Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

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To cite this Article Hayashi, Naoto , Yamaguchi, Kumiko and Matsumoto, Kiyoshi(2001) 'Inclusion Properties and Crystal Structure of Clathrates Constructed Based on "π-sandwich"', Supramolecular Chemistry, 13: 1, 45 — 52

To link to this Article: DOI: 10.1080/10610270108034881

URL: http://dx.doi.org/10.1080/10610270108034881

SUPRAMOLECULAR CHEMISTRY, Vol. 13, pp. 45–52
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Inclusion Properties and Crystal Structure of Clathrates Constructed Based on "π-sandwich"

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Inclusion behavior of structurally similar host compounds, 1,4-bis[1-(9-anthryl)-3-propen-1-on-3-yl]benzene (1) and 1,4-bis[3-(9-anthryl)-3-propen-1-on-1-yl]benzene (2), has been studied. Both hosts preferred cyclic, non-branched small molecules as a guest component, to yield 1 : 2 clathrates specifically. X-ray powder diffraction studies revealed that those 1 : 2 clathrates of 1 and 2 were respectively isostructural. X-ray analyses of (1)(THF)$_2$ ($P\bar{1}$, $a = 10.910(2)$, $b = 19.656(5)$, $c = 9.172(4)$ Å, $\alpha = 95.58(3)$, $\beta = 93.67(2)$, $\gamma = 103.30(2)°$, $D_{\mathrm{calc}} = 1.195\,\mathrm{g\,cm^{-3}}$, $Z = 2$, and $R = 0.067$ for 8644 observed reflections) and (2)(1,4-dioxane)$_2$, ($P2_1/n$, $a = 5.661(1)$, $b = 17.971(3)$, $c = 18.619(3)$ Å, $\beta = 91.37(2)°$, $D_{\mathrm{calc}} = 1.254\,\mathrm{g\,cm^{-3}}$, $Z = 2$, and $R = 0.097$ for 4353 observed reflections) illuminated that their guest preference should be ascribed to the commonly observed "π-sandwich" structure, in which guest molecules are enclathrated between two anthracene planes of the host molecules.

Keywords: X-ray structure; Clathrate; Crystal engineering; π-sandwich

INTRODUCTION

Although control of crystal structure was thought to be difficult [1], it has been recognized that, when a molecule has a substituent capable of strong intermolecular interactions, it is possible that molecular arrangement in crystalline is controlled. A number of examples have been reported, in which hydrogen bond [2], $\pi-\pi$ interaction [3], or metal coordination [4] control the crystal structure. On the other hand, when strong intermolecular interactions are not available, it remains quite difficult to control crystal structure. This is because crystal structure is determined by summation of various forces. Prediction of crystal structure on the analogue of known ones is also difficult. The reason is as follows. When the molecular structure is changed, the change will affect intermolecular interactions. In most cases, it causes a change in the balance of various forces, and consequently the packing structure will no longer be identical. For example, it is known that, although a C–F group is similar to a C–H group in size and shape, when they replace each other, the packing structure is generally different [5]. However, it is also important to know the principles of molecular

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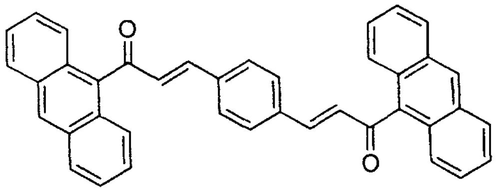
*Corresponding author. e-mail: hayashi@alchemy.jinkan.kyoto-u.ac.jp arrangement controlled by weak intermolecular interactions.

In order to study the relationship between molecular arrangement and weak intermolecular interactions, the authors have investigated inclusion behavior and crystal structures of clathrates comprised of structurally similar host molecules [6, 7]. We consider that clathrates should be useful for this purpose. Since the packing structure of clathrates is mainly governed by host compounds, they often afford isomorphic crystals for structurally similar guests. On the other hand, for various guest molecules, they easily yield a wide variety of polymorphs. In the present study, we have designed two molecules, **1** and **2**, for the hosts of clathrates (Scheme 1). These molecules have a "wheel-and-axle" structure [8], which was developed by Toda and has become widely known as the typical structure of clathrate host molecules. The molecular structures of **1** and **2** are similar but distinct. No matter which is observed, similar or distinct inclusion behavior and packing structures, the results will be helpful in understanding the packing principles of structurally similar molecules. If, in spite of their different packing structures, a common structure is observed among those clathrates, it will provide important information to engineer crystals by means of weak intermolecular interactions.

