

Guest-Binding Properties of Organic Crystals Having an Extensive Hydrogen-Bonded Network: An Orthogonal Anthracene–Bis(resorcinol) Derivative as a Functional Organic Analog of Zeolites

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Abstract: When recrystallized from an appropriate solvent, orthogonal bis(resorcinol)–anthracene compound **1a** as host forms molecular sheets involving an extensive hydrogen-bonded network. This generates supramolecular cavities which incorporate two molecules of recrystallization solvent such as ketones and esters as guests via host–guest hydrogen-bonding. The guest incorporation under competitive recrystallization conditions is highly selective; even a difference by one methylene group in the guests can be discriminated. The supramolecular cavities with included guest molecules are connected with each other, giving more or less continuous channels. Heating host–guest adducts in vacuo affords polycrystalline guest-free apohost. The apohost binds ketone and ester guests not only as liquids but also as gases and solids. The host:guest stoichiometry is 1:2 in most cases. Solid-state complexation using a 1:3 or 1:4 (host to guest) mixture affords 1:2 host–guest cocrystals and 1 or 2 equiv of unreacted guest simply remains as such. The adducts **1a**·2(guest) thus obtained under solid–liquid, solid–gas, or solid–solid conditions exhibit essentially the same powder X-ray diffraction patterns as their authentic single crystals. Apohost **1a** also binds hydrocarbons and haloalkanes such as benzene, *p*-xylene, and chloroform again in a 1:2 (host to guest) molar ratio. These results demonstrate that guest molecules can diffuse in the crystal lattices of apohost **1a**. As compared with the corresponding recrystallization processes, guest-binding to preformed apohost is apparently far less selective with respect to the guests. This is due to a kinetic preference for smaller guests, even without a hydrogen-bonding site as in hydrocarbons, which are capable of more facile lattice diffusion. The sorption–desorption of liquid and gaseous guests can be repeated many times. The guest-binding properties of apohost **1a** is discussed from a viewpoint of a functional organic counterpart of porous inorganic crystal zeolites.

Introduction

Zeolites are a class of porous inorganic polymers composed of aluminosilicate tetrahedra with a variety of cations.² They are capable of sorbing various guest molecules in the pores or cavities. This is a basis of a wide range of their practical uses. Is it possible to construct an organic analog of zeolites?³ This is all the present work is concerned with. An organic zeolite should first be capable of reversible guest-binding in a sto-

ichiometric manner. The guest molecules should be kept in internal cavities, which may be constructed^{4–6} by using intermolecular interactions such as hydrogen-bonding^{7–12} and metal coordination.¹³ The cavities should hopefully be maintained in the absence of any guest.^{14,15} From a functional point of view, however, this may not be essential; cavities that have

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(1) Responsible for the determination of crystal structures.

(2) Breck, D. W. *Zeolite Molecular Sieves, Structure, Chemistry, and Use*; John Wiley and Sons: New York, 1974.

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been collapsed due to crystal packing forces¹⁶ could be restored upon guest-binding.

We have recently introduced the *orthogonal aromatic-triad strategy* for the preparation of porous organic crystals.¹⁷ An orthogonal anthracene-bis(resorcinol) tetraol **1a** (Chart 1) as host forms an extensive hydrogen-bonded network to give a molecular sheet containing large supramolecular cavities, which incorporate two molecules of a recrystallization solvent as guests. In the present work, we investigated the guest-binding

(7) There are numerous previous examples of lattice inclusion compounds of aliphatic bicyclic or tricyclic diols having either ellipsoidal cavities (ellipsoidal clathrate type) or helical canals (helical tubulate type) (ref 8), cholic acid derivatives having channel-like cavities (ref 9), tetrahedrally substituted derivatives having diamondoid networks together with large internal chambers (ref 10), and others (ref 11). Phenols, alcohols, and amide derivatives having some level of rigidity are also 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 12).

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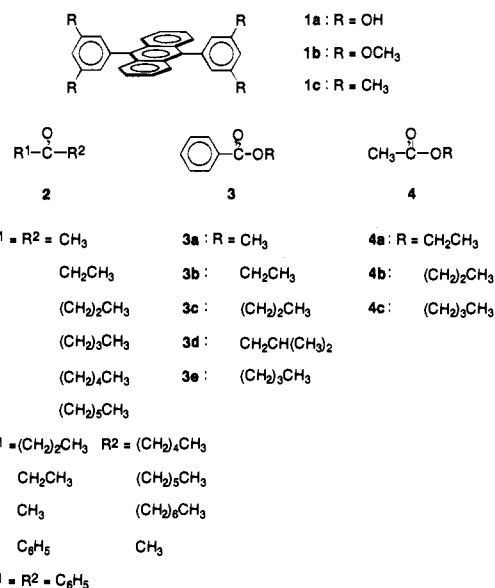
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Chart 1



properties of preformed guest-free apohost **1a**. One of fundamental questions pertaining to this work is how molecules diffuse in the solid.¹⁸ We report here that a great variety of polar and apolar guest molecules in various physical states (liquid, gas, and solid) can be bound to **1a** in a stoichiometric manner.⁷

Results and Discussion

Cocrystallization. Compound **1a** (Chart 1) is slightly soluble at elevated temperatures in more or less polar solvents such as ketones and esters. Crystals that separate upon cooling such a solution always contain solvent molecules as guests. The host-guest stoichiometry is 1:2 for such guests as ketones **2c–e, g, j, k** (vide infra), alkyl benzoates **3a–d**,¹⁷ alkyl acetates **4a–c** (Chart 1), and aromatic compounds including *m*-dimethoxybenzene, nitrobenzene, and *N,N*-dimethylaniline. On the other hand, smaller ketones such as acetone (**2a**) and 3-pentanone (**2b**) gave rise to a 1:4 (for **2a**) or 1:3 (for **2b**) host/guest ratio, while a larger ketone 7-tridecanone (**2f**) failed to give stable cocrystals. The IR spectra for the ketone adducts **1a**·**2**(**2**) in KBr pellets showed a significant shift (~ 20 cm^{-1}) in $\nu_{\text{C=O}}$ to a lower wavenumber as a result of host-guest hydrogen-bonding as in the case of ester adducts.^{17b}

The structure of the benzophenone adduct **1a**·**2**(**2k**) (monoclinic, $P2_1/n$) as a representative ketone adduct was determined by single-crystal X-ray diffraction. Characteristic aspects are as follows: (1) The anthracene and resorcinol rings in host **1a** are nearly perpendicular with each other. (2) Host **1a** forms an extensive hydrogen-bonded (O–H \cdots O–H) network with an O \cdots O distance of 2.73 Å, to give a molecular sheet composed of zigzag arranged polyresorcinol chains and face-to-face stacked anthracene columns (Figure 1a), where the face-to-face and center-to-center anthracene–anthracene distances and the column–column distance are $l_{\text{a-a}}^{\text{f}} = 13.34$ Å, $l_{\text{a-a}}^{\text{c}} = 13.88$ Å,

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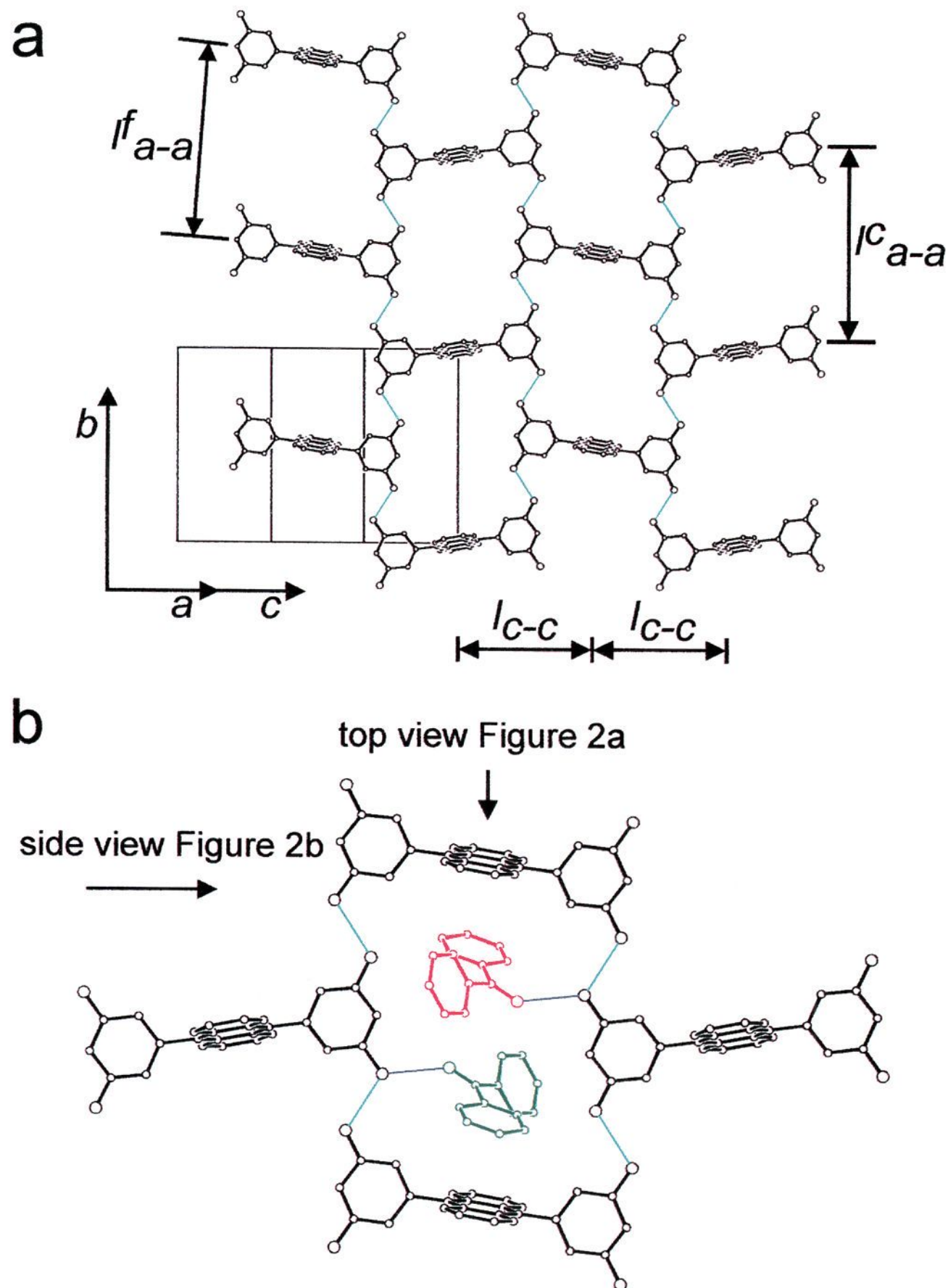


