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Hydrogen-bonded network and enforced supramolecular cavities in molecular crystals: An orthogonal aromatic-triad strategy. Guest binding, molecular recognition, and molecular alignment properties of a bisresorcinol derivative of anthracene in the crystalline state

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Crystallization of an *orthogonal* resorcinol-anthracene-resorcinol compound 1a (host) from an ester solvent such as alkyl benzoate (guest) affords a 1:2 host-guest adduct 1a•2(ester). An essential aspect of the crystal structures of ethyl, propyl, and isobutyl benzoate adducts (space group, $P2_1/n$) and also that of methyl benzoate adduct ($C2/c$) is an extensive hydrogen-bonded network of host 1a, leading to a molecular sheet composed of hydrogen-bonded polyresorcinol chains and anthracene columns. This network generates well-defined, cyclophane-like supramolecular cavities, which incorporate two alkyl benzoate molecules in a highly selective manner via a combination of essential host-guest hydrogen-bonding and what may be called the cavity-packing effect. The selectivity factor between methyl benzoate (the lowest-affinity guest) and isobutyl benzoate (the highest-affinity guest) is 1:70 under competitive conditions. The actual geometry of the cavity is somehow dependent on and hence induced-fit adjustable to the guest structures by manipulating the intramolecular (anthracene-resorcinol dihedral angle) and intermolecular conformation (tilt angle between two hydrogen-bonded resorcinol rings) of compound 1a as well as the sheet-to-sheet distance. The adducts 1a•2(guest) can also be obtained by solid-state guest-exchange or guest-binding, respectively, using a preformed adduct or guest-free apohost dipped *in an appropriate guest solvent.* The methyl benzoate adducts obtained in these ways exhibit the same X-ray powder diffraction pattern as the genuine single-crystal obtained by direct crystallization of host 1a from methyl benzoate. Thus, even internal supramolecular cavities maintained by the hydrogen-bonded network are readily accessible to molecules in bulk solution. In addition, they undergo an induced-fit adjustment to a guest molecule newly added by the guest-exchange or the guest-binding process, during which the crystallinity is maintained. The potential use of symmetrical and divergent multiple hydrogen-bonding sites with an orthogonal aromatic spacer (orthogonal aromatic-triad strategy) is discussed in terms of a tool to construct a new class of porous organic crystals that show novel molecular recognition, crystalline-state guest-binding, and crystalline-phase molecular alignment properties.

INTRODUCTION

The intermolecular forces that govern the crystal structures of organic molecules may be conveniently classified into two categories. One is attractive intermolecular interactions and the other is the so-called crystal packing. In porous ionic crystals, interionic interaction between cation (metal) and anion (oxide) is strong enough to give an extensive electrostatic or metal-coordination network. In molecular crystals, however, intermolecular interactions are usually weak. In such cases, molecules

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in crystals tend to be packed so as to leave a minimal volume of empty space or cavity. The actual mode of crystal packing must be very complicated, since it depends on the molecular shape in a delicate manner. It is therefore not easy at present to predict or design a particular crystal structure.[2,3]

If, on the other hand, the intermolecular interaction is multidirectional and strong enough, the resulting interaction-network might primarily govern the crystal structure; a significant volume of empty space or cavity left would be filled with appropriate guest (usually solvent) molecules. Hydrogen bonding is a potential tool to control crystal structures.[4–8] We originally planned to design simple molecules having divergent[9] (exo[4b] or outwardly-directed[5g]) hydrogen-bonding sites[10] that lead to an extensive hydrogen-bonded network with well-defined supramolecular cavities.[11–14] In Figure 1 is schematically shown the expected crystal structure for a particular class of compounds having four symmetrically-arranged hydrogen-bonding sites (X) in a plane perpendicular with respect to an appropriate aromatic spacer (S) (Chart I). We report here that an anthracene derivative having two resorcinol moieties (**1a**, Chart I) essentially forms such a network[15] and the supramolecular cavities generated show remarkable solid-state guest-binding behavior in both static and dynamic senses.[16]

RESULTS AND DISCUSSION

1:2 host-guest adduct formation upon cocrystallization

Compound **1a**, mp > 360°C, is not soluble in hydrocarbon or halomethane solvents but is slightly soluble at higher temperatures in more or less polar solvents such as aromatic and aliphatic esters. Crystals recovered upon cooling the solution were found to contain exactly two molecules of solvent per mole of host **1a** in every case.[17] On the other hand, recrystallization of the tetramethyl reference compound **1b** (Chart I) from such a polar solvent gave homocrystals of **1b** without incorporation of the solvent molecules.[15]

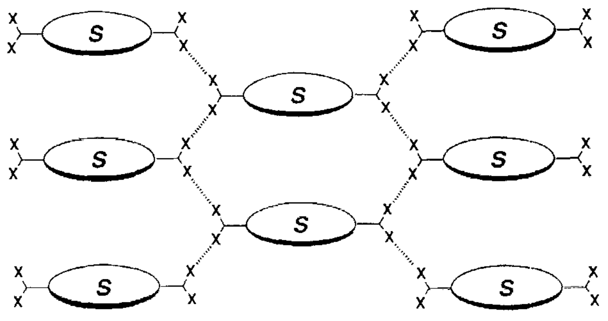
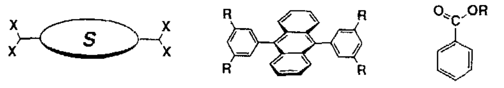


Figure 1 Schematic representation of an extensive hydrogen-bonded network.



1a : R = OH
1b : R = CH_3

2a : R = CH_3
2b : R = CH_2CH_3
2c : R = $CH_2CH_2CH_3$
2d : R = $CH(CH_3)_2$
2e : R = $CH_2CH_2CH_2CH_3$
2f : R = $CH_2CH(CH_3)_2$
2g : R = $C(CH_3)_3$

Chart I

The IR spectra for the adducts **1a**•2(ester) derived from alkyl benzoates (**2**, Chart I) and methyl cyclohexanecarboxylate in KBr pellets showed a significant shift in $\nu_{c=o}$ to a lower wavenumber, $\Delta\nu_{c=o}$ being rather constant at 37–46 cm^{-1} except for methyl benzoate (**2a**) for which $\Delta\nu_{c=o}$ was much smaller (30 cm^{-1}) (Table 1). When a mixture of an ester guest and propylbenzene was used as a crystallization solvent, two molecules of the former were always included exclusively (Table 2, entries 1 and 2). This fact, coupled with the above IR results, indicates that hydrogen bonding is essential for the guest incorporation in the crystals of host **1a**.

Selectivity in the guest binding was evaluated by a competitive method using an equimolar mixture of guests A and B. The results are summarized in Table 2, where the molar ratios A/**1a** and B/**1a** in recovered crystals and the selectivity factors A/B are listed. The total molar ratios of guest to host, (A+B)/**1a**, are always 2. The affinities of alkyl benzoates change with respect to the alkyl groups in the order **2a** (methyl) < **2b** (ethyl) < **2c** (propyl) > **2e** (butyl) (entries 3, 4, and 6); clearly, there is an optimal alkyl chain-length at the propyl group. The affinity of propyl benzoate (**2c**) is further enhanced by the methyl branching at the terminal position; **2c** (propyl) < **2f** (isobutyl) (entry 8). The selectivity factor between the lowest-affinity guest **2a** and the highest-affinity one **2f** is as large as 1:70 (entry 10). The selectivities are also remarkable between geometrical isomers of dimethyl 1,4-cyclohexanedicarboxylate (cis >> trans, entry 11) and methyl toluate (para >> ortho, entry 12). Another notable selectivity is among methyl esters having different acyl moieties. The affinities of cyclohexanecarboxylate, pivalate, benzoate, and pentanoate decrease in this order (entries 13–16).[18]

Crystal structure of isobutyl benzoate adduct

The crystal structures of selected alkyl benzoate adducts and homocrystals of reference **1b** were determined by single-crystal X-ray diffraction (Figures 2 – 10 and Table 1). In Figure 2 is shown the structure for **1b**, in which each molecule of **1b** is heavily packed via intermolecular methyl-anthracene contacts without formation

Table 1 Crystallographic Data, Important Crystal-Structure Parameters, and Infrared Carbonyl-Stretching Frequencies for Adducts **1a**•2(**2a**), **1a**•2(**2b**), **1a**•2(**2c**), and **1a**•2(**2f**), and compound **1b**[a]

	1a•2(2a)	*1a•2(2b)*	*1a•2(2c)*	*1a•2(2f)*	*1b*
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*2$_1$/*n*	*P*2$_1$/*n*
a, Å	13.396(1)	9.033(1)	9.325(1)	9.534(6)	9.184(5)
b, Å	20.395(1)	13.885(1)	13.704(1)	13.479(4)	8.159(2)
c, Å	13.918(1)	15.244(1)	15.615(1)	15.572(4)	15.284(8)
β, deg	117.012(5)	104.32(1)	102.600(6)	100.77(5)	100.14(2)
V, Å^3	3387.9	1852.5	1947.5	1966.0	1127.3
Z	4	2	2	2	1
R	0.048	0.137	0.069	0.096	0.049
R_W	0.055	0.167	0.090	0.131	0.076
no. rflcn. used	1760	1341	1486	2433	2266
no rflcn. obsd.	3439	3353	3149	4443	3621
$d_{H\text{-}G}$, g/cm^3	1.31	1.25	1.23	1.27	
d_H, g/cm^3	0.77	0.71	0.67	0.67	1.14
φ, deg	72.4	72.4	80.0	89.8	
φ' deg	58.3	72.4	80.0	89.8	
ϕ, deg	49.36	14.57	33.60	43.85	
$l^c_{a\text{-}a}$, Å	13.40	13.89	13.70	13.48	
$l^f_{a\text{-}a}$, Å	13.35	12.43	12.02	12.22	
$l_{c\text{-}c}$, Å	10.20	9.77	9.93	9.86	
$l_{s\text{-}s}$, Å	6.20	6.83	7.16	7.40	
$l_{o\text{-}o}$, Å	2.71	2.66	2.72	2.78	
$l_{o\text{-}oc}$, Å	2.67	2.74	2.68	2.72	
$\nu_{c=o}$, cm^{-1}	1695	1678	1679	1679	
$\Delta\nu_{c=o}$, cm^{-1} [b]	30	42	40	41	