RESULTS AND DISCUSSION

Compound **1** was quantitatively obtained by aldol condensation of 9-acetylanthracene and telephthalaldehyde. By slow evaporation, **1** afforded a wide variety of clathrates. The results (Tab. I) can be summarized as follows: (1) the host **1** preferred cyclic, non-branched small molecules as a guest component, (2) the host-to-guest ratios were mainly 1 : 2, along with a few samples of 1 : 4 stoichiometry. Interestingly, X-ray powder diffraction (XRPD) study revealed that 1 : 4 and 1 : 2 clathrates were respectively isostructural. One may remember the clathrates of *N,N'*-ditosyl-*p*-phenylenediamine [9], in which similar guest preference was observed. But, while the hydrogen bond between the host



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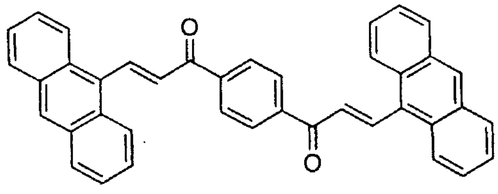


2

SCHEME 1

TABLE I Host-guest ratios of clathrates of the host **1** (1 : x)

Guest	**1**
THF	2
1,3-dioxolane	2
tetrahydrothiophene	2
thiophene	2
furan	2
pyrrole	4
2-methylfuran	0
2-methylthiophene	0
1,4-dioxane	4
tetrahydropyran	2
benzene	^{a}
pyridine	^{a}
fluorobenzene	0
toluene	0
acetone	0
methanol	0
diethyl ether	0
chloroform	0

[a] Cannot be determined because of unstability of clathrates in air.

and guests was mainly responsible for the guest preference in those clathrates, such strong intermolecular interaction is obviously not available in the present study. To investigate the inclusion behavior related to intermolecular interaction, we performed single crystal X-ray diffraction study of (**1**)(THF)$_2$.

Figure 1(a) shows the packing structure of (**1**)(THF)$_2$. There exist one independent host and two independent guest molecules (i.e., guest A and B). Each anthracene plane makes a right angle with the central phenyl moiety, and thus **1** is in C shape [10]. Two molecules of **1** form a dimer to provide an inclusion cavity in its center, where a pair of the guest A's is seized. It is noted that the enclathrated guests are sandwiched between two anthracene moieties of the host molecules (Fig. 1(b)). Two anthracene planes face each other in parallel with an interplanar distance of 9.41 Å. Although the atomic positions of the guest A were not determined precisely because of their disorder, the nearest π(anthryl)-C(guest) distance is estimated at approximately 3.4 Å, which indicates the presence of CH/π interaction [12] between guest A and the host. Guest B seems to be accommodated simply by packing forces.

As we reported previously [13, 14], a π-sandwich structure was also observed in (**1**)(1,4-dioxane)$_4$. The packing structure of (**1**)(1,4-dioxane)$_4$, as depicted in Figure 2(a), is different from (**1**)(THF)$_2$. Two side arms of the