Figure 1. Crystal structure of adduct **1a·2(2k)**. Hydrogen-bonded network in a molecular sheet (a) and packing geometry for two benzophenone molecules incorporated in the supramolecular cavity (b). Hydrogen bonds are shown in blue and included guest molecules are shown in red and green.

and $l_{c-c} = 9.83 \text{ \AA}$. (3) Each supramolecular cavity thus generated binds two molecules of benzophenone via hydrogen-bonding ($\text{O}-\text{H}\cdots\text{O}-\text{H}\cdots\text{O}=\text{C}$) between a pair of hydrogen-bonded OH groups of the host and the carbonyl group of the guest with an $\text{O}\cdots\text{O}=\text{C}$ distance of 2.65 \AA (Figure 1b). (4) As shown in Figure 2, parts a (top view) and b (side view), molecular sheets are layered in a staggered manner with sheet-sheet distance of $l_{s-s} = 7.06 \text{ \AA}$. Thus, neighboring sheets slide laterally from each other (Figure 2a), while there is no slide or deviation in the longitudinal or vertical direction (Figure 2b). The supramolecular cavities in neighboring sheets similarly slide, as schematically shown in Figure 3a. As a consequence, the cavities in layered sheets along the a axis shown by an arrow in Figure 2a form a continuous channel or canal, as shown by the perspective view from this direction (Figure 4). The observed structure is essentially the same as those for ethyl,

propyl, and isobutyl benzoate adducts **1a·2(3b)**, **1a·2(3c)**, and **1a·2(3d)** (monoclinic, $P2_1/n$).^{17b}

Alkanone adducts **1a·2(2c)**, **1a·2(2d)**, and **1a·2(2e)** were also shown to have very similar crystal structures with respect to the hydrogen-bonded network. The crystal parameters will be shown later in Table 4. Unfortunately, however, refinement of crystal structures was hampered by an extensive disorder or enhanced mobility of the alkyl groups of included ketone guests (vide infra).

In marked contrast to host **1a**, the tetramethoxy and tetramethyl derivatives **1b**, **c** (Chart 1) as non-hydrogen-bonding reference hosts showed no guest-binding ability at all. Recrystallization of compound **1b** or **1c** from 5-nonanone (**2d**) or isobutyl benzoate (**3d**) as a highest-affinity guest only gave homocrystals of **1b** or **1c** without incorporation of the guest. These results clearly indicate that the guest-binding or enclath-

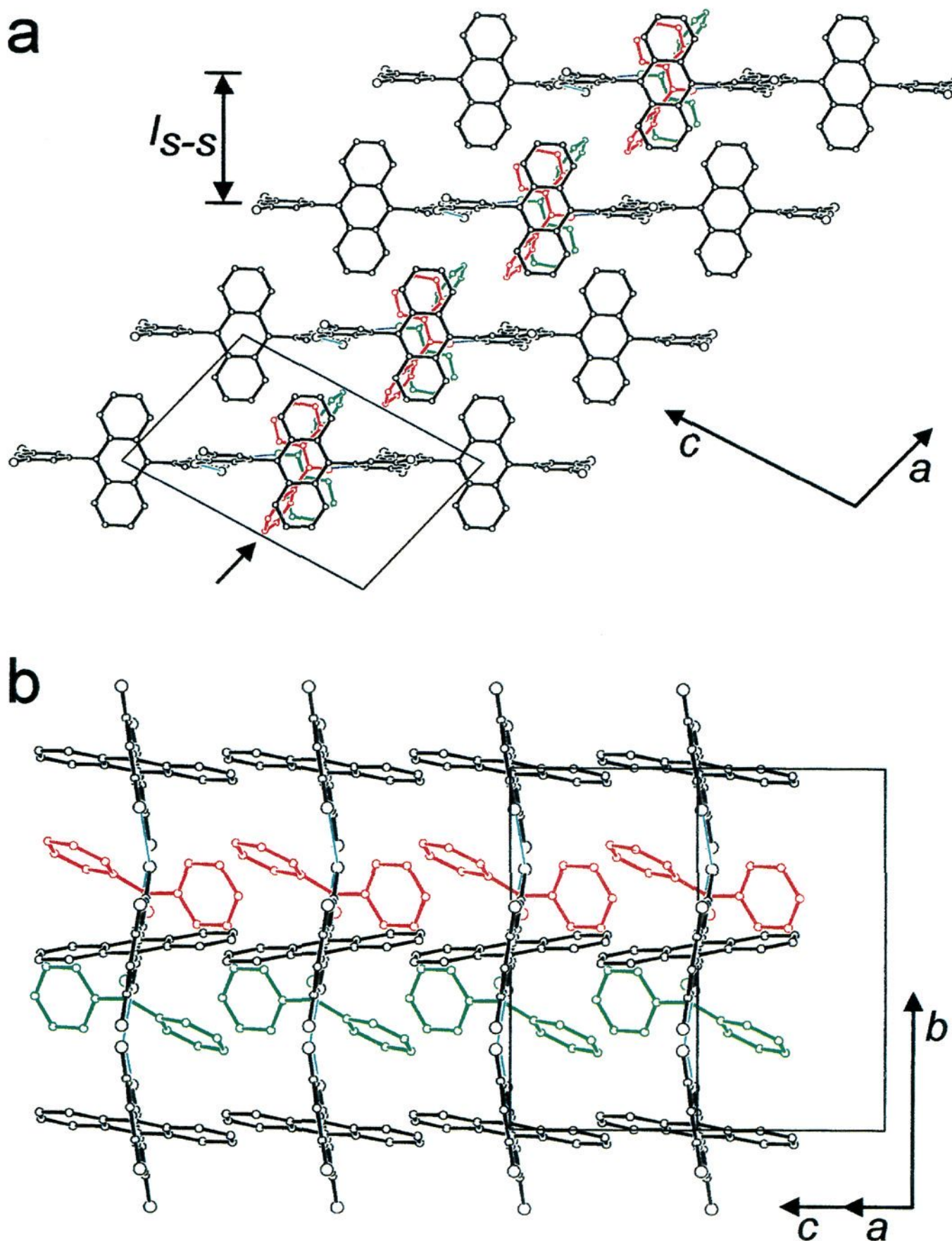


Figure 2. Arrangement of four adjacent guest-binding supramolecular cavities in four neighboring molecular sheets in the crystal of adduct **1a**·**2(2k)**: top view (a) and side view (b). Hydrogen bonds are shown in blue and included guest molecules are shown in red and green.

ration of host **1a** is due to the presence of cavity-forming hydrogen-bonded network. The crystal structure of compound **1c** has been determined:¹⁷ each molecule of **1c** is heavily packed via intermolecular methyl–anthracene contacts without formation of any cavity.

Host **1a** can also be recrystallized from a ketone or ester solvent diluted with an aromatic hydrocarbon, where the fate of the latter depends on the types of polar solvents.¹⁹ Recrystallization from a 1:1 mixture of benzene and **2c** or **2d** afforded exclusively the ketone adduct **1a**·**2(2c)** or **1a**·**2(2d)** without incorporation of the benzene. Recrystallization from an equimolar mixture of benzene and methyl or ethyl benzoate (**3a** or **3b**) resulted in the incorporation of one benzene molecule and gave a ternary adduct **1a**·**2(3a)**·C₆H₆ or **1a**·**2(3b)**·C₆H₆. When less bulky ethyl acetate (**4a**) was used in place of alkyl benzoate,

1:2:2 cocrystals **1a**·**2(4a)**·2(C₆H₆) were obtained. Single-crystal X-ray diffraction revealed that the two ester molecules are hydrogen-bonded to the host in a manner similar to that above and that the two benzene molecules are located so as to fill the empty space, one in the cavity and the other between sheets.^{17a}

Selectivity in Cocrystallization. The guest binding to host **1a** turned out to be very selective. In Table 1 are shown the guest/host molar ratios in cocrystals obtained under competitive

(19) Host **1a** is not soluble in benzene at all and hence cannot be recrystallized therefrom.

(20) One of the reviewers suggested that even the complexation of gaseous guests can be a result of condensation of the guests on the solid surface of apohost, followed by reconstruction of the surface, recrystallization, and concomitant enclathration. The present guest-binding, however, is not a simple surface phenomenon. In addition, there is a fundamental difficulty in defining the mechanism of *local* enclathration. Suppose that limited numbers of host and guest molecules locally interact and eventually form clathrates. How can we define “local mixing” or “local solution” of host and guest? How can we differentiate these events from “mutual diffusion” of host and guest and more importantly, how can we distinguish these two mechanisms experimentally?