[a] Definitions are follows. $d_{H\text{-}G}$, density of adducts; d_H, density of hypothetical host crystal with exclude guest molecules; φ and φ', anthracene-resorcinol dihedral angle (referring to Figure 3c and 7c); ϕ, tilt angle between two hydrogen-bonded resorcinol rings (referring to Figure 3c and 7c); $l^c_{a\text{-}a}$, center-to-center anthracene-anthracene distance (referring to Figure 4 and 8); $l^f_{a\text{-}a}$, face-to-face anthracene-anthracene distance (referring to Figure 4 and 8); $l_{c\text{-}c}$, column-to-column distance (referring to Figure 4 and 8); $l_{s\text{-}s}$, sheet-to-sheet distance (referring to Figure 5 and 9); $l_{o\text{-}o}$, O-O distance for the O-H•O-H moiety for the hydrogen-bonded two resorcinol groups (referring to Figure 3a, 6a, 7a, and 10a); $l_{o\text{-}oc}$, O-O distance for the O-H•O=C moiety in the hydrogen-bonded host-guest adduct (referring to Figure 6a and 10a); $\nu_{c=o}$, carbonyl stretching frequency for the incorporated ester guest in the adduct; $\Delta\nu_{c=o}$, shift to lower wavenumber in $\nu_{c=o}$ accompanying the adduct formation ($\nu_{c=o}$(free ester)-$\nu_{c=o}$(adduct)).

[b] $\Delta\nu_{c=o}$ values for other adducts are 46 (**1a**•2(**2d**)), 37 (**1a**•2(**2e**)), and 40 cm^{-1} (**1a**•2(methyl cyclohexanecarboxylate)).

of any cavity. As detailed below, on the other hand, the most characteristic feature in the structure for the isobutyl benzoate adduct of host **1a**, **1a**•2(**2f**), is the formation of an extensive hydrogen-bonded network with concomitant generation of supramolecular cavities, which incorporate two guest molecules.

The anthracene and resorcinol rings in compound **1a** are almost perpendicular with each other (anthracene-resorcinol dihedral angles are φ = φ' = 89.8°). The OH groups in the two neighboring molecules of **1a** form a hydrogen bond (O-H•O-H), leaving one OH-proton free. The O•O distance is $l_{o\text{-}o}$=2.78 Å (Figure 3). The two re-

Table 2 Competitive Cocrystallization of Host 1a.

entry	*guest A*	*guest B*	*A/1a*	*B/1a*	*A/B*
1	2a	$C_6H_5C_3H_7$	~2	~0	vl[a]
2	$C_6H_{11}CO_2CH_3$	$C_6H_5C_3H_7$	~2	~0	vl[a]
3	**2b**	**2a**	1.6	0.4	4
4	**2c**	**2b**	1.3	0.7	2
5	**2c**	**2d**	1.3	0.7	2
6	**2c**	**2e**	1.5	0.5	3
7	**2f**	**2e**	1.7	0.3	6
8	**2f**	**2c**	1.2	0.8	1.5
9	**2g**	**2e**´	1.3	0.7	2
10	**2f**	**2a**	1.97	0.03	70
11	C_6H_{10}-1,4-$(CO_2CH_3)_2$				
	cis	*trans*	~2	~0	vl[a]
12	CH_3-C_6H_4-CO_2CH_3				
	para	*ortho*	1.96	0.04	50
13	$C_6H_{11}CO_2CH_3$	**2a**	1.8	0.2	9
14	**2a**	$CH_3(CH_2)_3CO_2CH_3$	1.9	0.1	19
15	$C_6H_{11}CO_2CH_3$	$(CH_3)_3CCO_2CH_3$	1.4	0.6	2
16	$C_6H_{11}CO_2CH_3$	$CH_3(CH_2)_3CO_2CH_3$	~2	~0	vl[a]

[a] Very large.

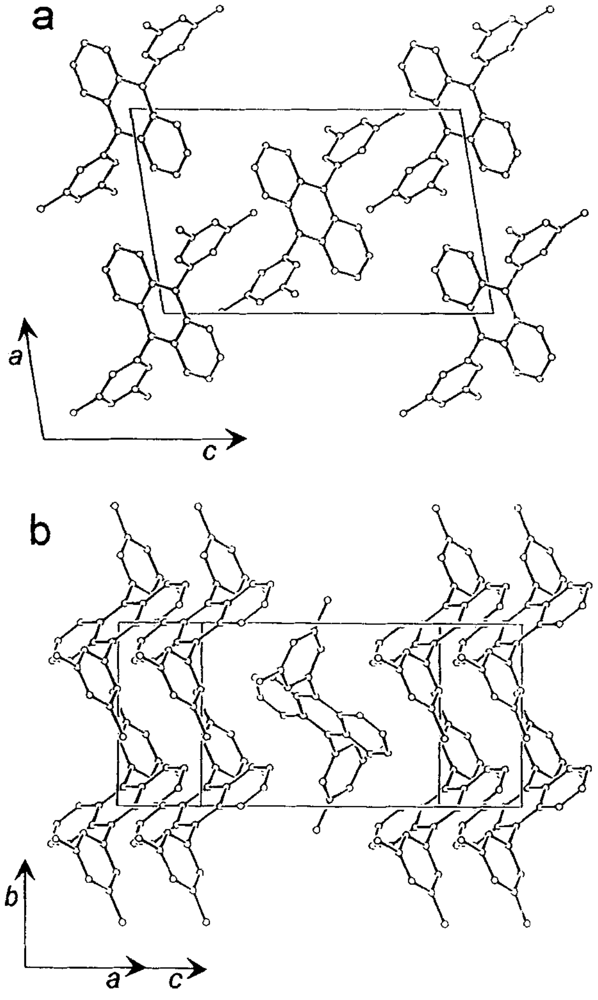


Figure 2 Crystal structure of the homocrystal of compound **1b**, viewed from two different directions (a and b).

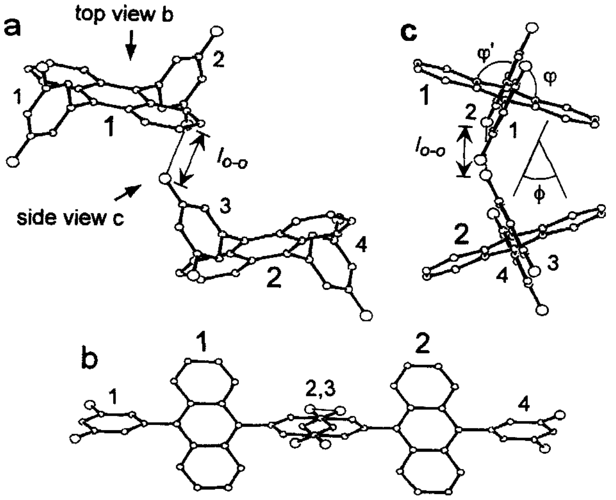


Figure 3 Unit hydrogen-bonding (a) between two molecules of host **1a** in adduct **1a**•2(**2f**) and its top view (b) and side view (c). The anthracene and resorcinol rings having the same number in views a-c correspond to each other.

sorcinol rings linked by the hydrogen bond are not coplanar with a tilt angle of ϕ=43.85°. As a consequence, the two anthracene rings are not parallel, the tilt angle being 43.85-2(90-89.8)=43.45°. Extension of the hydrogen bonding leads to a molecular sheet composed of zigzag-arranged hydrogen-bonded polyresorcinol chains and anthracene columns. The column-to-column distance is $l_{c\text{-}c}$=9.86 Å (Figure 4). The anthracene rings in a column are parallel with each other but not perpendicular with respect to the molecular sheet. The center-to-center anthracene-anthracene distance is $l^{c}_{a\text{-}a}$=13.48 Å and the face-to-face anthracene-anthracene distance is $l^{f}_{a\text{-}a}$=12.22 Å (Figure 4). Two neighboring sheets slide from each other so as to give a *staggered* arrangement

