcohol only as an acceptor when interacting with each other in the present complex. At the same time, the guest disorder induces disorder for the host hydroxyl hydrogens as well. Depending on the proton arrangement, either one or the other terminal OH group of a host dimer becomes capable of donating a proton to a guest, thus yielding a 2 : 1 host-guest associate. In this way a finite H-bonding pattern is created without full hydrogen bond saturation. The H-bonded heteromolecular 2 : 1 units are then held together in the crystal by ordinary van der Waals' forces.

In the **4**·pyridine (2 : 3) compound (Figure 3) the host-guest interaction yields 1 : 1 host-guest associates. Packing of these H-bonded 1 : 1 units gives rise to solvent-accessible voids of 221.0 $Å^3$ volume [13] around the inversion centres in the structure, where additional guest molecules are trapped by lattice forces only (Figure 3). These latter guests raise the packing density [13, 14] of the crystal from 63.8% (without space filling guests) to 66.7%. The packing coefficient for normal close-packed organic crystals is usually within the interval 0.65–0.77 [14]. Nevertheless, the latter pyridine guest has to occupy at least two centrosymmetrically related disorder positions due to the space group symmetry requirement. Thus, the assumed disorder model for that loosely bound guest comprises two partly overlapping disorder positions, which have opposite in-plane orientations (Figure 5b) and occur with equal probability.

We have seen earlier that host **1** (R = H) forms H-bonded 2 : 2 host-guest associates with an ethanol guest [2], with full hydrogen-bond saturation. The present study revealed host **3** (R = CH_3) to form H-bonded 2 : 1 aggregates with methanol, and host **4** (R = *t*-Bu) to create a 1 : 1 associate with pyridine. The two latter structures do not have full H-bond saturation. Moreover, additional pyridine guests have to be included in the **4**·pyridine (2 : 3) crystal in order to fill up the voids between the H-bonded host-guest entities. It seems likely that the increasing size of the diarylmethanol groups (or the entire host molecule) leads to a decreasing number of molecules forming the hydrogen-bonded supramolecular unit. It is apparent that the directional requirement of a hydrogen bond, together with the increasing size of the H-bonded unit, enhances the difficulty of reaching a crystal packing with

acceptable density. As a consequence, the structure will contain smaller H-bonded units without full H-bond saturation, which, however, are capable of packing with enough density. This conclusion is in agreement with our earlier observations, e.g., on different 9-substituted fluoren-9-ols [15, 16].

The toluene inclusion crystal of **3** (R = CH_3, Figure 4) was found to have the same highly symmetrical orthorhombic space group (*Fddd*) as the pentan-2-ol inclusion compound of host **2** (R = Cl) [5]. We found this somewhat surprising, because only the host molecules have similar sizes and shapes, not the guests, and both the hosts and the guests are supposed to differ in polarity and proton donor/acceptor ability, which might affect the sensitive balance of intermolecular interactions that determine the organisation of molecular crystals.

The relationship between these two crystal structures was proved by calculating the three descriptors of isostructurality [i.e., Π, $I_i(n)$ and $I_i(n^*)$] following Kálmán *et al.* [10]. Although the two compounds were studied at different temperatures [293 K for **3**·toluene (1 : 1) and 193 K for **2**·pentan-2-ol (1 : 1)], using different radiations [Mo$K\alpha$ for the toluene complex and Cu$K\alpha$ for the pentan-2-ol containing crystal], their unit cell similarity index, Π, is as low as 0.0055 (mean elongation ϵ = 0.0046). Furthermore, the isostructurality index of the host framework, $I_i(24)$, calculated by comparing the 24 unique non-H atom positions of hosts **2** and **3** yielded the value 98.7%, and the molecular isometricity index, $I_i(24^*)$, which is a direct measure of the degree of approximate isomorphism of molecules, reached the value 99.1% (ΔR_i of the least-squares fitting was 0.0445). Accordingly, the calculated values indicate high homeostructurality [10] for these two inclusion crystals.

Chloro ($V_{Cl} \approx 20$ Å^3) and methyl ($V_{CH3} \approx 24$ Å^3) substituents are known to have similar volumes [17, 18]. Hence, in molecular crystals which follow Kitaigorodskii's close-packing model [14], these substituents may be able to replace each other without changing the crystal structure ('chloro-methyl exchange rule' [18]). However, only a limited number of compounds, either containing large, irregularly shaped molecules or comprising a small number of Cl substituents, were found to obey the 'chloro-methyl exchange rule'. At the same time, numerous examples are known in which involvement of the chloro substituents in weak but directional interactions (e.g., Cl···Cl bonds) leads to altered packing relations for the chloro homologue. These latter observations suggest that CH_3 and Cl substituents may carry different charges, and while the methyl groups function as substituents of a certain volume, the halogens act rather through specific anisotropic electronic effects [18].