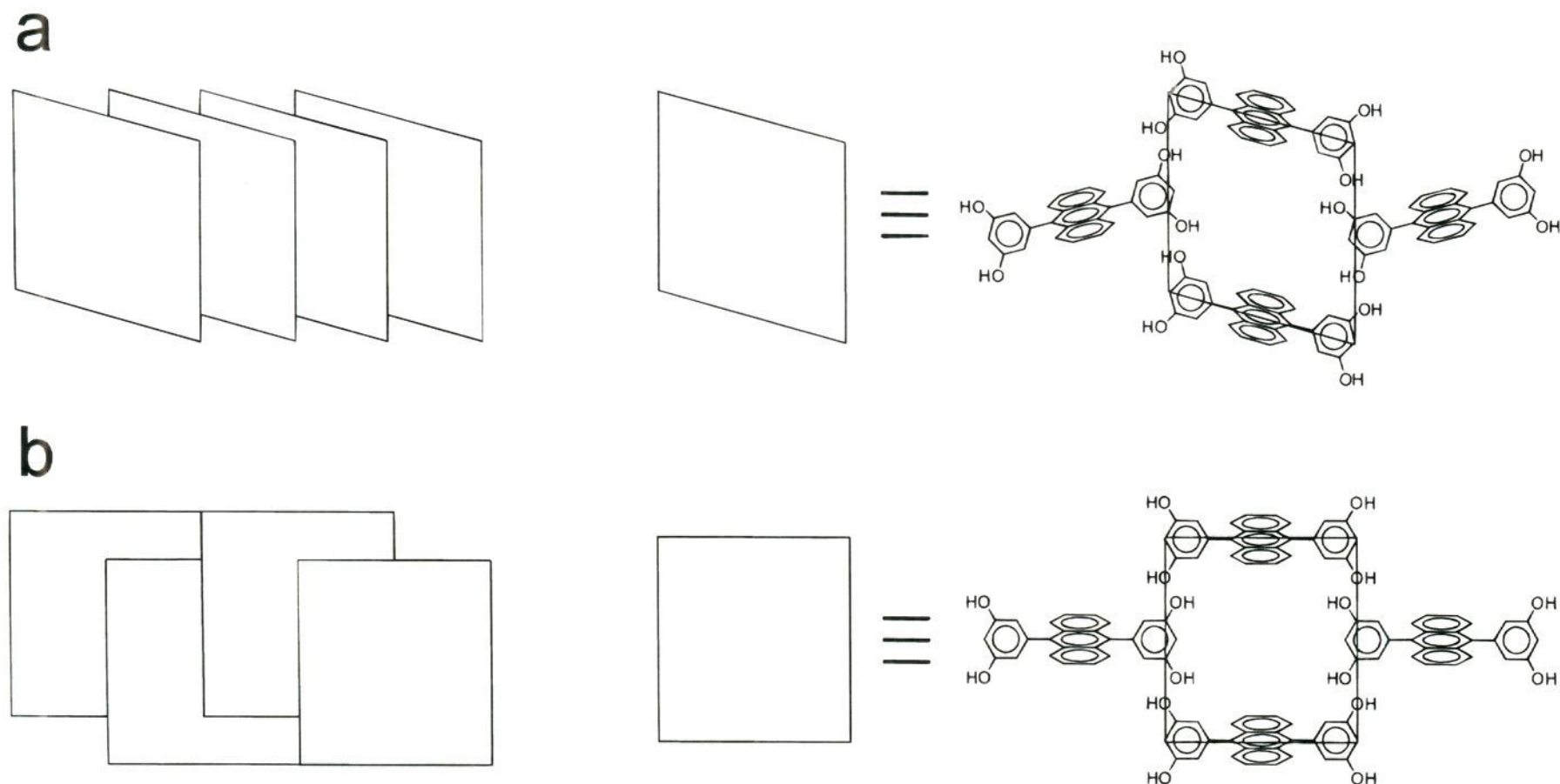


Figure 3. Schematic representation of the arrangement of four supramolecular cavities in four neighboring molecular sheets in the crystals of adducts **1a**·2(**2k**) (a) and **1a**·2(**3a**) (b).

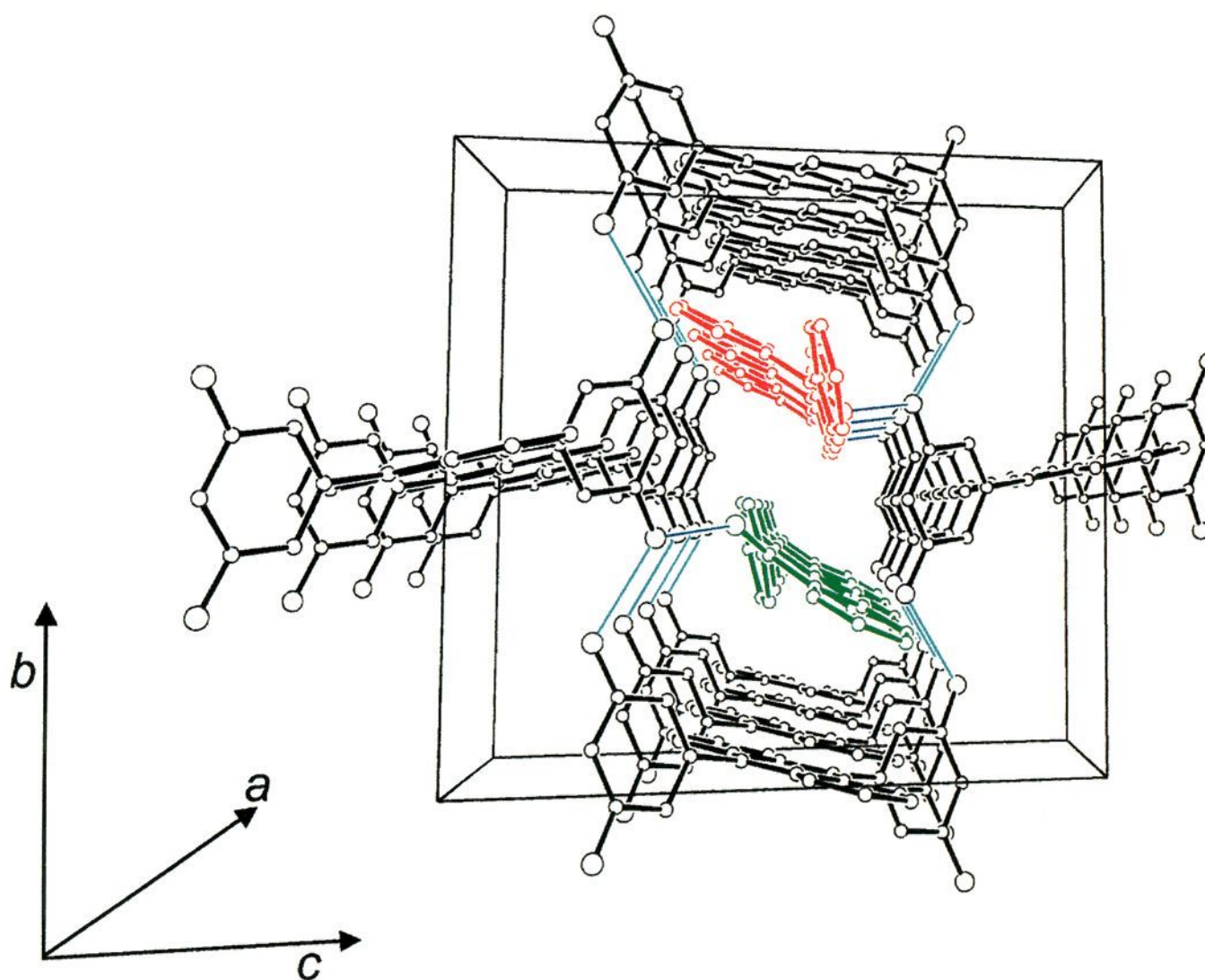


Figure 4. Perspective view along the *a* axis of the guest-binding supramolecular cavities in the crystal of adduct **1a**·2(**2k**). Hydrogen bonds are shown in blue and included guest molecules are shown in red and green.

recrystallization conditions using an equimolar mixture of two solvents A and B. First of all, the total guest/host molar ratio $(A + B)/1a$ in the present ternary systems is always 2.

The results in Table 1 indicate that the chain length of a carbonyl guest is a decisive factor that governs the selectivity. Thus, the competition between dibutyl or 4,4-ketone **2d** and dipentyl or 5,5-ketone **2e** results in an exclusive binding of the former (entry 2). That between **2d** (4,4-ketone) and **2c** (3,3-ketone) is in favor of the former by a factor of 1.7:0.3 (entry

1). The latter, on the other hand, is exclusively incorporated in the competition with guest **2e** (entry 3). Similar selectivity is noted also in the alkyl benzoate series; an alkyl benzoate may be regarded as a phenyl alkoxy ketone, and the phenyl ring is a C_4 moiety as far as chain elongation is concerned. Thus, propyl benzoate (**3c**) and isobutyl benzoate (**3d**) as 4,4-ketones exhibit significantly higher affinities than butyl benzoate (**3e**, 4,5-ketone) or ethyl benzoate (**3b**, 4,3-ketone); the binding of methyl benzoate (**3a**, 4,2-ketone) is weakest (entries 7–12).