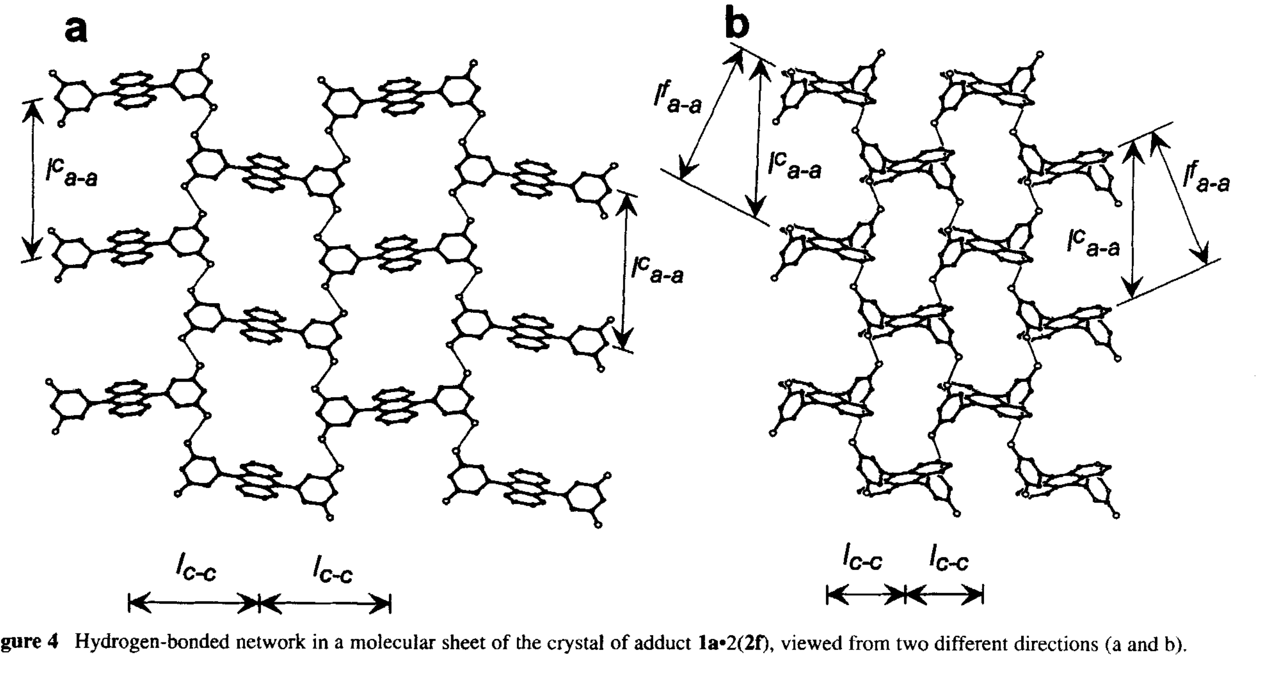


Figure 4 Hydrogen-bonded network in a molecular sheet of the crystal of adduct **1a**•2(**2f**), viewed from two different directions (a and b).

of the anthracene moieties (Figure 5). The sheet-to-sheet distance is $l_{s\text{-}s}$=7.40 Å. The crystal data and important structural parameters are summarized in Table 1.

Each supramolecular cavity has two anthracene rings as a ceil and a floor and two polar walls, in the left and right, composed of four pairs of hydrogen bonded OH groups (O-H•O-H) of the host (Figure 6). Two of them have their *free* OH-protons inwardly directed. They are not located in the mean plane of the molecular sheet; one is in front of it and the other behind it because of the zigzag nature of the hydrogen-bonded resorcinol rings. The front and rear sides of the cavity are covered by the resorcinol moieties of neighboring sheets (cf Figure 5), which are not shown in Figure 6 for clarity. Two molecules of isobutyl benzoate as a guest are incorporated in the cavity in a *parallel* manner with respect to the anthracene rings[19] and also in an antiparallel manner with respect to each other (Figure 6).[20] The carbonyl oxygen atoms of the guest are hydrogen-bonded to the free OH-protons of the host with an O•O distance of $l_{o\text{-}oc}$ = 2.72 Å, while the benzene ring and the isobutyl moiety of the guest are within distances of van der Waals interactions with the anthracene rings of the host.[19] The top view and the side view of Figure 6 are shown in Figure 5 for three adjacent guest-binding cavities in three neighboring molecular sheets.

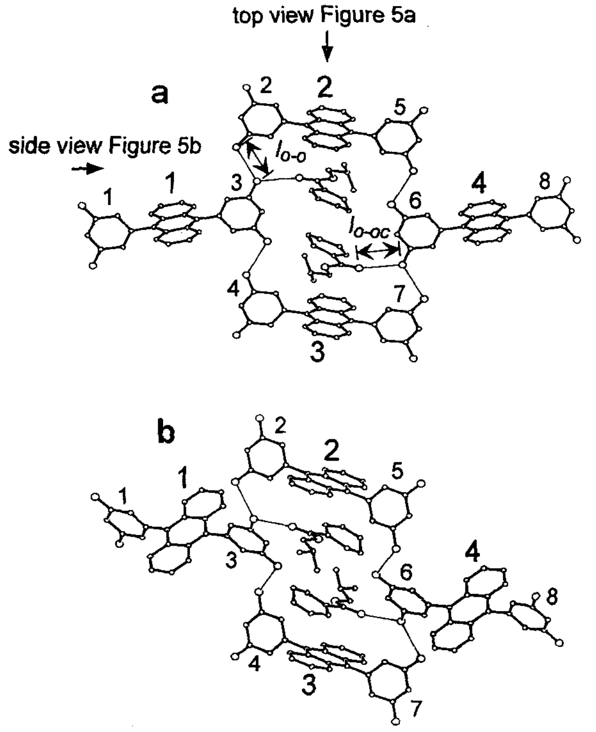


Figure 6 Packing geometry for two isobutyl molecules incorporated in the supramolecular cavity in the crystal of adduct **1a**•2(**2f**), viewed from two different directions (a and b). The anthracene and resorcinol rings having the same number in this Figure (a and b) and Figure 5 (a and b) correspond to each other.

Crystal structure of methyl benzoate adduct

The crystal structure of the methyl benzoate adduct **1a**•2(**2a**) belongs to a space group ($C2/c$) different from that ($P2_1/n$) for the isobutyl benzoate adduct described above. It exhibits a similar overall feature as far as the zigzag-arranged hydrogen-bonded network is concerned; the tilt angle between two resorcinol rings linked by a hydrogen bond is φ = 49.36° (Figure 7), which is close to φ = 43.85° for the isobutyl benzoate adduct (Figure 3).

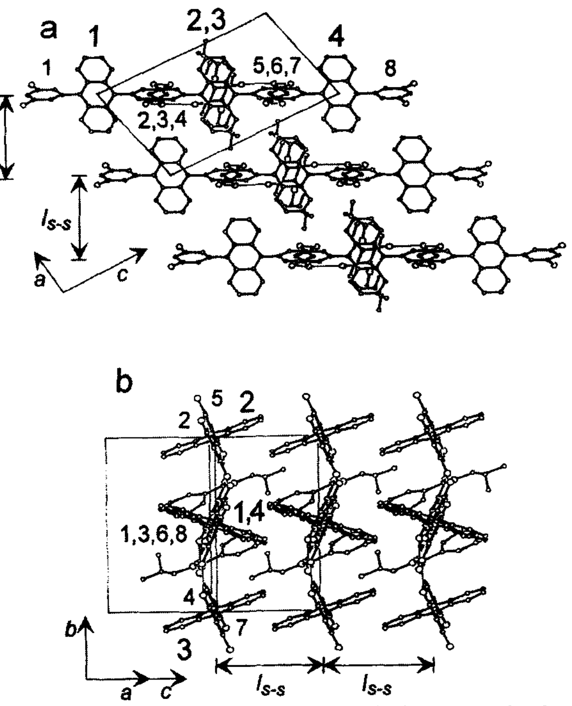


Figure 5 Arrangement of three adjacent guest-binding supramolecular cavities in three neighboring molecular sheets in the crystal of adduct **1a**•2(**2f**); top view (a) and side view (b). The anthracene and resorcinol rings having the same number in this Figure (a and b) and Figure 6 (a and b) correspond to each other.

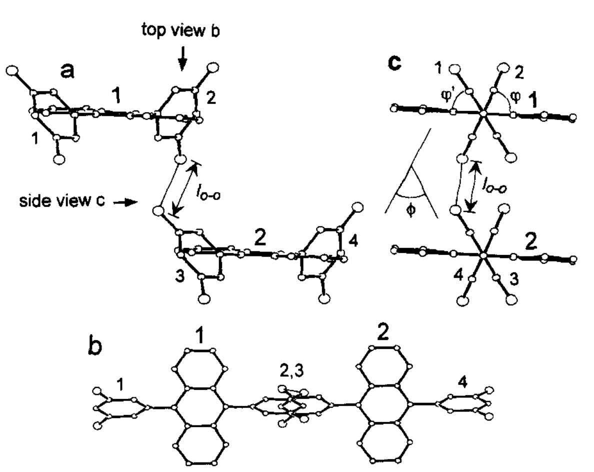


Figure 7 Unit hydrogen-bonding (a) between two molecules of host **1a** in adduct **1a**•2(**2a**) and its top view (b) and side view (c). The anthracene and resorcinol rings having the same number in views a-c correspond to each other.

The two resorcinol rings in compound **1a** are not perpendicular with respect to the anthracene ring, the dihedral angles being $\varphi = 72.4°$ or $\varphi' = 58.3°$. This twisting is in such a way ($180 - (\varphi + \varphi') \cong \phi$) that the two anthracene rings in a pair of hydrogen-bonded molecules of **1a** become parallel with each other (Figure 7). This leads to a molecular sheet in which the anthracene columns are composed of face-to-face stacked anthracene rings which are perpendicular to the molecular sheet ($l^c_{a-a} = 13.40$ Å, $l^f_{a-a} = 13.35$ Å, and $l_{c-c} = 10.20$ Å) (Figure 8 and Table 1). The neighboring sheets are interpenetrating with each other to some extent (Figure 9). Otherwise, the staggered arrangement of the anthracene moieties is similar to that for the isobutyl benzoate adduct (Figure 5).

In the supramolecular cavity are incorporated two molecules of methyl benzoate (**2a**) in a *perpendicular* manner with respect to the anthracene rings and also in an antiparallel manner with respect to each other, as shown in Figure 10. The carbonyl oxygen atoms of incorporated guest **2a** are hydrogen-bonded to the free OH protons of host **1a** ($l_{o-oc} = 2.67$ Å), as above, and the methyl groups in **2a** are in van der Waals contacts with the anthracene rings of **1a**. The benzene rings in **2a**, on the other hand, undergo partial stacking with resorcinol rings of host **1a** in neighboring sheets (cf Figure 9), which are not shown again in Figure 10 for clarity.