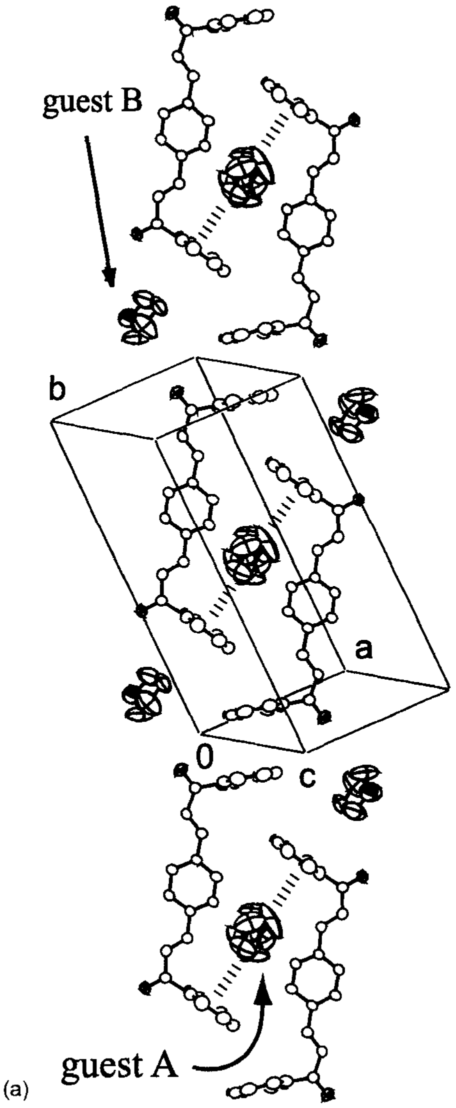


FIGURE 1 Packing illustration (a) and perspective view of the "π-sandwich" structure (b) of (**1**)(THF)$_2$. For clarity, guest molecules and oxygen atoms of the host are represented by discriminated ellipsoids, and hydrogen atoms are omitted. CH/π interactions are specified by dotted lines.

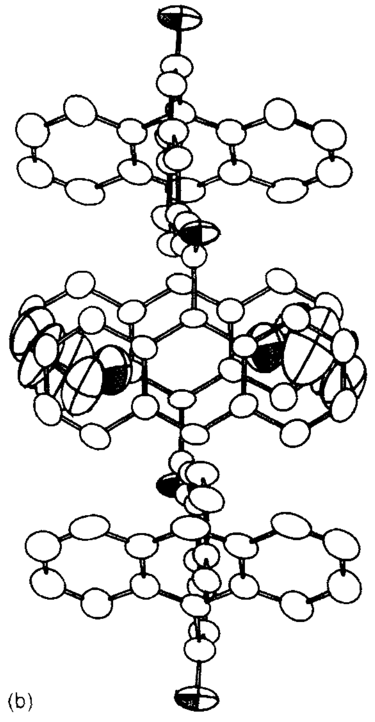


FIGURE 1 (Continued).

host adopt *trans* orientation in (**1**)(1,4-dioxane)$_4$, while *cis* is used for (**1**)(THF)$_2$. Consequently, the host molecules are in S shape so that they cannot form the dimeric structure but instead stack one-dimensionally. There is enclathrated only one independent guest molecule, whereas there are two for (**1**)(THF)$_2$. Nevertheless, the guest molecules in (**1**)(1,4-dioxane)$_4$ are also sandwiched between two parallel planes of anthracenes (Fig. 2(b)). The interplanar distance (9.7 Å) and the nearest π(arom)–C(guest) distance (3.6 Å) are very close to those of (**1**)(THF)$_2$, respectively.

We assumed that this "π-sandwich" structure may control the packing structure of the clathrates of the host **1**, in which no strong intermolecular interaction can exist. To prove the hypothesis, we designed a new host compound **2**, the molecular structure of which is close to **1**. The difference between **1** and **2** is the direction of enone moiety. Thus, the inclusion behavior of **2** was expected to be similar to that