Table 1. Competitive Cocrystallization of Host **1a**

entry	guest A	guest B	A/1a	B/1a	(A + B)/1a	A/B	ref
1	2d	2c	1.7	0.3	2	5.7	this work
2	2d	2e	~2	~0	2	v1 ^a	this work
3	2c	2e	~2	~0	2	v1 ^a	this work
4	2d	2g	1.5	0.5	2	3	this work
5	2d	2h	~2	~0	2	v1 ^a	this work
6	2d	2i	~2	~0	2	v1 ^a	this work
7	3b	3a	1.6	0.4	2	4	17b
8	3c	3b	1.3	0.7	2	1.9	17b
9	3c	3e	1.5	0.5	2	3	17b
10	3d	3e	1.7	0.3	2	5.7	17b
11	3d	3c	1.2	0.8	2	1.5	17b
12	3d	3a	1.97	0.03	2	~70	17b
13	3a	<i>p</i> -CH ₃ C ₆ H ₄ CO ₂ CH ₃	1.3	0.7	2	1.9	this work
14	3a	CH ₃ CO ₂ C ₆ H ₅	~2	~0	2	v1 ^a	this work
15	3b	CH ₃ CH ₂ CO ₂ C ₆ H ₅	~2	~0	2	v1 ^a	this work

^a Very large.

The affinity-lowering effect of a chain length ≥ 5 can be further demonstrated. (1) Methyl benzoate (4,2-ketone) can be bound more strongly than methyl *p*-toluate (5,2-ketone) (entry 13). (2) In marked contrast to methyl and ethyl benzoates (4,2- and 4,3-ketone), which show moderate affinities, their alkyl-aryl exchanged isomers phenyl acetate (1,5-ketone) and phenyl propionate (2,5-ketone) are hardly bound (entries 14 and 15). (3) An interesting selectivity is among regioisomers of nonanone. There is a significant reduction in the affinities on going from **2d** (4,4-ketone) to **2g** (3,5-ketone) (entry 4). 2,6-Ketone **2h** and 1,7-ketone **2i** are hardly bound (entries 5 and 6).

These results indicate that the affinity of a carbonyl compound as guest is very sensitive to the chain lengths of two moieties bound to the carbonyl group and that the optimal chain length is 4. The carbonyl group of a guest stays in a molecular sheet so as to be hydrogen-bonded to the host. The two alkyl/aryl/alkoxy groups then occupy the cavity and extend to neighboring sheets (cf. Figure 2). Competition between unfavorable non-bonded steric interactions and favorable high-efficiency crystal packing^{16a} would be best balanced at chain length 4. Analysis of the crystal structures of adducts **1a**·2(**3b**), **1a**·2(**3c**), and **1a**·2(**3d**) supports this view.^{17b} It is remarkable that the difference by one methylene unit in either total chain length or position of the carbonyl group of the ketonic guests can be discriminated fairly well.

Guest Exchange. Single crystals of host-guest adducts are not soluble in the present types of ketones or esters at room temperature. When dipped in such a solvent, they underwent guest exchange with varying efficiencies.^{20,21} A typical example is the ethyl benzoate to methyl benzoate exchange, i.e., the conversion of ethyl benzoate adduct **1a**·2(**3b**) dipped in methyl benzoate to methyl benzoate adduct **1a**·2(**3a**).^{17b} This conversion is complete within 24 h, during which a total 1:2 host-guest stoichiometry is always maintained. Intermediate ternary adducts **1a**·*x*(**3b**)·*y*(**3a**) ($x + y = 2$, $0 \leq x, y \leq 2$) exhibit a powder X-ray diffraction pattern which is simply sum of those of *x***1a**·2(**3b**) and *y***1a**·2(**3a**). The exchange in the reverse direction is much slower. Methyl benzoate adduct **1a**·2(**3a**) dipped in ethyl benzoate under otherwise identical conditions underwent a limited extent of guest-exchange, giving a ternary adduct **1a**·0.4(**3b**)·1.6(**3a**) after 24 h; only 0.4 mol of guests had exchanged. This is rather surprising since competitive recrystallization prefers ethyl ester **3b** to methyl ester **3a** by a factor

of 4:1 (Table 1, entry 7). Crystal structures seem to provide a clue for better understanding of different guest-exchange capabilities.

The structure of ethyl benzoate adduct **1a**·2(**3b**) is essentially the same as that of benzophenone adduct **1a**·2(**2k**) (Figures 1, 2, 3a, and 4). Supramolecular cavities in layered sheets in fact form a continuous channel which is very similar to that shown in Figure 4. In the case of methyl benzoate adduct **1a**·2(**3a**), which belongs to a different space group (monoclinic, *C2/c*), neighboring sheets slide not only laterally but also vertically.^{17b} As a result, cavities in layered sheets overlap with each other to a lesser extent (Figure 3b) and the channel becomes narrower. Incorporated methyl benzoate molecules would be less mobile in the channel as compared with ethyl benzoate in adduct **1a**·2(**3b**). This may be why adduct **1a**·2(**3a**) is more resistant toward guest-exchange than adduct **1a**·2(**3b**), although the mechanism of guest-exchange still remains to be further elucidated.

Apohost and Its Complexation with Liquid Guests. Volatile guest molecules trapped in the cavity can be removed by heating the corresponding cocrystals in vacuo. The guest-free apohost thus obtained is a polycrystalline material, whose powder X-ray diffractions are shown in Figure 5a. This rather complicated powder pattern can be completely reproduced for all preparations of apohost under different conditions with respect to the guest molecule in starting cocrystals and time of heating. The IR spectrum indicates that the OH groups of apohost **1a** are extensively hydrogen-bonded ($\nu_{\text{OH}} = 3400 \text{ cm}^{-1}$). This fact, however, cannot be taken as evidence that the cavities are left vacant; they are possibly distorted and partially filled via conformational change of compound **1a** and interpenetration¹⁰ of neighboring sheets. What is important is the potential guest-binding ability of the apohost.²¹

The apohost is not soluble at room temperature in ketones or esters of the present type. When dipped in such a solvent as 4-heptanone (**2c**), 5-nonanone (**2d**), methyl benzoate (**3a**), ethyl benzoate (**3b**), and isobutyl benzoate (**3d**), it picked up two molecules of the solvent as guest. The guest-binding to apohost is very fast, being complete in seconds, in marked contrast to the guest-exchange which takes hours even for a best combination of guests. The resulting adducts **1a**·2(guest) exhibit powder X-ray diffractions which are, without exception, identical to those of the corresponding single crystals obtained by direct recrystallization. These results demonstrate that solvent molecules as guests penetrate into polycrystals of apohost **1a**, thereby inducing an adjustment of the crystal structure to newly added guest molecules. From a strictly mechanistic point of view, however, there is no *a priori* confirmation that this is really a solid-state phenomenon; the binding of liquid guest to

(21) 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*, 446–447. (b) Miyata, M.; Sada, K.; Hori, S.; Miki, K. *Mol. Cryst. Liq. Cryst.* **1992**, *219*, 71–74. For solid-state adsorption of gases, see the paper of Barrer and Shanson shown in ref 3.