Crystal structures of ethyl benzoate and propyl benzoate adducts

The crystal structures of the ethyl and propyl benzoate adducts **1a**•2(**2b**) and **1a**•2(**2c**) are similar to that of adduct **1a**•2(**2f**) in respect to the space group ($P2_1/n$) and the mode of guest binding (parallel).[20] The anthracene-resorcinol dihedral angles ($\varphi = \varphi'$, referring to Figures 3c and 7c) in regard to incorporated guest molecules decrease in the order **2f** > **2c** > **2b**. The tilt angles (ϕ, referring to Figures 3c and 7c) between two hydrogen-bonded resorcinol rings decrease in the same order; **2f** > **2c** > **2b**. Because of this compensation in φ and ϕ, the anthracene-anthracene distances (l_{a-a}) are kept rather constant among adducts **1a**•2(**2b**), **1a**•2(**2c**), and **1a**•2(**2f**). On the other hand, the decreasing sizes of bound guests **2f** > **2c** > **2b** > **2a** are sensitively reflected on the sheet-to-sheet distances (l_{s-s}). All the actual values are shown in Table 1.

Power pattern X-ray diffraction and solid-state guest-binding properties

The crystallinity of an organic solid can be conveniently evaluated by X-ray powder diffraction. All the single crystals of the adducts obtained by direct recrystallization exhibited sharp diffraction patterns, as typically shown in Figure 11a and b for adducts **1a**•2(**2a**) (space group, $C2/c$) and **1a**•2(**2b**) ($P2_1/n$), respectively. Adducts **1a**•2(**2c**) and **1a**•2(**2f**), which belong to the same space group ($P2_1/n$) as **1a**•2(**2b**), show more or less similar diffraction patterns as **1a**•2(**2b**). They exhibit characteristic diffractions at $2\theta \cong 13°$ and 8° (cf Figure 11b) with calculated spacings of $d \cong 7$Å and 10 Å ($2d\sin\theta = \lambda$), respectively. They may correspond to the sheet-to-sheet (l_{s-s}) and column-to-column (l_{c-c}) distances. The actual values of d/Å are 6.93 and 10.3 (**1a**•2(**2b**)), 7.2–7.3 and 10.36 (**1a**•2(**2c**)), and 7.45 and 10.18 (**1a**•2(**2f**)), which are in fact close to the corresponding l_{s-s} and l_{c-c} values (Table 1).

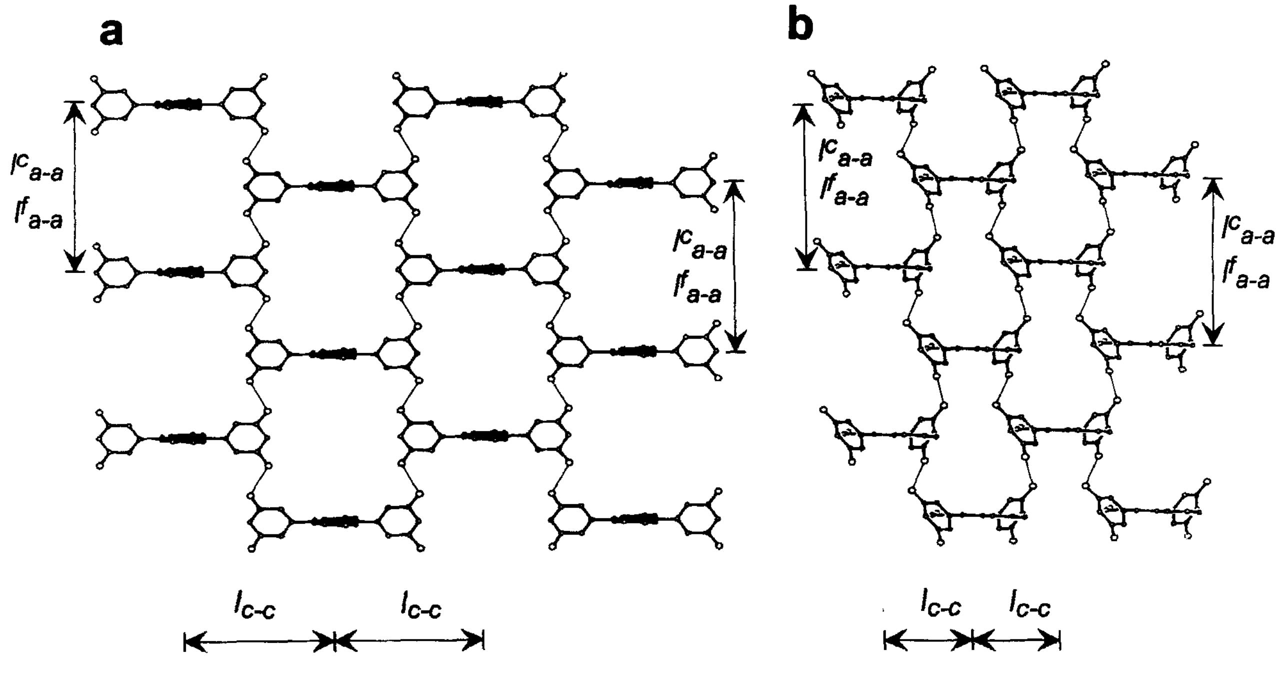


Figure 8 Hydrogen-bonded network in a molecular sheet of the crystal of adduct **1a**•2(**2a**), viewed from two different directions (a and b).

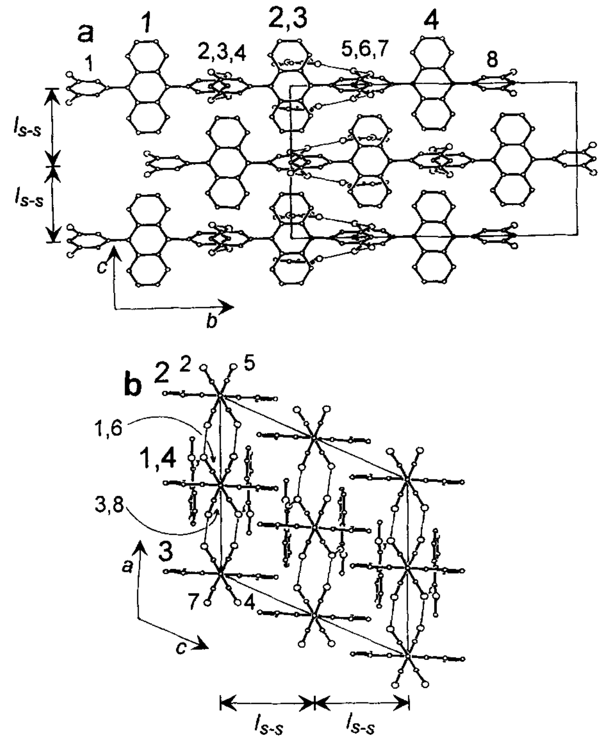


Figure 9 Arrangement of three adjacent guest-binding supramolecular cavities in three neighboring molecular sheets in the crystal of adduct **1a**•2(**2a**); top view (a) and side view (b). The anthracene and resorcinol rings having the same number in this Figure (a and b) and Figure 10 (a and b) correspond to each other.

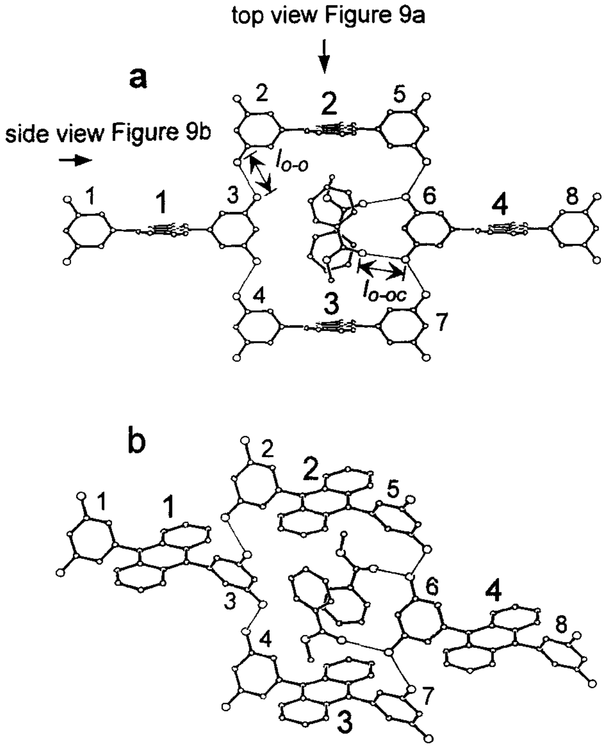


Figure 10 Packing geometry for two methyl benzoate molecules incorporated in the supramolecular cavity in the crystal of adduct **1a**•2(**2a**), viewed from two different directions (a and b). The anthracene and resorcinol rings having the same number in this Figure (a and b) and Figure 9 (a and b) correspond to each other.

We could so far never obtain single crystals of host **1a** without any included guest molecules. Recrystallization of **1a** from a low-boiling solvent such as ethyl acetate or a mixture of ethyl acetate and benzene afforded single crystals **1a**•2($CH_3CO_2CH_2CH_3$) or **1a**•2($CH_3CO_2CH_2CH_3$)•2(C_6H_6)$_2$,[15] respectively. Upon heating in vacuo, they lost most of guest molecules, giving **1a**•0.5($CH_3CO_2CH_2CH_3$) whose diffraction pattern is shown in Figure 11c. There are a set of diffractions including those at $2\theta = 11.33°$ ($d = 7.82$ Å) and $7.93°$ ($d = 11.16$ Å), corresponding to $l_{a\text{-}a}$ and $l_{c\text{-}c}$, respectively. Thus, this solid material, **1a**•0.5($CH_3CO_2CH_2CH_3$), still possesses a significant degree of crystallinity and the supramolecular cavities are preserved.[21] This material, when dipped in methyl benzoate (**2a**), rapidly picked up two molecules of **2a** with concomitant loss of the acetate, giving rise to adduct **1a**•2(**2a**)[22], whose diffraction pattern is shown in Figure 11d.