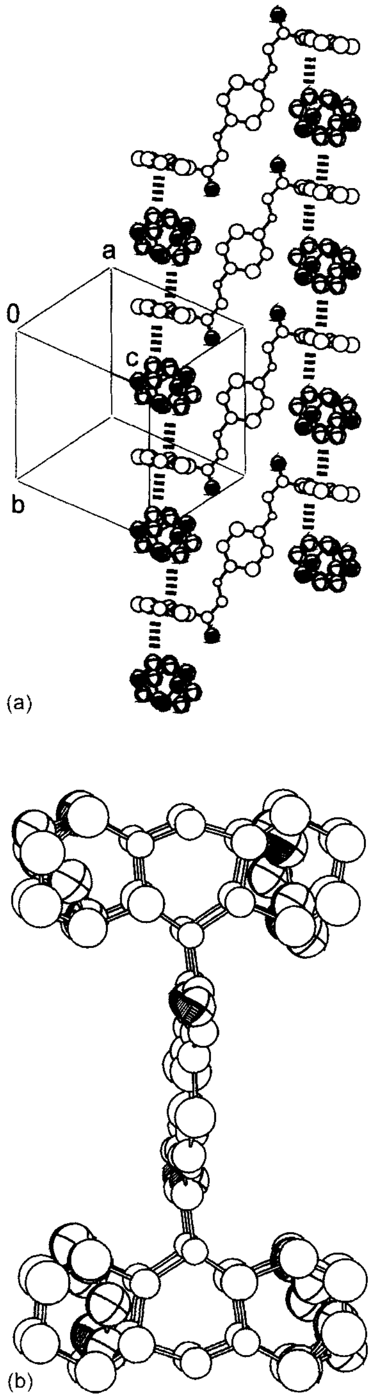


FIGURE 2 Packing illustration (a) and perspective view of the "π-sandwich" structure (b) of (**1**)(1,4-dioxane)$_4$. For clarity, guest molecules and oxygen atoms of the host are represented by discriminated ellipsoids, and hydrogen atoms are omitted. CH/π interactions are specified by dotted lines.

of **1**. Compound **2** was also yielded by aldol condensation of corresponding aldehyde and ketone. As expected, this compound also behaved as a host of clathrates. Like **1**, **2** didn't afford clathrates with hexane, dichloromethane, ether, or acetone but enclathrated cyclic, non-branched small molecules, such as thiophene and 1,4-dioxane. Compared with **1**, however, the host **2** was much more selective. Neither benzene, tetrahydrothiophene, furan, nor pyran was enclathrated as a guest.

By X-ray studies, the obtained clathrates with 1 : 2 stoichiometry, (**2**)(1,4-dioxane)$_2$ and (**2**)(thiophene)$_2$, were revealed to be isostructural. To understand the inclusion behavior of **2**, we performed a single crystal X-ray analysis of (**2**)(1,4-dioxane)$_2$. Figure 3(a) shows that (**2**)(1,4-dioxane)$_2$ packs differently from (**1**)(THF)$_2$ or (**1**)(1,4-dioxane)$_4$. The host molecules array in such a manner that a "wheel" of a host fits in a crevice of another host. No parallel-facing anthracenes are found. Nevertheless, it is again observed that enclathrated guest molecules are sandwiched between two π-planes (Fig. 3(b)). These findings seem strongly to support our hypothesis of a "π-sandwich" which is a principal motif controlling the packing structure.

Before preparing clathrates of the host **2**, we had anticipated that structurally similar **1** and **2** would yield isomorphic crystals. Against expectation, in spite of structural similarity, **1** and **2** pack differently in their clathrates. The reason is explainable in terms of the conformation of enone moieties of the host molecules. As shown in Figures 1 and 2, the host **1** always adopted *s-trans* conformation, whereas **2** took *s-cis* (see Fig. 3). Obviously, **2** cannot adopt *s-trans* conformation, owing to steric repulsion of hydrogens (Scheme 2). In contrast, it is not clear why **1** prefers *s-trans* over *s-cis*. A semi-empirical calculation (PM3) [15] of the model compound [1-(9-anthryl)-3-phenyl-3-propen-1-one] showed that *s-trans* is more stable. However, the energetic difference between two conformers is small ($\Delta H_f = -72.349\,\text{kcal mol}^{-1}$ for *s-trans*, while $-71.570\,\text{kcal mol}^{-1}$ for *s-cis*, thus $\Delta\Delta H_f = 0.779\,\text{kcal mol}^{-1}$).