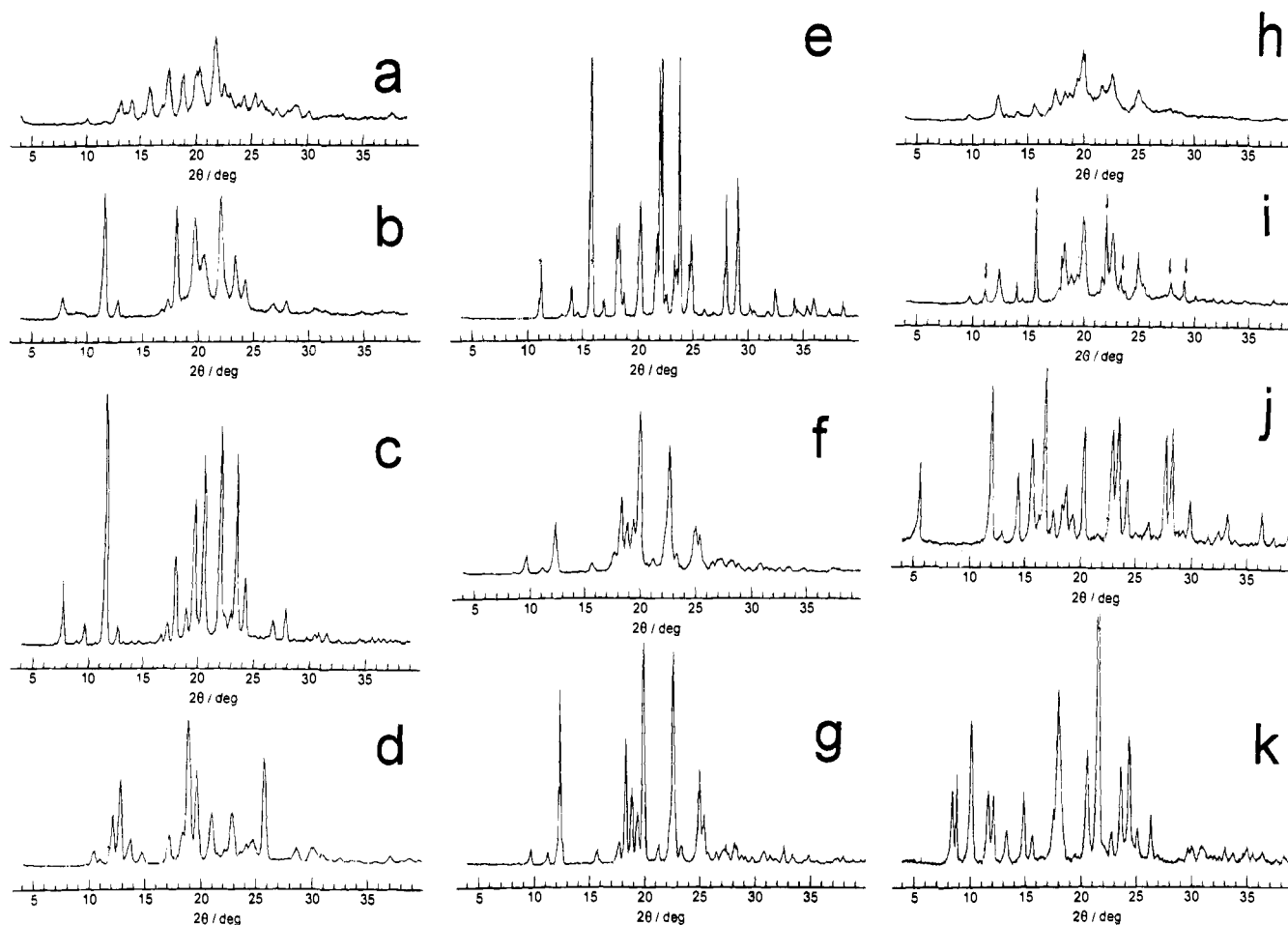


Figure 5. Powder X-ray diffraction patterns for apohost **1a** (a), adduct **1a·2(2d)** obtained by solid–gas complexation (b), single crystals of adduct **1a·2(2d)** (c), adduct **1a·2(p-xylene)** obtained by solid–gas complexation (d), single crystals of guest **2k** (e), 1:2 mixture of apohost **1a** and guest **2k**, which was coground for 5 min and left at 25 °C for 20 h (f), single crystals of adduct **1a·2(2k)** (g), 1:1 mixture of apohost **1a** and **2k**, which was coground for 5 min and left at 25 °C for 20 h (h), 1:4 mixture of apohost **1a** and **2k**, which was coground for 5 min and left at 25 °C for 20 h (i, where diffractions with marks are for uncomplexed ketone **2k** and others correspond to adduct **1a·2(2k)**), 1:2 mixture of apohost **1a** and benzoquinone, which was coground for 5 min and left at 45 °C for 20 h (j), and 1:2 mixture of apohost **1a** and *cis*-1,2-cyclohexanediol, which was coground for 5 min and left at 45 °C for 20 h under ultrasonic irradiation (k). See text for details of the preparation of samples.

solid apohost could be due to local and instantaneous dissolution of the host in the liquid phase followed by rapid recrystallization. This possibility cannot be ruled out, although it is important to note that the apohost binds not only liquid but also gaseous and solid guests.²⁰

Complexation of Gaseous Guests. Solid–gas experiments^{21,22} were carried out at 25 °C by using a sealed vessel containing a liquid ketone **2** or ester **3** and apohost **1a** placed in the gas phase, so that the latter was in contact with the vapor of the guest at its vapor pressure at 25 °C. Typical time courses of the binding of isomeric nonanones **2d,g–i** under these conditions are shown in Figure 6. There are three characteristic aspects. (1) The host–guest stoichiometry is ~1:2 in every case, as in solid–liquid complexation.²³ The resulting adducts **1a·2(guest)** show powder X-ray diffractions which are identical or at least very similar to those of single crystals, as shown in Figure 5b,c for adduct **1a·2(2d)**. (2) The amounts of guest bound increase linearly with time almost up to the very point of 100% binding, as detailed for guest **2d**. (3) The rates of

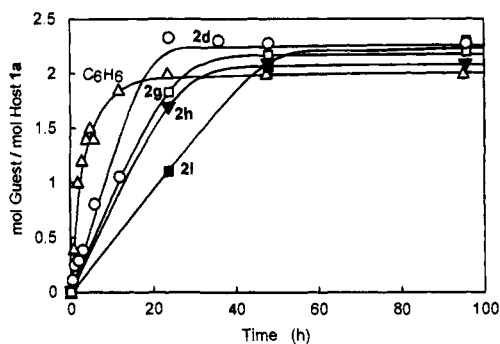


Figure 6. Time courses of solid–gas complexation of apohost **1a** with ketones **2d, g–i** or benzene at 25 °C.

guest-binding in the decreasing order **2d** > **2g** > **2h** > **2i** show only a very modest dependence on the position of the carbonyl group. The selectivity among these guests in competitive recrystallization is much more dramatic (Table 1, entries 4–6).

Item 1 above suggest a common mechanism for both the solid–gas and solid–liquid complexation. Whatever the mecha-

(22) For solid–gas complexation using quinol^a and imidazole derivatives^{b–e} as hosts, see: (a) Palin, D. E.; Powell, H. M. *J. Chem. Soc.* **1947**, 208–221. (b) Inouye, Y.; Sakaino, Y. *Acta Crystallogr., Sect. C* **1985**, *41*, 1106–1108. (c) Sakaino, Y.; Takizawa, T.; Inouye, Y.; Kakisawa, H. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1623–1629. (d) Sakaino, Y.; Inouye, Y.; Kakisawa, H.; Takizawa, T. *Mol. Cryst. Liq. Cryst.* **1988**, *161*, 255–281. (e) Sakaino, Y.; Fuji, R.; Fujisawa, T. *J. Chem. Soc., Perkin Trans. 1* **1990**, 2853–2854.

(23) Adducts of ketone obtained by solid–gas complexation often gave a guest/host ratio slightly larger than 2. When left under an air atmosphere for 30 min, these adducts gave a value of 2. The excess amount of guest might have been weakly absorbed on the surface of adduct. Adducts obtained by solid–liquid complexation, on the other hand, were carefully wiped with a filter paper in order to remove a trace of surface-bound guest; they gave a guest/host ratio of 2. See the Experimental Section for details.

Table 2. Solid-Gas Host-Guest Complexation Using Ketones and Esters and Vapor Pressures (*P*) of the Guests at 25 °C

entry	guest	guest/1a ^a	<i>P</i> (mmHg) ^b
1	2a	3.1	231
2	2b	3.0	35
3	2c	2.3	<5
4	2d	2.2	<1
5	2j	2.0	0.31
6	3a	1.4	0.35
7	3b	1.0	0.17
8	3c	0.31	0.16 ^c
9	3d	0.23	<0.15
10	3e	0.10	<0.15

^a The molar ratio of guest bound to host used after 30 h of solid-gas host-guest contact at 25 °C. ^b Calculated by the Antoine equation: $\log P = A - (B/T + C)$, where *P* is vapor pressure (mmHg), *T* is temperature (°C), and *A*, *B*, and *C* are Antoine constants. ^c Calculated by the Clausius-Clapeyron equation: $\log P = A - (B/T)$, where *P* is vapor pressure (mmHg), *T* is temperature (K), and *A* and *B* are constants.

nistic details may be, guest molecules are ultimately captured in each cavity as in single crystals via hydrogen-bonding. In a kinetic sense, however, hydrogen-bonding plays only a minor role, as suggested by item 3.

The binding of most of volatile ketones up to C₉, including acetophenone (**2j**), reaches a plateau region in 30 h. The host/guest molar ratios are ~1:2,²³ except for small ketones such as acetone (**2a**) and 3-pentanone (**2b**) which give a 1:3 stoichiometry (Table 2). Alkyl benzoates **3** are less volatile and, except for methyl benzoate, require a longer time to reach a saturation level. The molar ratios of guest bound to host used after 30 h of solid-gas host-guest contact are shown in Table 2, together with vapor pressures of the guests. The highest affinity, among alkyl benzoates, of the least bulky methyl benzoate (**3a**) seems to be primarily ascribed to its high vapor pressure, but steric factors may also come into play.

Incorporation of Hydrocarbons and Haloalkanes. Guest-free apohost was found to readily incorporate around two molecules of benzene when dipped in it as a neat liquid or allowed to be in contact with the vapor of it under conditions described above.²⁴ The solid-liquid complexation is almost instantaneous; molar ratios of benzene bound to apohost used at appropriate time intervals are 2.3 (10 s), 2.4 (5 min), 1.9 (1 h), 2.2 (2 h), 2.4 (3 h), 2.4 (4 h), and 2.0 (24 h). The time course of the solid-gas complexation is included in Figure 6.

Other hydrocarbons including alkanes and their halogenated derivatives can also be bound under the solid-gas conditions. The amounts of guest bound increase with time and reach a plateau region after 30 h. The guest/host molar ratios at this point are shown in Table III (supporting information). These values for different guests cannot be compared directly because different guests have different vapor pressures at 25 °C, at which

(24) For inclusion compounds of hydrocarbon guests with cholic acid,^a deoxycholic acid,^{b-f} perhydrotris(phenylene),^g tris(*o*-thiomide),^{h,i} hydrocarbons,^{j,k} or tris(*o*-phenylenedioxy)cyclotrisphosphazene,^l see: (a) Nakano, K.; Sada, K.; Miyata, M. *Chem. Lett.* **1994**, 137-140. (b) Fieser, L. F.; Newman, M. S. *J. Am. Chem. Soc.* **1935**, 57, 1602-1605. (c) Rheinboldt, H.; Braun, P.; Flume, E.; König, O.; Lauber, A. *J. Prakt. Chem.* **1939**, 153, 313-316. (d) Huntress, E. H.; Phillips, R. F. *J. Am. Chem. Soc.* **1949**, 71, 458-460. (e) Cilent, G. *Ibid.* **1950**, 72, 4272-4273. (f) Herndon, W. C. *J. Chem. Educ.* **1967**, 44, 724-728. (g) Farina, M. *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: New York, 1984; Vol. 2, p 69. (h) Ollis, W. D.; Stoddart, J. F. *Inclusion Compounds*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds.; Academic Press: New York, 1984; Vol. 2, p 169. (i) Arad-Yellin, R.; Green, B. S.; Knossow, M.; Rysanek, N.; Tsoucaris, G. *J. Inclusion Phenom.* **1985**, 3, 317-333. (j) Weber, E.; Ahrendt, J.; Czugler, M.; Csoeregh, I. *Angew. Chem.* **1986**, 98, 719-721. (k) Mak, T. C. W.; Wong, H. N. C. *Top. Curr. Chem.* **1987**, 140, 141-164. (l) Allcock, H. R. *Acc. Chem. Res.* **1978**, 11, 81-87.