Another interesting observation is the guest exchange. The alkyl benzoate adducts as well as **1a**•0.5($CH_3CO_2CH_2CH_3$) are not soluble in an alkyl benzoate solvent at room temperature. When, for example, single crystals of the ethyl benzoate adduct **1**•2(**2b**) were dipped in methyl benzoate (**2a**), they were converted to the methyl benzoate adduct **1**•2(**2a**)[23,24], whose diffraction pattern is shown in Figure 11e. The diffraction patterns in Figures 11d and 11e are nearly identical with that for the *single-crystalline* sample of this adduct obtained by direct recrystallization (Figure 11a), although diffractions in the former are somewhat broader than those in the latter and relative intensities of various diffractions are not necessarily the same between these two cases. Both the crystalline adducts obtained by solid-state guest-binding and guest-exchange must have the same crystal structure as the genuine single crystal of this adduct.

Crystallization of host **1a** from an equimolar mixture of methyl benzoate (**2a**) and ethyl benzoate (**2b**) affords a mixed adduct **1a**•0.4(**2a**)•1.6(**2b**) (vide supra, Table 2, entry 3), whose diffraction pattern is shown in Figure 11f. This is very similar to that for the *pure* adduct **1a**•2(**2b**) (Figure 11b); there is almost no sign of the diffractions characteristic of adduct **1a**•2(**2a**) (Figure 11a). These results are indicative of the homogeneity of the structure of the mixed adduct. It possesses the **2b**-induced hydrogen-bonded network and supramolecular cavities incorporating the more-favored (**2b**) and the less-favored (**2a**) guests with different affinities.

DISCUSSION

Hydrogen-bonded network and supramolecular cavities

Host **1a** forms a hydrogen-bonded network. This necessarily generates *large* cavities ceiled and bottomed by

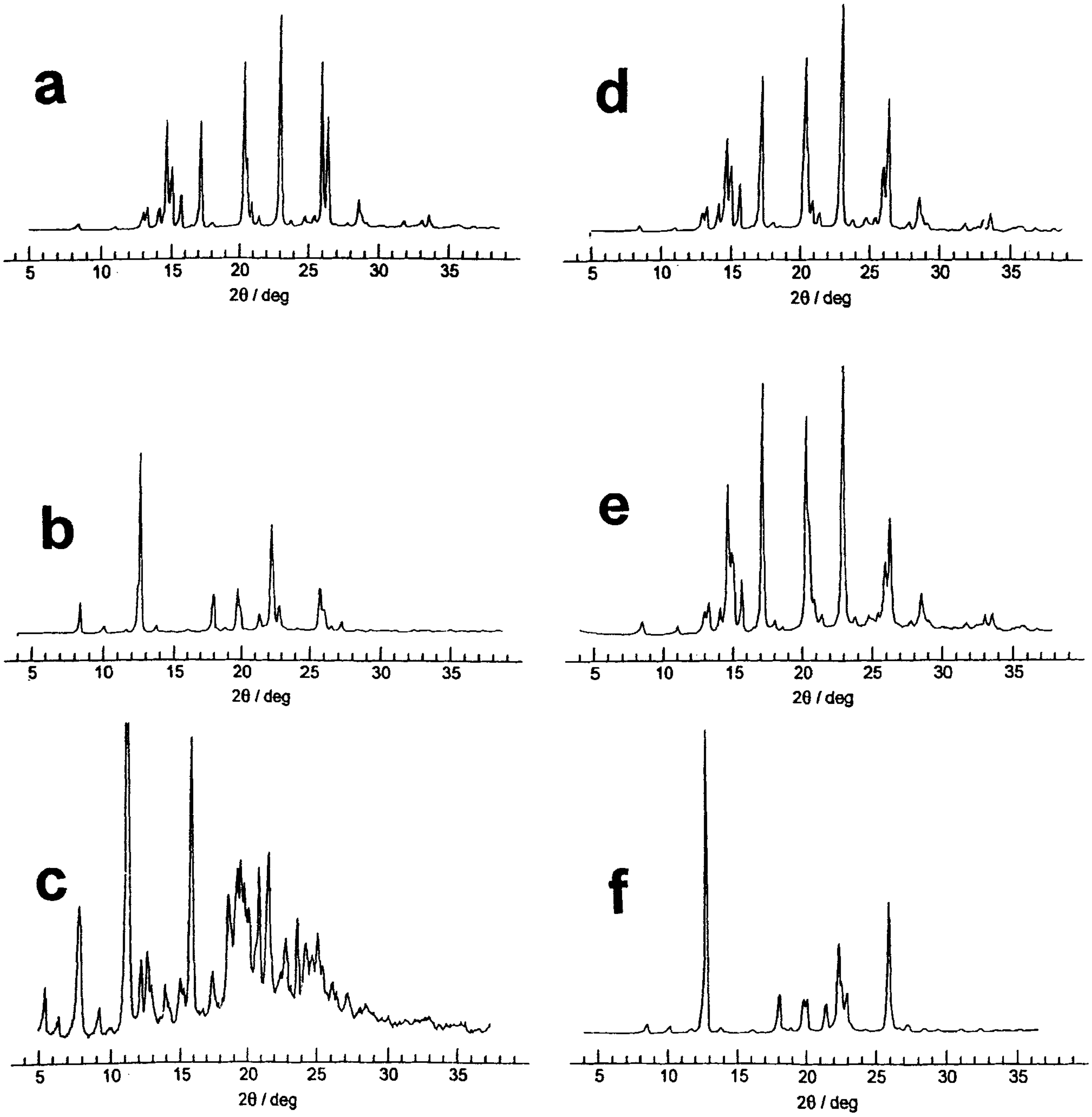


Figure 11 Powder-pattern X-ray diffractions for single crystals of adduct **1a**•2(**2a**) (a), single crystals of adduct **1a**•2(**2b**) (b), crystalline materials of apohost **1a**•0.5($CH_3CO_2CH_2CH_3$) (c), adduct **1a**•2(**2a**) obtained by the crystalline-phase guest-exchange (d), adduct **1a**•2(**2a**) obtained by the crystalline-phase guest-binding (e), and mixed adduct **1a**•0.4(**2a**)•1.6(**2b**) (f). See text for the details of the preparation of samples.

the (nearly) orthogonal anthracene rings. The cavities are filled with guest molecules. The calculated densities for the adducts are d_{HG} = 1.23–1.31 g/cm^3 (Table 1). Those for the hypothetical host crystal with excluded guest molecules are d_H = 0.67–0.77 g/cm^3 (Table 1), consistent with the highly porous nature.[25] The high-melting (mp > 360 °C) thermal stability and the low-density porous nature of the crystals of host **1a** are of the same origin, i.e., the novel and strong hydrogen-bonded network. The basic structures of the network are similar for various alkyl benzoate adducts. They contain staggered-layered molecular sheets composed of zigzag-arranged polyresorcinol chains and parallel-aligned anthracene columns. In this respect, the supramolecular cavities are rather rigid as far as the present variation in the alkyl groups of alkyl benzoates as guests is concerned. At the same time, however, they still exhibit some degree of flexibility to allow induced-fit adjustments to guest structures.[26] This is done by manipulating the intramolecular (anthracene-resorcinol dihedral angle) and intermolecular conformation (tilt angle between two hydrogen-bonded resorcinol rings) of compound **1a** on one hand and the sheet-to-sheet distance in the crystal on the other.

Molecular recognition in supramolecular cavities

The 1:2 (host-to-guest) stoichiometry is readily understood in terms of essential host-guest hydrogen bonding as confirmed by both crystallography and IR spectroscopy;[18] there are two such hydrogen-bonding sites in each cavity. The hydrogen bonding, however, must not be the sole governing factor, since there is a notable selectivity in the guest binding or adduct formation for a series of closely related guest esters, e.g., 1:70 between methyl benzoate (**2a**) and isobutyl benzoate (**2f**). A control experiment using a piece of single crystal of the methyl benzoate adduct dipped in a saturated solution of host **1a** in an equimolar mixture of methyl benzoate and isobutyl benzoate indicates a preferential crystal growth of the isobutyl benzoate adduct on the crystal surface with concomitant methyl-to-isobutyl guest-exchange in the crystalline phase. Furthermore, the mixed adduct **1a**•0.4(**2a**)•1.6(**2b**) obtained by competitive crystallization shows an X-ray powder diffraction patterns which is very similar to that of the pure adduct **1a**•2(**2b**). An indication of this is that even the less-favored guest **2a** is entrapped in the cavities suited for the more-favored one **2b**. These results demonstrate that the observed selectivity should be ascribed not to any difference in the rate processes, such as nucleation, of crystallization but to molecular recognition in the supramolecular cavities.

The isobutyl benzoate molecule as a guest is slightly longer than the long axis of the anthracene moiety of compound **1a**. When the benzene ring of the former sits on one of the terminal benzene rings of the latter, the two terminal methyl groups in the former, i.e., the guest, extend beyond the anthracene ring (Figure 5). In this way, not only the supramolecular cavity but also the space between neighboring sheets can be nicely filled or packed with two molecules of isobutyl benzoate (**2f**) (Figures 5 and 6). The cavity packing would also be sensitively controlled by the face-to-face anthracene-anthracene distance ($l^{f}_{a\text{-}a}$). The latter in turn depends on the tilt angle (ϕ, Figure 3) between the resorcinol rings in the hydrogen-bonded polyresorcinol chain. The zigzag nature of the latter may have this significance.