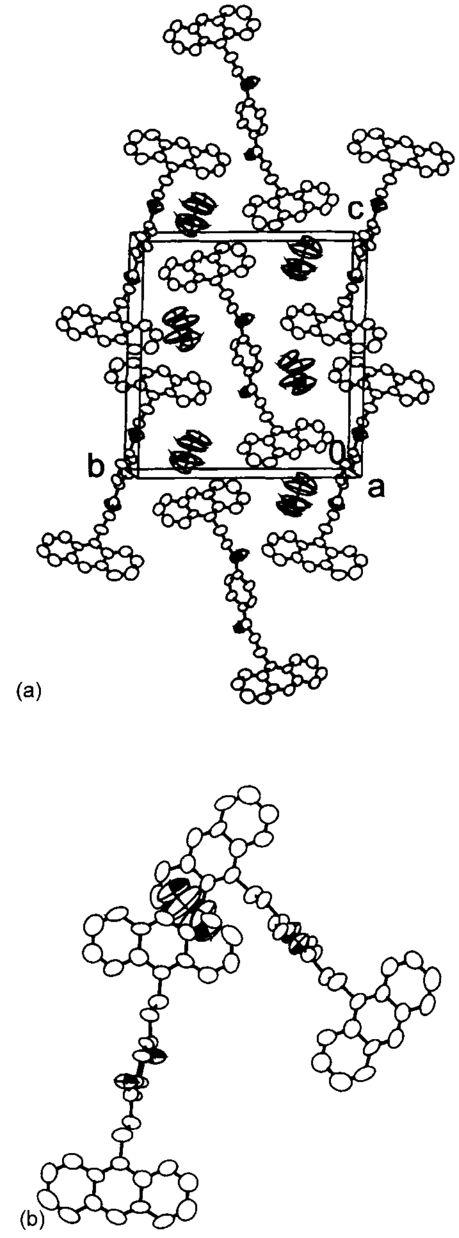
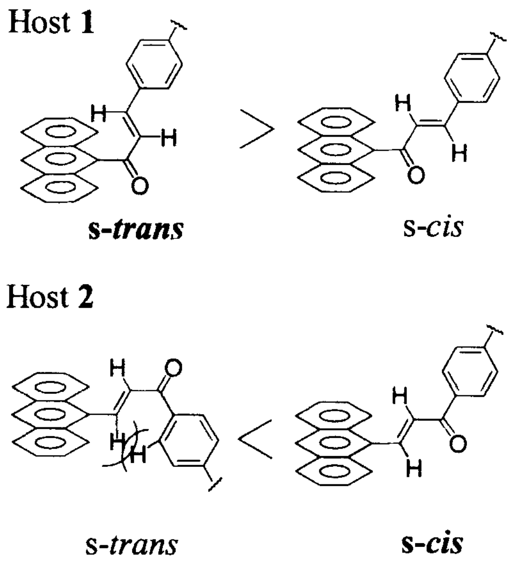


FIGURE 3 Packing illustration (a) and perspective view of the "π-sandwich" structure (b) of (**2**)(1,4-dioxane)$_2$. For clarity, guest molecules and oxygen atoms of the host are represented by discriminated ellipsoids, and hydrogen atoms are omitted.

Conclusively, we found an example of clathrates in which the packing structure was



SCHEME 2

constructed with a motif of the "π-sandwich". The "π-sandwich" appears to control the guest preference as well. The energetic advantage of the "π-sandwich" may be small, since solely cyclic, non-branched molecules were enclathrated, which are fitted to the inclusion cavity so as to give the "π-sandwich". It was not successful in obtaining good guest-free crystals of **1** and **2**. This finding seems to indicate the importance of the "π-sandwich" in constructing the crystal structures presented here.

EXPERIMENTAL

Synthesis of 1,4-bis[1-(9-anthryl)-3-propen-1-on-3-yl]benzene (1)

To a mixture of 7.73 g of 9-acetylanthracene [16] and 2.49 g of telephthalaldehyde in 115 mL of THF was added dropwise a solution of lithium diisopropylamide (prepared from 5.20 mL of diisopropylamine and 23.2 mL of n-butyllithium solution (hexane, 1.6 mol dm^{-3}) in 75 ml of THF) during 40 minutes at 0°C in an argon atmosphere. After overnight stirring, water was added to the reaction mixture. The yielded yellow powder was collected by suction filtration. The crude **1** (11.10 g, quantitative) was used without further purification. ^{1}H-NMR: δ_H 8.55 (s, 2H, arom), 8.1–7.8 (m, 8H, arom), 7.6–7.4 (m, 12H, arom), 7.24 (*d*, $J = 16$ Hz, 2H, vinyl), 7.20 (*d*, $J = 16$ Hz, 2H, vinyl). IR: 675 (s), 816 (w), 887 (w), 895 (w), 966 (m), 1109 (m), 1119 (m), 1151 (m), 1171 (m), 1194 (m), 1221 (m), 1300 (w), 1417 (m), 1585 (s), 1618 (s), 1645 (s). Anal. Calcd for $C_{40}H_{26}O_2$: C, 89.19; H, 4.87. Found: C, 88.97; H 4.95.