solid-gas experiments were carried out. Nevertheless, a number of comments are worthwhile. (1) Among various guests investigated, only chloroform, benzene, and *p*-xylene have molar ratios of guest/host ≈ 2 (entries 3, 19, and 23). (2) Unsaturation in the six-membered ring is affinity-enhancing (entries 16-19). (3) Other guests have more or less similar guest/host ratios, despite a big span in the vapor pressures; 0.1-0.2 for haloethanes (entries 1 and 2), 0.4-1.3 for haloethanes (entries 4-6), 0.1-0.6 for alkanes ranging from C₅ to C₉ (entries 7-14, and 16), and 0.1-0.6 for alkylbenzenes and halobenzenes (entries 20-22, and 24-36). This may be due to compensation between complexation-promoting vapor-pressure effects (favoring more volatile and less bulky guests) and decomplexation-suppressing cavity-packing effects (favoring less volatile and more bulky guests). Exceptional stabilities of the chloroform, benzene, and *p*-xylene adducts suggest that cavity packing is still delicately controlled by a slight change in guest structures.²⁵

The incorporated hydrocarbon and haloalkane guests can be readily removed. The 1:2 host-guest adducts of benzene (bp 80 °C), *p*-xylene (bp 138 °C), and chloroform (bp 61 °C) lost 1.5, 0.2, and 1.0 molecules of included guest, respectively, when left in atmosphere for 10 min at 25 °C. Thus, the guest/host ratios shown in Table III (supporting information) must represent equilibrium values, reflecting the complexation and decomplexation rates at a particular vapor pressure of a given guest at 25 °C. The lability of hydrocarbons and haloalkanes is undoubtedly due to lack of host-guest hydrogen-bonding interaction. More drastic conditions at 190 °C in vacuo for 48 h are required to remove entrapped ethyl acetate molecules (**4a**, bp 77 °C) from the hydrogen-bonded adduct **1a**·2(**4a**). In a manner similar to those of ketone and ester adducts, the *p*-xylene adduct **1a**·2(H₃C-C₆H₄-CH₃) exhibits sharp powder diffractions (Figure 5d) which are again identical with those of the corresponding single crystals. The latter was accidentally obtained by recrystallizing host **1a** from a 1:2 mixture of *p*-xylene and a low-affinity ketone **2i** (cf. entry 6 of Table 1), where no incorporation of the ketone was observed. The sorption/desorption of hydrocarbons, haloalkanes, and haloarenes is reversible and can be repeated many times, while bringing no change in respective diffraction patterns.

Guest-Binding to Apohost Using Benzene Solutions. When dipped in a dilute benzene solution of ketone **2** or ester **3**, apohost **1a** preferentially binds benzene. The results are summarized in Table 3, where the guest/host molar ratios are listed for competitive runs using benzene solutions ([benzene] ≈ 11 M) of an equimolar (0.1 M) mixture of two ketones A and B or two esters A and B. Thus, under these conditions of [benzene]/[A] = [benzene]/[B] ≈ 110, approximately two molecules of benzene are bound together with smaller amounts of guests A and B. The total guest/host ratios (A + B + benzene)/host are in the range 2.2-3.0.

The relative affinities of ketones (entries 1-4) follow the decreasing order **2d** (4, 4) > **2g** (3, 5) > **2c** (3, 3) > **2e** (5, 5) >> **2i** (1, 7). Those of alkyl benzoates (entries 5-8) decrease in the order **3d** (isobutyl) > **3b** (ethyl) > **3a** (methyl). Ethyl benzoate (**3b**) has a significantly higher affinity than phenyl propionate (entry 9). These orders of affinity are the same as those found in competitive recrystallization (Table 1, entries 1-6, 7-12, and 15, respectively). However, the selectivities in the guest-binding to apohost are far less pronounced as compared with those in recrystallization.

(25) It is interesting to note that only benzene and *p*-xylene among guests in Table III (supporting information) have exceptionally high melting points (5.5 and 12 °C, respectively).

Table 3. Competitive Binding to Apohost **1a** Using Benzene Solutions of Polar Guests

entry	guest A ^a	guest B ^a	A/1a	B/1a	C ₆ H ₆ /1a	(A + B + C ₆ H ₆)/1a	A/B
1	2d	2c	0.39	0.32	1.5	2.2	1.2
2	2d	2e	0.34	0.12	2.0	2.5	2.8
3	2d	2g	0.26	0.23	2.1	2.6	1.1
4	2d	2i	0.50	~0	2.5	3.0	vl ^b
5	3b	3a	0.41	0.26	1.9	2.6	1.6
6	3c	3b	0.55	0.42	1.2	2.2	1.3
7	3d	3b	0.36	0.26	1.6	2.2	1.4
8	3d	3a	0.45	0.17	2.2	2.8	2.7
9	3b	CH ₃ CH ₂ CO ₂ C ₆ H ₅	0.80	0.08	1.6	2.5	10

^a [A] = [B] = 0.1 M in C₆H₆ (~11 M). ^b Very large.

Solid–Solid Complexation. Benzophenone (**2k**) is a solid member of the present ketonic guests. A 1:2 mixture of apohost **1a** (mp > 360 °C) and ketone **2k** (mp 48.5 °C) was coground with an agate mortar and an agate pestle for 5 min and then allowed to stand at 25 °C for 20 h. The powder X-ray diffraction pattern immediately after mixing was simply a sum of those for host **1a** (Figure 5a) and guest **2k** (Figure 5e). The powder pattern, however, gradually changed with time until that shown in Figure 5f for adduct **1a**·2(**2k**) resulted. This is essentially identical with that (Figure 5g) for the single crystals of this adduct obtained by recrystallization of host **1a** from a solution of guest **2k** in 3-pentanone (**2b**),²⁶ where no incorporation of the latter was observed. This particular preference for a 4,4-ketone **2k** over the 2,2-ketone **2b** provides another example of the C₄ selectivity discussed above. Figure 5h shows the powder pattern for a 1:1 (host to guest) mixture. When guest is in excess as in a 1:3 or 1:4 mixture, 1:2 adduct **1a**·2(**2k**) is readily formed, while 1 or 2 equiv of the guest **2k** in excess remains simply as such. The powder pattern for a 1:4 mixture is shown in Figure 5i; diffractions with marks are for **2k** (referring to Figure 5e) and others corresponding to the 1:2 adduct (referring to Figure 5g). There is thus a strict 1:2 host-guest stoichiometry also in the case of solid–solid complexation²⁷ as in solid–liquid or solid–gas complexation as well as recrystallization.

Benzoquinone (mp 115 °C) can be complexed in a similar manner at a slightly elevated temperature 45 °C. The resulting adduct **1a**·2(benzoquinone) exhibits powder diffractions (Figure 5j) which are again identical with those of the corresponding single crystals obtained by recrystallization of host **1a** from diethyl ether.²⁸ In marked contrast, anthraquinone (mp 286 °C) is inert toward apohost **1a**. The powder diffraction pattern of a coground 1:2 mixture of apohost **1a** and anthraquinone remained to be the sum of those of the two components and showed no change even after 7 days at 55 °C under ultrasonic irradiation. On the other hand, recrystallization of host **1a** from an ether solution of anthraquinone readily afforded adduct **1a**·2-(anthraquinone).²⁸ These results may provide another example

(26) We have never encountered any literature which unambiguously demonstrates that a coground solid–solid mixture gives rise to an essentially single-crystal structure. Recently, however, Ohashi, et al., reported that a coground 1:1 mixture of hexadecyltrimethylammonium chloride and *o*-iodophenol first gives a solid solution and then affords powders whose powder X-ray diffractions are identical with those of the corresponding single crystals formed from an aqueous solution (Kitamura, T.; Sekine, A.; Uekusa, H.; Ohashi, Y.; Iimura, N.; Hirata, H. Presented at the 67th Annual Meeting of the Chemical Society of Japan, March 1994, Tokyo, Abstr. 1A538).

(27) 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, see: (a) Toda, F. *Top. Curr. Chem.* **1987**, *140*, 43–69. (b) Tanaka, K.; Toda, F. *Nippon Kagaku Kaishi* **1988**, 1643–1656. (c) Toda, F. *Advances in Supramolecular Chemistry*; Gokel, G. W., Ed.; JAI Press: Greenwich, CT, 1992; Vol. 2, pp 141–191. (d) Toda, F.; Tanaka, K.; Sekikawa, A. *J. Chem. Soc., Chem. Commun.* **1987**, 279–280.

(28) Adducts **1a**·2(benzoquinone) and **1a**·2(anthraquinone) have quite different single-crystal structures. Details will be reported shortly.

of size selectivity as for the guests. 1,2-Cyclohexanediol, either cis (mp 99–101 °C) or somewhat more reluctantly trans (mp 101–104 °C), can be complexed only under ultrasonic conditions at 45 °C. In marked contrast, monosaccharides such as D-glucose (mp 149–151 °C) and D-xylose (mp 144–145 °C) fail to complex even under such conditions. The diffraction pattern for the 1:2 adduct derived from the cis isomer of cyclohexanediol is shown in Figure 5k. Strict requirement of the 1:2 host–guest stoichiometry in the solid-state complexation of benzoquinone and cyclohexanediol was confirmed as above.