The crystal packing would not be so good with ethyl benzoate (**2b**) or propyl benzoate (**2c**) as a guest. The sheet-to-sheet distance ($l_{s\text{-}s}$, referring to Figures 5 and 9) for adduct **1a**•2(**2b**) is smaller than those for adducts **1a**•2(**2c**) or **1a**•2(**2f**) only by 0.33 or 0.57 Å (Table 1), respectively, which is much shorter than a carbon-carbon bond distance, i.e., the difference in alkyl chain-lengths between guests **2b** and **2c** or **2f**. Along these lines is understandable the selectivity in the binding of alkyl benzoates, which is characterized by the optimal alkyl-chain length at propyl, the affinity-enhancing effects of methyl branching, and the highest-affinity occurring at the isobutyl group. A full interpretation of the selectivity, however, should be deferred until much information is available as to the competition between unfavorable nonbonded steric interactions and favorable high-efficiency crystal packing.[2a]

It is also interesting to note that the present guest-binding in the supramolecular cavity bears a striking resemblance to the guest-binding to the resorcinol cyclic tetramer host in homogeneous solutions.[27] Both systems involve a cooperation of hydrogen-bonding and what may be called the cavity packing.[18] The hydrogen-bonding sites in the host are provided by a pair of hydrogen-bonded OH groups of the resorcinol moieties. The cavity packing may actually be a combination of π-π stacking and CH-π interactions.[27d]

The methyl benzoate molecule seems to be too small in size to allow a good face-to-face interaction with the anthracene moiety. In order to avoid a lot of empty space to be generated, this small guest is perpendicularly bound in the quadratic prism-like cavity of proper size. This induced-fit adjustment of the cavity is a result of a remarkable cooperation of the intramolecular (anthracene-resorcinol dihedral angle) and intermolecular (tilt angle between two hydrogen-bonded resorcinol rings) conformational changes and a significant shrinkage of the sheet-to-sheet distance ($l_{s\text{-}s}$) (Table 1). This binding mode allows methyl-anthracene CH-π contacts (Figure 9) but seemingly weakens the host-guest hydrogen-bonding, the shift in carbonyl stretching frequency ($\Delta\nu_{C=O}$ = 30 cm^{-1}) being 7–16 cm^{-1} smaller as compared with those for other alkyl benzoate adducts (Table 1).

SUMMARY AND CONCLUDING REMARKS

There are many examples of porous inorganic crystals, where an extensive electrostatic or metal-coordination network leads to the formation of channel- (as in rutile), layer- (as in clay and graphite), or cage-like (as in zeolite) cavities.[28] The present work may provide a general strategy for the design of *porous organic crystals*.[29] Compound **1a** is an aromatic triad having two hydrogen-bonding responsible aromatic (resorcinol) rings with an intervening (nearly) orthogonal aromatic (anthracene) spacer. The symmetrically and divergently arranged OH groups in the former form an extensive hydrogen-bonded network with *enforced* anthracene columns (orthogonal aromatic-triad strategy). The resulting molecular sheets are layered to generate well-defined supramolecular cavities. Thus, host **1a** affords novel crystals having a high thermal stability, a porous nature, and a sheet (layer) structure. Each cavity incorporates two molecules of a variety of polar guest compounds via essential host-guest hydrogen-bonding. The binding of alkyl benzoates is highly selective with respect to the alkyl groups, depending on how they can fill or pack the supramolecular cavity as well as the space between neighboring sheets.

The structure of the supramolecular cavity is primarily governed by the *rigid* hydrogen-bonded network. It is, however, not completely rigid but is capable of "breathing" or undergoing a finer (induced-fit) adjustment to guest structures by manipulating the three freedoms left, i.e., the intramolecular conformation of host **1a**, the intermolecular geometry of two hydrogen-bonded resorcinol rings, and the crystal-phase sheet-to-sheet distance. In this respect, the present supramolecular cavity bears relevance to the active sites of enzymes. The cavity is of the cyclophane type. In this respect, it bears relevance to the covalently-constructed synthetic cyclophane hosts which occupy a central position in the current molecular recognition studies.

The present strategy may open the way to the prediction and design of particular crystal structures at least of the present type. Such important crystal-structure parameters as the anthracene-anthracene distance ($l_{a\text{-}a}$), the column-to-column distance ($l_{c\text{-}c}$), and, to some extent, even the sheet-to-sheet distance ($l_{s\text{-}s}$), and the size, shape, and nature of the supramolecular cavities are predictable on the basis of the molecular structure of host **1a**. These characteristic aspects suggest a potential use of this type of porous organic crystalline solids as a new class of receptors, catalysts, and adsorbents, i.e., as an organic counterpart of a variety of inorganic porous materials such as zeolites.

Another important implication of this work is that the present strategy would also provide a clue to achieve molecular alignments in crystals. By proper choice of incorporated guest molecules, one may achieve an anthracene-guest donor-acceptor alternation along the column. The aromatic spacers and hydrogen-bonding sites could be changed in various ways. The targets in further work which is now under way in our laboratory include (1) shortening of the face-to-face aromatic-aromatic distance, (2) alternation of different types of columns such as donor column and acceptor column,[30] and (3) construction of three-dimensional hydrogen-bonded networks, thereby giving rise to highly-structured molecular polymers.

EXPERIMENTAL SECTION

General procedures

^{1}H NMR spectra were taken on a JEOL-GX 270 or a JEOL EX 400 spectrometer. IR spectra were obtained with a JASCO IR-810 spectrophotometer. Microanalyses were performed at the microanalysis center of Kyoto University.

X-ray crystal structure determinations

Single-crystals of adducts **1a**•2(**2a**), **1a**•2(**2b**), **1a**•2(**2c**), and **1a**•2(**2f**) suitable for X-ray analysis were obtained by crystallization of host **1a** from respective guest solvents (vide infra). Crystal data are summarized in Table 1. Diffraction data were obtained with an Enraf Nonius CAD4 four-circle automated diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Selected crystals were mounted in glass capillaries. The reflection intensities were monitored by three standard reflections every 2 h; the decays of intensities for all crystals were within 2%. Intensity data were corrected for both Lorentz and polarization effects. An absorption correction was applied in each case with the program DIFABS.[31]

The structures were solved by use of the program SIR88[32] and refined anisotropically for non-hydrogen atoms by full-matrix least-squares calculations. Each refinement was continued until all shifts were smaller than one-third of the standard deviations of the parameters involved. Atomic scattering factors and anomalous dispersion terms were taken from International Tables for X-ray Crystallography.[33] Hydrogen atoms except for disordered ones were introduced at calculated positions (C-H = 0.95 Å) and their parameters were isotropically refined. The final R and R_w values of all crystals were summarized in Table 1. The weighting scheme $w^{-1} = (\sigma^2(Fo) + (0.015Fo)^2)$ was employed for all crystals. The positions of disordered guest molecules in adducts **1a**•2(**2b**) and **1a**•2(**2f**) were not located.[20] The calculations were performed on a micro VAX 3100 computer by using the Enraf-Nonius SDP[34] set of computer programs.

9,10-Bis(3,5-dihydroxy-1-phenyl)anthracene (1a) and 9,10-Bis(3,5-dimethyl-1-phenyl)anthracene (1b)

Compound **1a** was obtained by the nickel-catalyzed coupling reaction of 9,10-dibromoanthracene and 3,5-dimethoxy-1-phenylmagnesium chloride,[35] followed by demethylation of the resulting tetramethoxy derivative with BBr_3.[36] Thus, a THF solution (30 mL) of the Grignard reagent prepared from 1-chloro-3,5-dimethoxybenzene (10.0 g, 57.9 mmol) and magnesium (2.11 g, 86.9 mmol) was added dropwise under nitrogen into a solution of 9,10-dibromoanthracene (5.83 g, 15.3 mmol) and $NiCl_2$•bis(diphenylphosphinopropane) (0.19 g, 0.15 mmol) in a mixture of benzene (220 mL) and THF (150 mL) at 40°C in a period of 24 h. The mixture was stirred at room temperature for 12 h, poured into water, and extracted with ether. The ether extract was washed with aqueous HCl (2 N), water, saturated aqueous $NaHCO_3$, water, and saturated aqueous NaCl in this order and dried (Na_2SO_4). Removal of the ether gave the crude product which was reprecipitated from dichloromethane-hexane, chromatographed on silica gel with a mixed solvent of hexane, ether, and dichloromethane (5:1:1) as eluent, and finally recrystallized from a mixture of hexane and dichloromethane to afford pale-yellow crystals of 9,10-bis(3,5-dimethoxy-1-phenyl)anthracene (2.9 g, 37%): mp 280°C; (1^{H} NMR (DMSO-d_6) δ 3.87 (s, 12 H, OCH_3), 6.48 (t, 2 H, Ar-H), 6.73 (d, 4 H, Ar-H), 7.35 (double d, 4 H, Ar-H), 7.78 (double d, 4 H, Ar-H).

Into a CH_2Cl_2 solution (80 mL) of the tetramethoxy derivative thus obtained (2.59 g, 5.75 mmol) was added dropwise a CH_2Cl_2 solution (40 mL) of BBr_3 (3.2 mL, 34.5 mmol) in a period of 12 h at 0 °C. The mixture was poured into water and extracted with ether. The ether extract was washed with aqueous saturated $NaHCO_3$, water, and aqueous saturated NaCl in this order and dried (Na_2SO_4). Removal of the ether gave the crude product which was chromatographed on silica gel with a mixed solvent of hexane and ethyl acetate (5:1) as eluent, treated with active charcoal, and recrystallized from a mixture of ethyl acetate and benzene (vide infra) to afford single crystals of adduct **1a**$\bullet 2(CH_3CO_2CH_2CH_3)\bullet 2(C_6H_6)$ (2.0 g, 92%): ^{1}H-NMR (DMSO-d_6) δ 6.23 (d, 4 H, Ar-H), 6.40 (t, 2 H, Ar-H), 7.39 (doubled d, 4 H, Ar-H), 7.68 (double d, 4 H, Ar-H), 9.45 (s, 4 H, OH), 1.17 (t, 6 H, CH_2CH_3), 1.99 (s, 6 H, CH_3CO), 4.01 (q, 4 H, CH_2), 7.32 (s, 12 H, C_6H_6). When the single crystals thus obtained (approximate size, 2 × 1 × 1 mm^3) were heated at 80 °C in vacuo for 10 h, most of the solvent molecules were removed to leave a turbid solid with a composition of **1a**$\bullet 0.5(CH_3CO_2CH_2CH_3)$. This material was ground into fine powders and heated again at 80 °C in vacuo for 10 h to give solvent-free **1a**: mp > 360 °C. Anal. Calcd for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 78.88; H, 4.44.