Synthesis of 1,4-bis[3-(9-anthryl)-3-propen-1-on-1-yl]benzene (2)

To a mixture of 2.43 g of 9-anthracenealdehyde and 0.95 g of *p*-diacetylbenzene [17] in 30 mL of THF was added dropwise a solution of lithium diisopropylamide (prepared from 1.70 mL of diisopropylamine and 7.40 mL of *n*-butyllithium solution (hexane, 1.6 mol dm^{-3}) in 20 ml of THF) during 15 minutes at 0°C in an argon atmosphere. After overnight stirring, water was added to the reaction mixture. The yielded

TABLE II Selected crystal data and structure refinement for (1)(THF)$_2$, (2)(1,4-dioxane)$_2$

Clathrate	(1)(THF)$_2$	(2)(1,4-dioxane)$_2$
Molecular formula	$C_{48}H_{42}O_4$	$C_{48}H_{48}O_6$
Molecular weight	682.82	714.82
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell parameters		
a, Å	10.910(2)	5.661(1)
b, Å	19.656(5)	17.971(3)
c, Å	9.172(4)	18.619(3)
α, °	95.58(3)	90
β, °	93.67(2)	91.37(2)
γ, °	103.30(2)	90
V, Å^3	1897.5(10)	1896.6(6)
Z	2	2
$F(000)$	724	756
D_{calc}, g cm^{-3}	1.195	1.254
Crystal size, mm	0.40 × 0.10 × 0.10	0.55 × 0.10 × 0.10
Scan speed (deg mim^{-1})	4	4
$2\theta_{\max}$, °	55	55
Unique data measured	8644	4353
data with $> 2\sigma$	1705	738
Number of variables	469	244
R value	0.067	0.097
constant g in weighting scheme[a]	0.1051	0.1223
$wR(F^2)$	0.285	0.341
S	0.883	0.853
Residual extrema in final difference map, eÅ^{-3}	+0.237, −0.211	+0.353, −0.150
largest and mean Δ/σ	0.047, 0.003	0.014, 0.002

[a] $w = 1/[\sigma^2(F_0) + (gP)^2]$, where $P = (F_0^2 + 2F_c^2)/3$.

orange powder was collected by suction filtration and washed by a small portion of ether. The crude **2** (2.62 g, 83%) was used without further purification. ^{1}H-NMR: δ_H 8.86 (d, $J = 13$ Hz, 2H, vinyl), 8.5–8.0 (m, 14H, arom), 7.63 (d, $J = 13$ Hz, 2H, vinyl), 7.6–7.5 (m, 8H, arom). IR: 692 (w), 702 (w), 843 (m), 881 (m), 929 (w), 1011 (m), 1034 (w), 1217 (w), 1223 (w), 1265 (s), 1290 (w), 1593 (s), 1661 (s). Anal. Calcd for $C_{40}H_{26}O_2$: C, 89.19; H, 4.87. Found: C, 89.15; H 4.60.

X-ray Study

Clathrate crystals suitable for X-ray diffraction study were obtained by slow recrystallization. Information concerning the crystallographic data and structure determination of the three clathrates are summarized in Table II. Intensities were collected using the ω-technique on a RIGAKU AFC-5S diffractometer using Mo-K_α radiation ($\lambda = 0.71069$ Å) at 291 K.

All calculations were performed on a Linux computer with the SHELX-97 program packages [18]. The structures were solved by direct methods and all non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were generated at ideal positions, assigned appropriate isotropic temperature factors, and included in the structure-factor calculations.

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