In reference to the conditions required, the affinities of solid guests follow the decreasing order of benzophenone (**2k**, monoketone) > benzoquinone (dione) > cyclohexanediol (diol) ≫ monosaccharides (polyols). This order suggests that cohesive intermolecular interaction is an important factor that governs the affinity of a solid guest to apohost **1a**. In contrast to the former two guests as carbonyl compounds, the latter two guests, especially the last one, as hydroxyl compounds are intermolecularly hydrogen-bonded.

Packing Coefficients and Guest-Loading Abilities. Control runs using resorcinol or anthracene in place of apohost showed no guest-binding at all under the solid–liquid, solid–gas, or solid–solid conditions. Thus, the cavity-forming hydrogen-bonded network of the apohost seems to play an essential role in the guest-binding thereto. Table 4 shows the packing coefficients (K_{HG}) for the host–guest adducts **1a**·2(**2c**), **1a**·2(**2d**), **1a**·2(**2e**), **1a**·2(**3a**),^{17b} **1a**·2(**3b**),^{17b} **1a**·2(**3c**),^{17b} **1a**·2(**3d**),^{17b} and **1a**·2(**4a**)·2(C₆H₆),^{17a} whose single-crystal parameters are known. The packing coefficient is defined as $K_{HG} = (V_h Z_h + V_g Z_g)/V$, where V_h and V_g are calculated volumes of host and guest,²⁹ Z_h and Z_g are numbers of host and guest molecules in a unit cell, and V is the volume of a unit cell. The values of $K_{HG} = 0.67–0.73$ may be compared with those for simple aromatic compounds such as benzene (0.681), naphthalene (0.702), and anthracene (0.722).³⁰ Table 4 also contains the packing coefficients of $K_H = 0.3–0.4$ for the hypothetical apohost with excluded guest molecules; $K_H = V_h Z_h/V$.

It is important to note that there is no correlation between packing coefficients and affinities of included guest molecules in the competitive cocrystallization processes. For example, methyl benzoate (**3a**) has a high value of K_{HG} as compared with those of other alkyl benzoates (**3b,c,d**). Guest **3a**, however, has the lowest affinity (Table 1, entries 7–12). Symmetrical alkanones **2c,d,e** have comparable K_{HG} values, although the affinities decrease dramatically in the order **2d** > **2c** ≫ **2e** (Table 1, entries 1–3). Full interpretation of these results should be deferred until much information is available as to why a highest-affinity adduct **1a**·2(**2d**) and a lowest-affinity adduct **1a**·2(**3a**)

(29) The molecular volumes of host and guest were calculated by using the HyperChem-ChemPlus set of computer programs which is based on a grid method (Bodor, N.; Gabanyi, Z.; Wong, C. *J. Am. Chem. Soc.* **1989**, *111*, 3783–3786) with atomic radius data (Gavezzotti, A. *J. Am. Chem. Soc.* **1983**, *105*, 5220–5225).

(30) References 16a,b.

Table 4. Crystallographic Data and Packing Coefficients for Various Adducts^a

adduct	1a·2(c)	1a·2(d)	1a·2(e)	1a·2(k)	1a·2(3a) ^b	1a·2(3b) ^b	1a·2(3c) ^b	1a·2(3d) ^b	1a·2(4a)·2(C ₆ H ₆) ^c
crystal system	monoclinic	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	<i>P2₁/n</i>	<i>Pbcn</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>C2/c</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/n</i>	<i>P2₁/c</i>
<i>a</i> , Å	8.973(4)	13.750(2)	9.375(2)	9.644(1)	13.396(1)	9.033(1)	9.325(1)	9.534(6)	16.579(4)
<i>b</i> , Å	13.739(3)	19.425(2)	13.519(2)	13.882(2)	20.395(1)	13.885(1)	13.704(1)	13.479(4)	14.272(2)
<i>c</i> , Å	15.320(2)	15.058(2)	17.547(3)	14.864(4)	13.918(1)	15.244(1)	15.615(1)	15.572(4)	18.391(2)
β , deg	104.11(0)		92.36(0)	104.62(2)	117.012(5)	104.32(1)	102.600(6)	100.77(5)	111.15(1)
<i>V</i> , Å ³	1831.8	4022.0	2222.2	1925.6	3387.8	1852.6	1947.4	1966.1	4058.6
<i>d</i> _{HG} , g/cm ³	1.13	1.12	1.10	1.31	1.31	1.25	1.23	1.26	0.901
<i>d</i> _H , g/cm ³	0.715	0.651	0.589	0.680	0.773	0.707	0.672	0.666	0.645
<i>V</i> _h , Å ³	349.90	349.90	349.90	349.90	349.90	349.90	349.90	349.90	349.90
<i>V</i> _g , Å ³	133.09	167.40	201.63	177.33	128.96	146.10	163.18	180.24	89.20, 87.15
<i>Z</i> _h	2	4	2	2	4	2	2	2	4
<i>Z</i> _g	4	8	4	4	8	4	4	4	8, 8
<i>K</i> _{HG}	0.672	0.681	0.677	0.731	0.717	0.693	0.694	0.722	0.692
<i>K</i> _H	0.382	0.348	0.314	0.363	0.413	0.377	0.359	0.356	0.345

^a Definitions are as follows: *d*_{HG}, density of adduct; *d*_H, density of hypothetical apohost with excluded guest molecules; *V*_h and *V*_g, calculated volumes of host and guest, respectively (cf. footnote 29); *Z*_h and *Z*_g, numbers of host and guest molecules, respectively, in a unit cell; *K*_{HG}, packing coefficient of adduct ($K_{HG} = (V_h Z_h + V_g Z_g)/V$); *K*_H, packing coefficient of hypothetical apohost ($K_H = V_h Z_h/V$). ^b Lattice parameters have been reported in ref 17b. ^c Lattice parameters have been reported in ref 17a.

Table 5. Guest-Loading Abilities of Host 1a^a

adduct	guest/host (wt/wt) (g/g)	guest/host (vol/wt) (mL/g)	guest/adduct ^b (vol/vol)
1a·4(2a)	0.589	0.745	
1a·3(2b)	0.655	0.808	
1a·2(2c)	0.578	0.706	0.504
1a·2(2d)	0.721	0.879	0.573
1a·2(2e)	0.863	1.04	0.613
1a·2(2k)	0.924	0.842	0.572
1a·2(3a)	0.690	0.633	0.489
1a·2(3b)	0.761	0.724	0.512
1a·2(3c)	0.832	0.816	0.549
1a·2(3d)	0.903	0.903	0.602
1a·2(4a)·2(C ₆ H ₆)	0.842	0.949	0.612
1a·2(3b)·(C ₆ H ₆)	0.959	0.951	
1a·2(C ₆ H ₆)	0.396	0.453	
1a·2(H ₃ CC ₆ H ₄ CH ₃)	0.538	0.621	
1a·2(CHCl ₃)	0.605	0.405	
1a·16(H ₂ O) ^c	0.730	0.730	
1a·2(<i>cis</i> -1,2-cyclohexanediol)·3–5(H ₂ O) ^c	0.726–0.817	0.757–0.848	
MS 4A ^d with H ₂ O, CO ₂ , or O ₂ as guest	0.24–0.29	0.21–0.29	0.33–0.45 ^e
MS 5A ^d with H ₂ O or O ₂ as guest	0.28–0.31	0.24–0.31	0.38–0.48 ^e
MS 5A ^d with butane as guest	0.13	0.23	0.35 ^e
MS 13X ^d with H ₂ O, CO ₂ , or O ₂ as guest	0.36–0.40	0.36–0.40	0.45–0.51 ^e
MS 13X ^d with isooctane as guest	0.19	0.19	0.39 ^e

^a Volume of bound guest is calculated from its weight and density in the liquid state. ^b Total volume of bound guest molecules in a unit cell divided by the volume of the unit cell. ^c See footnote 32. ^d MS, molecular sieves. ^e Reference 34.

have space groups (*Pbcn* and *C2/c*, respectively) different from the standard *P2₁/n*.³¹ It is the extents of disorder or mobility of included guest molecules that the packing coefficients seem to be better correlated with. Such adducts as 1a·2(2k), 1a·2(3a),^{17b} and 1a·2(3d)^{17b} having *K*_{HG} ≥ 0.72 are almost free from disorder of the included guest molecules. Adducts 1a·2(3b) and 1a·2(3c) having 0.70 > *K*_{HG} > 0.69 exhibit some degree of disorder with regard to the orientation of the benzene ring and the alkyl group.^{17b} On the other hand, the alkanone adducts 1a·2(2c), 1a·2(2d), and 1a·2(2e) have *K*_{HG} ≤ 0.68. The alkyl groups of included ketone molecules seem to be rather extensively disordered around the fixed C=O bond.

The guest-loading abilities of host 1a are shown in Table 5, where the guest/host ratios in terms of weight/weight and volume/weight and the guest/adduct ratios in terms of volume/volume are listed for typical host–guest adducts including hydrated host.³² Here, the volume (*V*) of bound guest is calculated according to $V = w/d$, where *w* is weight of bound

guest and *d* is density of guest in the liquid state.³³ This is the standard method to obtain the pore size of zeolites.³⁴ Thus, 1 g of the host can accommodate 0.40–0.96 g or 0.41–1.0 mL³⁵ of guest. The ratios of the volume occupied by guest in adduct are in the range 0.48–0.61. Table 5 also contains the corresponding values for molecular sieves (MS) 4A (pore diameter,

(32) Apohost 1a extracts two molecules of guest such as cyclohexanol, cyclohexanediol, and alkyl acetate from an aqueous solution. In the absence of any guest, it is hydrated. The resulting adducts 1a·2(guest)·*x*(H₂O) (*x* = 3–5) and hydrated host 1a·*y*(H₂O) (*y* = 16) are essentially single crystals as judged from their powder X-ray diffractions (Aoyama, Y.; Imai, Y.; Endo, K.; Kobayashi, K. *Tetrahedron* 1995, 51, 343–352).