Reference compound **1b** was prepared in a yield of 50% by the coupling reaction of 9,10-dibromoanthracene and 3,5-dimethyl-1-phenylmagnesium chloride in a similar manner as above: mp 250 °C (decomp.); ^{1}H NMR (CD_2Cl_2) δ 2.40 (s, 12 H, CH_3), 7.08 (d, 4 H, Ar-H), 7.21 (t, 2 H, Ar-H), 7.33 (double d, 4 H, Ar-H), 7.69 (double d, 4 H, Ar-H). Anal. Calcd for $C_{30}H_{26}$: C, 93.22; H, 6.78. Found: C, 93.24; H, 6.77.

Recrystallization

The crude product of compound **1a** (ca. 1 g) was dissolved in ethyl acetate (30 mL). Benzene (30 mL) was added slowly with careful stirring to avoid precipitation of **1a** on the wall of the flask. The resulting solution was kept in an atmosphere of benzene vapor in a sealed container. Single crystals of adduct **1a**$\bullet 2(CH_3COI_2CH_2CH_3)\bullet 2(C_6H_6)$ of an approximate size of 2 × 1 × 1 mm^3 separated in a couple of days.

Guest-free compound **1a** (ca. 20 mg) was dissolved in 10–15 mL of a high-boiling guest solvent such as alkyl benzoate or an equimolar mixture of two such guest solvents at 140–150 °C under nitrogen. The resulting solution was allowed to cool down at a rate of 1 °C/min. Crystals of the host-guest adduct(s) (approximate size, 2 × 1 × 1 mm^3) which separated, in most cases, at temperatures < 70 °C were collected by filtration. They were washed with propylbenzene and wiped with a filter paper. The washing-wiping cycle was repeated two or three times to remove a trace of solvent on the crystal surface. At least ten pieces of such crystals were combined and dissolved in DMSO-d_6 for ^{1}H NMR analysis for the amount(s) of guest molecule(s) incorporated.

Guest exchange and guest binding in the solid state

Into an appropriate guest solvent (X, 30 mL) was added ca. 200 mg of the single crystals of adduct **1a**•2(Y) or **1a**$\bullet 2(CH_3CO_2CH_2CH_3)\bullet 2(C_6H_6)$. The single crystals were of a similar size (approximately 2 × 1 × 1 mm^3). The mixture was left at room temperature without stirring. About ten pieces of the crystals were picked up at appropriate time intervals and got rid of the solvent on the surface as above. They were analyzed by ^{1}H NMR for the amounts of guest molecules incorporated to allow the extent of guest exchange to be evaluated. The yield in terms of weight of the recovered crystal was ~ 100% in every case, indicating that there had been no dissolution-loss of host **1a** during the guest-exchange process.

Pieces of apohost **1a**$\bullet 0.5(CH_3CO_2CH_2CH_3)$ were obtained by heating single crystals (approximate size, 2 × 1 × 1 mm^3) of adduct **1a**$\bullet 2(CH_3CO_2CH_2CH_3)\bullet 2(C_6H_6)$ at 80 °C in vacuo (vide supra). Although they became no longer transparent but turbid, they appeared to retain the shape and size of the original single crystal. The solid-state binding of methyl benzoate to the apohost thus obtained was carried out similarly as above.

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REFERENCES AND NOTES

1 Responsible for the X-ray crystal structure determinations.

2 (a) Kitaigorodsky, A.I. *Molecular Crystals and Molecules*; Academic press: New York, **1973**. (b) Wright, J.D. *Molecular Crystals*, Cambridge University Press: Cambridge, **1987**. (c) Desiraju, G.R. *Crystal Engineering: The Design of Organic Solids*, Elsevier: New York, **1989**.

3 Gavezzotti, A. *J. Am. Chem. Soc.*, **1991**, *113*, 4622.

4 (a) Etter, M.C., *Acc. Chem. Res.*, **1990**, *23*, 120. (b) Lehn, J.-M. *Angew. Chem.*, **1990**, *102*, 1347; *Angew. Chem. Int. Ed. Engl.*, **1990**, *29*, 1304. (c) Whitesides, G.M.; Mathias, J.P.; Seto, C.T. *Science*, **1991**, *254*, 1312.

5 For recent examples of ordered structure formation for cocrystals arising from ditopic and complementary host and guest, see: (a) Lehn, J.-M.; Mascal, M.; Decian, A. Fischer, J. *J. Chem. Soc., Chem. Commun.*, **1990**, 479. (b) Ducharme, Y.; Wuest, J.D. *J. Org. Chem.*, **1988**, *53*, 5787. (c) Seto, C.T.; Whitesides, G.M. *J. Am. Chem. Soc.*, **1990**, *112*, 6409. (d) Etter, M.C.; Urbanczyk-Lipkowska, Z.; Zia-Ebrahimi, M.; Panunto, T.W. *Ibid.*, **1990**, *112*, 8415. (e) Zerkowski, J.A.; Seto, C.T.; Wierda, D.A.; Whitesides, G.M. *Ibid.*, **1990**, *112*, 9025. (f) Seto, C.T.; Whitesides, G.M. *Ibid.*, **1991**, *113*, 712. (g) Geib, S.J.; Hirst, S.C.; Vicent, C.; Hamilton, A.D. *J. Chem. Soc., Chem. Commun.*, **1991**, 1283. (h) Garcia-Tellado, F.; Geib, S.J.; Goswami, S.; Hamilton, A.D. *J. Am. Chem. Soc.*, **1991**, *113*, 9265. (i) Gallant, M.; Viet, M.T.P.; Wuest, J.D. *J. Org. Chem.*, **1991**, *56*, 2284. (j) Zerkowski, J.A.; Seto, C.T.; Whitesides, G.M. *Ibid.*, **1992**, *114*, 5473.

6 (a) Ermer, O. *J. Am. Chem. Soc.*, **1988**, *110*, 3747. (b) Zhao, X.; Chang, Y.-L.; Fowler, F.W.; Lauher, J.W. *Ibid.*, **1990**, *112*, 6627. (c) Simard, M.; Su, D.; Wuest, J.D. *Ibid.*, **1991**, *113*, 4696.

7 (a) Leiserowitz, L.; Tuval, M. *Acta Crystallogr.*, **1978**, *B34*, 1230. (b) Leiserowitz, L.; Hagler, A.T. *Proc. R. Soc. London A*, **1983**, *388*, 133. (c) Etter, M.C.; Adsmond, D.A. *J. Chem. Soc., Chem. Commun.*, **1990**, 589. (d) Etter, M.C.; Urbanczyk-Lipkowska, Z.; Zia-Ebrahimi, M.; Panunto, T.W. *J. Am. Chem. Soc.*, **1990**, *112*, 8415. (e) Etter, M.C.; Reutzel, S.M. *Ibid.*, **1991**, *113*, 2586.

8 (a) Toda, F. *Top. Curr. Chem.*, **1987**, *140*, 43. (b) Tanaka, K.; Toda, F. *Nippon Kagaku Kaishi*. **1988**, 1643. (c) Toda, F. In *Advances in Supramolecular Chemistry*; Gokel, G.W., Ed.; JAI Press: Greenwich, CT, **1992**; Vol. 2, pp 141 - 191.

9 Rebek, J. Jr.; Askew, B.; Killoran, M.; Nemeth, D.; Lin, F.-T. *J. Am. Chem. Soc.*, **1987**, *109*, 2426.

10 For the host-guest complexation involving convergent ortho hydroxyl groups, see: (a) Aoyama, Y.; Asakawa, M.; Yamagishi, A.; Toi, H.; Ogoshi, H. *J. Am. Chem. Soc.*, **1990**, *112*, 3145. (b) Aoyama, Y.; Asakawa, M.; Matsui, Y.; Ogoshi, H. *Ibid.*, **1991**, *113*, 6233.

11 For the lattice inclusion compounds of aliphatic bicyclic or tricyclic diols having either ellipsoidal cavities (the ellipsoidal clathrate type) or helical canals (the helical tubulate type), see: (a) Bishop, R.; Dance, I.G. *Inclusion Compounds*; Atwood, J.L.; Davies, J.E.D.; MacNicol, D.D., Ed.; Oxford University Press: Oxford, **1991**, Vol. 4, pp 1 - 26 and references therein. (b) Bishop, R.; Craig, D.C.; Dance, I.G.; Scudder, M.L.; Ung, A.T. *Supramolecular Chem.*, **1993**, *1*, 123. (c) Bishop, R.; Craig, D.C.; Dance, I.G.; Kim, S.; Mallick, M.A.I.; Pich, K.C.; Scudder, M.L.*Ibid.*, **1993**, *1*, 171. (d) Ung, A.T.; Bishop, R.; Craig, D.C.; Dance, I.G.; Scudder, M.L *Tetrahedron*, **1993**,. *49*, 639. (e) Bishop, R.; Craig, D.C.; Dance, I.G.; Scudder, M.L. *J. Chem. Soc., Perkin Trans. 2*, **1993**, 937.