Host **2** has four chloro substituents per molecule, and these were found to be involved in Cl···Cl as well as in Cl$\cdots\pi$ interactions in the **2**·pentan-2-ol (1 : 1) inclusion compound. The latter connections are most probably more crucial for the host–host recognition modes than the former ones [5]. Although the methyl-substitued analogue (**3**) is not capable of establishing interactions corresponding to those between the halogens, similar to the relatively short Cl$\cdots\pi$ connections

between host **2** molecules [5], noticeably short $C_{methyl}(H)\cdots\pi$ approaches were observed between neighbouring host **3** molecules in the toluene complex (Table II). The geometry of these latter connections is comparable to that previously published for $C(H)\cdots\pi$ bonds [19–21], thus indicating the possibility of $C(H)\cdots\pi$ host-host interactions in **3**·toluene (1 : 1).

It is interesting to note that careful comparison of the shorter Cl···Cl connections with the corresponding $C_{methyl}\cdots C_{methyl}$ distances (Table III) hints that the chloro substituents in **2** and the methyl groups in **3** probably have slightly different charges. Accordingly, intra- or intermolecular Cl···Cl contact distances involving symmetry-equivalent chloro substituents [3.703(2) Å and 3.708(2) Å, respectively], have about the same lengths, and are longer than the shortest intermolecular distance between non-equivalent Cl atoms [3.517(2) Å] (Table III). On the contrary, the intramolecular $C_{methyl}\cdots C_{methyl}$ distance involving symmetry-equivalent methyl groups [3.62(1) Å] is considerably shorter than the intermolecular contact distances between neighbouring molecules [3.93(1) Å and 3.91(1) Å], the latter ones being equal within experimental error, irrespective of the symmetry-equivalence or non-equivalence of the connected groups. Nevertheless, the observed $C(H)\cdots\pi$, $Cl\cdots\pi$ or Cl···Cl connections are certainly weak bonds [19–21]; therefore it is reasonable to assume that the highly symmetrical (*Fddd*) host frameworks are primarily results of shape recognition of the inconveniently shaped host molecules. Despite the assumed charge differences between the *R* groups and the Cl···Cl interactions in **2**·pentan-2-ol (1 : 1), the present two compounds follow the 'chloro-methyl exchange rule', hence evidencing the importance of dense packing in molecular crystals. At the same time, the host–host interactions, mediated *via* $C(H)\cdots\pi$ or $Cl\cdots\pi$ connections, respectively, certainly contribute in a similar way to the stabilisation of the isostructural host frameworks. The loosely bound toluenes, on the other hand, stabilise the **3**·toluene (1 : 1) crystals by filling up the voids in the host framework, just as the H-bonded pentan-2-ol guests seem to do in the **2**·pentan-2-ol (1 : 1) compound [5], irrespective of the different host–guest interaction modes and differences in characteristics, shapes and sizes of the guest molecules.

4. Conclusion

The present roof-shaped diol hosts constitute excellent examples of molecular recognition, by exhibiting two significantly different conformations mostly depending on the proton donor/acceptor ability of the guest component. In one of the forms, called 'active', the OH groups of the diol molecule form a rather short intramolecular hydrogen bond with each other, as a part of the H-bonding pattern in the crystal, whereas the 'inactive' conformation is possibly supported by weaker intramolecular $(O)H\cdots\pi$ and/or $\pi\cdots\pi$ type forces. The crystal structures of the **3**·methanol (2 : 1) and **4**·pyridine (2 : 3) compounds seem to be the result of simultaneous satisfaction of the tendency towards formation of hydrogen bonds

and the requirements of dense packing. The homeostructurality of two in many respect different inclusion compounds, namely **3**·toluene (1 : 1) and **2**·pentan-2-ol (1 : 1), exemplifies the situation where the chloro–methyl exchange does not alter the crystal structure. Despite the slightly different charges of the Cl and CH_3 groups and the differences in intermolecular interactions, host molecules **2** and **3** form isostructural frameworks, thus illustrating the crucial role that close packing plays in molecular crystals. Host–host interactions of the C(H)$\cdots\pi$ or Cl$\cdots\pi$ type, respectively, contribute in similar ways to the stabilisation of the packing arrangements.

The major significance of this and previous studies [2, 4, 5] on the present host family is the rather high precision with which supramolecular interaction modes can be predicted, making possible design of crystalline complexes and inclusion compounds using these compounds.

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