(33) The volume obtained in this way for two or more guest molecules in vicinity is usually ~50% larger than that based on calculated molecular volume²⁹ multiplied by the number of molecules involved. The volumes in Table 4 are based on the latter method, which, although less realistic, is applicable to molecules such as host 1a whose density in the liquid state is not known.

(34) (a) Breck, D. W.; Eversole, W. G.; Milton, R. M.; Reed, T. B.; Thomas, T. L. *J. Am. Chem. Soc.* 1956, 78, 5963–5971. (b) Reference 2, Chapter 8.

(35) The pore size (volume of empty space per gram of host) for hypothetical rigid apohost is calculated as $(1 - K_H)/d_H \approx 0.6/0.7 \approx 0.86$ mL/g.

(31) The major difference in the crystal structures of adducts 1a·2(2c) and 1a·2(2e) (space group, *P2₁/n*) and adduct 1a·2(2d) (space group, *Pbcn*) lies in how molecular sheets are layered.

4 Å), 5A (5 Å), and 13X (8 Å).³⁴ In reference to any guest/host or guest/adduct ratio, the present host exhibits higher guest-loading abilities than molecular sieves. In this respect, it is interesting to refer to the size of the guest-binding cavities of host **1a**; the column-column distance, the center-to-center anthracene-anthracene distance, and the sheet-sheet distance are $l_{c-c} = 9.77-9.93$ Å, $l_{a-a} = 13.48-13.89$ Å, and $l_{s-s} = 6.83-7.40$ Å (referring to Figures 1a and 2) for adducts **1a**·2-(**2k**), **1a**·2(**3a**), **1a**·2(**3b**), **1a**·2(**3c**), and **1a**·2(**3d**).^{17b}

Mechanism of the Guest-Binding to Apohost. The guest-binding to apohost has a number of characteristic aspects: (1) Not only liquid but also gaseous and solid guests can be bound in a 1:2 host/guest stoichiometry. (2) Irrespective of their initial states (liquid, gas, or solid), ketone and ester guests **2** and **3** afford 1:2 adducts **1a**·2(**2**) and **1a**·2(**3**), whose structures are essentially the same as recrystallization-obtained single crystals. Compared with recrystallization processes, guest-binding to apohost is less discriminate as for the guests. (3) There is a general preference for smaller guests even when they are hydrocarbons. (4) As for solid guests, less cohesive ketonic guests have higher affinities than alcoholic guests which are more cohesive.

Item 1 demonstrates that the present host-guest complexation is in fact a solid-state phenomenon. Guest molecules may be bound at the surface of apohost and then undergo translocation upon interaction with host molecules by the mechanism which is not clear.²⁰ This process is simply referred to as diffusion of guest molecules hereafter.²⁰ By doing so, we by no means try to claim that the apohost is porous. Porosity of apohost is neither proved nor assumed here. Item 2 indicates that apohost is induced-fit adjustable to newly added guest molecules, thereby restoring relaxed single-crystal structures. Item 3 suggests that guest-binding to apohost is kinetically controlled, where an essential factor is *not* host-guest hydrogen-bonding but facile lattice diffusion of the guest. In this respect, i.e., from a kinetic point of view, alkanes, arenes, and their halogenated derivatives are good guests. In the solid-solid complexation, another factor comes into play; each guest molecule has to be freed from bulk solid before entering lattice diffusion, as indicated by item 4.

As far as gaseous guests are concerned, the uptake of guest molecules looks as if it were zero-order with respect to apohost or, more precisely, *concentration* of the cavities (Figure 6). On the other hand, the guest-binding to apohost shows an expected dependency on [guest]. Solid-liquid complexation is complete in seconds, while solid-gas complexation takes hours to days with half-lives of 2–24 h for benzene and ketones **2d**, **g**–**i** (Figure 6). The difference in the rates of solid-liquid and solid-gas complexation should primarily be ascribed to the difference in [guest] in bulk phase: [benzene], for example, is ~11 M for neat liquid and ~0.006 M for gas at its vapor pressure (95 mmHg) at 25 °C. The simplest mechanism which is consistent with the observed kinetic aspects would involve an equilibrium Langmuir-type adsorption (with equilibrium constant K) of guest at the surface of apohost, followed by rate-determining diffusion (with rate constant k_D), from cavity to cavity, of surface-bound guest molecules into the interior of apohost;³⁶ $\text{rate} \propto k_D K [\text{guest}]$. In view of the apparently zero-order kinetics of guest binding (Figure 6), it is remarkable that there is no depth dependence of the cavities in their guest-binding abilities, where the depth of a cavity refers to how deep

it is from the surface. This may be another reflection or indication of the porosity of the present apohost.

Conclusions

Host **1a** forms an extensive hydrogen-bonded network in the solid state. This necessarily generates cyclophane-like supramolecular cavities, which are filled with guest molecules upon either direct recrystallization or solid-state complexation. Both methods give the same host-guest adducts with respect to not only 1:2 host/guest stoichiometry but also crystal structures. The basic structure of the hydrogen-bonded network and hence those of the cavities are rather rigid and not much dependent on the structures of included guest molecules.³⁷

The recrystallization process or crystal growth is an on-surface phenomenon and is controlled by a thermodynamic factor; polar guests of an appropriate size are favored, which allow simultaneous host-guest hydrogen-bonding and cavity packing. The solid-state complexation using preformed guest-free apohost is applicable to a great variety of guest molecules with respect to physical states covering liquid, gas, and solid as well as polarity characters ranging from hydrocarbons through common polar organic molecules to water.³² Guest-binding to apohost is an in-solid phenomenon involving rate-limiting diffusion of surface-bound guest molecules in the solid interior. The driving force of this process is to restore relaxed single-crystal structures with filled cavities. From a thermodynamic point of view, such guests as hydrogen-bond-forming polar molecules of an appropriate size are favored as above. From a kinetic viewpoint, however, small guests even without a hydrogen-bonding site are preferred. Hydrogen-bonding is not essential at all for the diffusion of the guest in porous polycrystals of the apohost. Benzene in fact is one of the best guests in a kinetic sense.

It is not clear at least from the present work whether the apohost is *really* porous and retains significant internal cavities. As far as functions are concerned, however, this point may not be so essential, since cavities can be restored upon guest binding. The present apohost of an orthogonal aromatic-triad tetraol **1a** may thus be regarded as a functional organic analogue of zeolites³ from the viewpoints of (1) general guest independence of the structure of the cavities, (2) diversity of applicable guest molecules, and (3) reversibility of sorption/desorption of the guest. The size of the guest-binding cavities of the present organic zeolite may be larger than the pore sizes of inorganic zeolites. The general preference for small molecules, unsaturated compounds, and polar guests, especially water, is also the characteristic aspects of zeolites. To the best of our knowledge, there is no organic host, other than **1a**, which incorporates as many as 16 water molecules.³² These characteristic aspects suggest potential uses of the present types of organic zeolites as a new class of adsorbents, separators, and catalysts.³ One of the most important practical advantages is the readiness of handling. No particular pretreatment, such as ultrapulverization, is needed. The crude synthetic product, after removal of solvent, is practically apohost which can be used for most purposes.

The present host might better be called a two-dimensional organic zeolite, since it is composed of layered molecular sheets. A potential future target in this area is to construct three-dimensional organic zeolites having a three-dimensional hydrogen-bonded network.^{10a-c} Such a work would also shed more light on the mechanism of in-solid diffusion of bound guest molecules. The hydrogen-bonded OH pairs (O–H···O–H) may

(36) This is not the sole mechanism consistent with the observed kinetic aspects. An alternative one, although seemingly less realistic, would assume rate-limiting adsorption of guest at the surface of apohost, followed by faster diffusion of bound guest molecules in the solid interior; $\text{rate} \propto k_a [\text{guest}]$, where k_a is the adsorption rate constant.

(37) For the guest control of diol inclusion host lattices, see: (a) Reference 8. (b) Ung, A. T.; Bishop, R.; Craig, D. C.; Dance, I. G.; Scudder, M. L. *Struct. Chem.* **1992**, *3*, 59–61. (c) Ung, A. T.; Bishop, R.; Craig, D. C.; Dance, I. G.; Scudder, M. L. *J. Chem. Soc., Chem. Commun.* **1993**, 322–323.

be converted to a covalent silicone bridge (O–Si–O) by using an appropriate silicone reagent. Crystal-phase *polymerization* of compound **1a** along this line is also an interesting extension of this work in the context of organic zeolites.

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Supporting Information Available: Table III (Solid-Gas Host–Guest Complexation Using Hydrocarbons, Haloalkanes, and Haloarenes and Vapor Pressures (*P*) of the Guests at 25 °C), Experimental Section with headings of General Procedures, X-ray Crystal Structure Determinations, Recrystallization and

Guest Exchange, Apohost and Its Complexation with Liquid and Gaseous Guests, and Solid–Solid Complexation, and tables of parameters and anisotropic temperature factors for non-hydrogen atoms, positional parameters for hydrogen atoms, bond lengths and angles, and torsion angles (14 pages); listings of observed and calculated structural factors for adduct **1a**·2(**2k**) (14 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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