12 For the lattice inclusion compounds of cholic acid derivatives having channel-like cavities, see: (a) Miyata, M.; Shibakami, M.; Takemoto, K. *J. Chem. Soc., Chem. Commun.*, **1988**, 655. (b) Miki, K.; Masui, A.; Kasai, N.; Miyata, M.; Shibakami, M.; Takemoto, K. *J. Am. Chem. Soc.*, **1988**, *110*, 6594. (c) Sada, K.; Kondo, T.; Miyata, M.; Tamada, T.; Miki, K. *J. Chem. Soc., Chem. Commun.*, **1993**, 753.

13 For the lattice inclusion compounds of a rigid tetrapyridone having a diamondoid network with large internal chambers, see ref 6c.

14 (a) Byrn, M.P.; Curtis, C.J.; Goldberg, I.; Hsiou, Y.; Khan, S.I.; Sawin, P.A.; Tendick, S.K.; Strouse, C.S. *J. Am. Chem. Soc.*, **1990**, *23*, 3331. (b) Gnaim, J.M.; Green, B.S.; Arad-Yellin, R.; Vyas, K.; Levy, J.T.; Frolow, F.; Keehn, P. *Ibid.*, **1992**, *114*, (1915). (c) Hayashi, N.; Mazaki, Y; Kobayashi, K. *Chem. Lett.*, **1992**, 1689.

15 The crystal structure for the 1:2:2 cocrystal of host **1a**, ethyl acetate, and benzene, **1a**•$2(CH_3CO_2CH_2CH_3)$•$2(C_6H_6)$, has been reported in a preliminary form: Kobayashi, K.; Endo, K.; Aoyama, Y.; Masuda, H. *Tetrahedron Lett.*, **1993**, *34*, 7929.

16 Toda and coworkers have been extensively studying the solid-state guest-binding properties of various phenols, alcohols, and amides as hosts (ref 8).

17 Host **1a** forms 1:2 adducts with acetophenone, diethyl ketone, nitrobenzene, and *N,N*-dimethylaniline in a similar manner as with ester guests.

18 Phenol, alcohol, and amide derivatives having some level of rigidity are known to form crystalline inclusion complexes with a variety of guest molecules. They often exhibit a remarkable selectivity arising from a combination of host-guest hydrogen-bonding and crystal packing (ref 8). Also see: (a) Toda, F.; Tanaka, K.; Mak, T.C.W. *Tetrahedron Lett.*, **1984**, *25*, 1359. (b) Toda, F.; Tanaka, K.; Mak, T.C.W. *Bull. Chem. Soc. Jpn.*, **1985**, *58*, 2221. (c) Toda, F.; Tanaka, K.; Mak, T.C.W. *J. Inclusion Phenomen*, **1985**, *3*, 225. (d) Toda, F.; Tanaka, K.; Nagamatsu, S.; Mak, T.C.W. *Isr. J. Chem.*, **1985**, *25*, 346. (e) Toda, F.; Tagami, Y.; Mak, T.C.W. *Chem. Lett.*, **1986**, 113. (f) Toda, F.; Tagami, Y.; Mak, T.C.W. *Ibid.*, **1986**, 1909. (g) Toda, F.; Kai, A.; Tagami, Y.; Mak, T.C.W. *Ibid.*, **1987**, 1393. (h) Goldberg, I.; Stein, Z.; Tanaka, K.; Toda, F. *J. Inclusion Phenomena*, **1988**, *6*, 15.

19 As shown in Figures 5 and 6, the benzene ring of isobutyl benzoate is not perfectly parallel with respect to the anthracene ring.

20 In all crystals except for **1a**•2(**2a**), the guest molecules showed some degree of disorder. That in propyl benzoate (**2c**) appeared in the terminal methyl groups. That in ethyl benzoate (**2b**) or isobutyl benzoate (**2f**) was with regard to the orientation of the benzene ring and the alkyl group. In addition to the normal and major binding mode as shown in Figure 5, a reversed and minor binding mode was also observed in which the aromatic and aliphatic moieties have been exchanged by undergoing a 180° rotation around the fixed C=O bond. The fraction of the minor binding mode was very small as compared with the major binding mode but could not be accurately determined.

21 Cavities in inclusion lattices often collapse in the absence of guest molecules. In some cases, however, such cavities are retained in their absence. See: (a) MacNicol, D.D.; McKendrick, J.J.; Wilson, D.R. *Chem. Soc. Rev.*, **1978**, *7*, 65. (b) Atwood, J.L.; Davies, J.E.D.; MacNicol, D.D. *Inclusion Compounds*; Academic Press: New York, **1983**, Vol. 1–3. (c) Ung, A.T.; Bishop, R.; Craig, D.C.; Dance, I.G; Scudder, M.L. *J. Chem. Soc., Chem. Commun.*, **1991**, 1012. (d) Bishop, R.; Craig, D.C.; Dance, I.G.; Scudder, M.L.; Ung, A.T. *Mol. Cryst. Liq. Cryst.*, **1992**, *211*, 141.

22 Toda, et al., have shown that the complexation not only between solid host and liquid guest but also between solid host and solid guest is a rather general phenomenon (ref 8). Also see: Toda, F., Tanaka, K.; Sekikawa, A. *J. Chem. Soc., Chem. Commun.*, **1987**, 279.

23 For the crystalline-phase guest-addition, -removal, and -exchange in the cholic acid intercalation crystals, see: (a) Miyata, M; Shibakami, M.; Chirachanchai, S.; Takemoto, K.; Kasai, N.; Miki, K. *Nature*, **1990**, *343*, 446. (b) Miyata, M.; Sada, K.; Hori, S.; Miki, K. *Mil. Cryst. Liq. Cryst.*, **1992**, *219*, 71. For adsorption of gases with diannin's compounds (4-*p*-hydroxyphenyl-2,3,4-trimethylchroman), see: Barrer, R.M.; Shanson, V.H. *J. Chem. Soc., Chem. Commun.*, **1976**, 333.

24 No guest-exchange took place when single crystals of ethyl benzoate adduct **1a**•2(**2b**) were dipped in propylbenzene.

25 The densities of simple aromatic compounds are definitely higher than 1.0. For examples, those of anthracene (monoclinic) and resorcinol (orthorhombic) are 1.248 and 1.278 (α form) or 1.327 (β form), respectively (*Crystal Data*, 3rd Ed., Vol. 1; Donnay, J.D.H., Ondik, H.M., Ed., US Department of Commerce, National Bureau of Standards, and the Joint Committee on Powder Diffraction Standards: 1972.

26 For the guest control of diol inclusion host lattices, see: (a) Ref 11. (b) Ung, A.T., Bishop, R.; Craig, D.C.; Dance, I.G.; Scudder, M.L. *Struct. Chem.*, **1992**, *3*, 59. (c) Ung, A.T., Bishop, R.; Craig, D.C.; Dance, I.G.; Scudder, M.L. *J. Chem. Soc., Chem. Commun.*, **1993**, 322.

27 (a) Aoyama, Y.; Tanaka, Y.; Sugahara, S. *J. Am. Chem. Soc.*, **1989**, *111*, 5397. (b) Kikuchi, Y.; Kato, Y; Tanaka, Y.; Toi, H.; Aoyama, Y. *Ibid.*, **1991**, *113*, 444. (c) Kikuchi, Y., Kobayashi, K., and Aoyama, Y. *Ibid.*, **1992**, *114*, 1351. (d) Kobayashi, K.; Asakawa, Y.; Kikuchi, Y.; Toi, H.; Aoyama, Y. *Ibid.*, **1993**, *115*, 2648.

28 See, for examples: (a) Whittingham, M.S.; Jacobson, A.J. *Intercalation Chemistry*; Academic Press: New York, **1982**. (b) Ref 24b.

29 Ref 6c and references cited therein.

30 The stacked (hetero) aromatic columns play essential roles in organic conductors and superconductors composed of electron

donor and acceptor. See, for examples: (a) Phillip, T.E.; Kistenmacher, T.L.; Ferraris, J.P; Cowan, D.O. *J. Chem. Soc., Chem. Commun.*, **1973**, 471. (b) Bechgaard, K.; Jacobson, C.J.; Mortensen, K.; Pedersen, H.J.; Thorup, N. *Solid State Commun.*, **1980**, *33*, 1119. (c) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K.; *J. Phys. Chem. (Paris)*, **1980**, *41*, 95. (d) Thorup, N.; Rindorf, G.; Soling, H.; Bechgaard, K. *Acta Cryst.*, **1981**, *B37*, 1236. (e) Jacobsen, C.S.; Tanner, D.B.; Bechgaard, K. *Phys. Rev. Lett.*, **1981**, *46*, 1142.

31 Walker, N.; Stuart, D.D. *Acta Crystallogr. Sect. A*, **1983**, *39*, 158.

32 Burla, M.C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Polidori, G.; Spagna, R.; Viterbo, D. *J. Appl. Cryst.*, **1989**, *22*, 389.

33 *International Tables for X-Ray Crystallography*, Ibers, J.A.; Hamilton, W.C., Ed.; Kynoch: Birmingham, **1974**. Vol. IV.

34 Frenz, B.A. Enraf-Nonius structure determination package. SPD users guide, Version 4. Enraf-Nonius, Delft, The Netherlands. **1985**.

35 Cf. Tamao, L.; Sumitani, K.; Kiso, Y.; Zembayashi, M.; Fujioka, A.; Kodama, S.; Nakajima, I.; Minato, A.; Kumada, M. *Bull. Chem. Soc. Jpn.*, **1976**, *49*, 1958.

36 Cf. McOmie, J.F.W.; West, D.E. *Organic Syntheses*; Wiley: New York, **1973**. Collec. Vol. V, pp 412 – 414.