Clathrate Formations with Isomeric Host Compounds Based on Thieno[3,2-*b*]thiophene and Thieno[2,3-*b*]thiophene: Inclusion Modes and Crystal Structures

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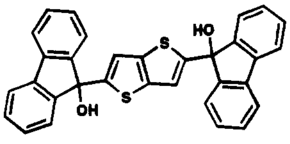
Two host compounds **1** and **2**, which are composed of isomeric thieno[3,2-*b*]thiophene and thieno[2,3-*b*]thiophene, respectively, afforded crystalline host−guest inclusion complexes. Benzene and DMSO were chosen as guest species capable of the least and the most intense host−guest interactions, respectively, and the X-ray crystal structures of their clathrates were investigated. Benzene was enclathrated in each of **1** and **2** with different host-to-guest ratios to give (**1**)$_3$(benzene)$_4$ and (**2**)(benzene). In both crystals, there are pairs of benzene molecules arranged in parallel offset. Crystal data: (**1**)$_3$(benzene)$_4$, triclinic, $P\bar{1}$, a = 13.940(5) Å, b = 15.537(2) Å, c = 13.040(4) Å, α = 104.13(2)°, β = 119.91(2)°, γ = 92.24(2)°, V = 2330(1) Å^3, Z = 1; (**2**)(benzene), triclinic, $P\bar{1}$, a = 12.427(4) Å, b = 13.041(4) Å, c = 10.733(2) Å, α = 92.97(2)°, β = 104.79(2)°, γ = 117.10(1)°, V = 1648.2(7) Å^3, Z = 2. The (**2**)(benzene) crystals eliminate the guest at significantly high temperature, 128 °C, which is discussed in light of the hydrogen-bonded rigid host lattices. The crystals including DMSO, (**1**)(DMSO)$_2$, and (**2**)(DMSO)$_2$ were isomorphous. Crystal data: (**1**)(DMSO)$_2$, triclinic, $P\bar{1}$, a = 12.618(1) Å, b = 13.161(2) Å, c = 11.615(3) Å, α = 115.41(2)°, β = 97.04(2)°, γ = 103.41(1)°, V = 1639.7(6) Å^3, Z = 2; (**2**)(DMSO)$_2$, triclinic, $P\bar{1}$, a = 12.613(1) Å, b = 13.383(3) Å, c = 11.601(2) Å, α = 115.49(1)°, β = 97.28(1)°, γ = 104.60(1)°, V = 1647.3(5) Å^3, Z = 2. The formation of the isostructural crystals is discussed on the basis of the strong hydrogen bonding between the host and guest molecules, which counteracts the structural and electronic differences between **1** and **2**. In line with this interpretation, the conformational preference of the OC−CS bonds due to the electrostatic O···S attraction was overcome in the DMSO inclusion crystals. In spite of the isostructural crystal packing, their thermal behavior of guest release, as investigated by DSC measurements, is rather different; (**1**)(DMSO)$_2$ loses the guest DMSO molecules stepwise at 111 and 138 °C, whereas (**2**)(DMSO)$_2$ does at 96 and 159 °C.

We have recently introduced a series of new host compounds including 2,5-bis(9-hydroxyfluoren-9-yl)thieno[3,2-*b*]thiophene (**1**) for crystalline inclusion complexes, generally designated as clathrate crystals.[1] These are composed of a linearly fused thiophene ring as a rigid backbone and two fluorenyl groups as highly bulky substituents.[2−5] As a part of our continuing work we have prepared 2,5-bis(9-hydroxyfluoren-9-yl)thieno[2,3-*b*]thiophene (**2**) as an isomeric host species of **1**.[6] The size and shape of these molecules are quite similar to each other. Thus, it is of interest to investigate the inclusion properties and crystal packings of the clathrate crystals composed of these two isomeric host compounds.



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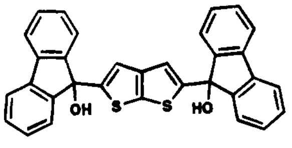

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In particular, we are interested in possible isomorphism of two-component crystals. Isomorphism is most frequently encountered in compounds of similar molecular shape.[7] Crystalline host−guest inclusion complexes frequently give isomorphous crystals for different guest molecules, since change of the guest component, especially of nonpolar guest compounds of small molecular size, causes only a slight perturbation of the whole host−guest crystal construction which is mainly controlled by the host lattices. A relevant example is reported recently for cholic acid enclathrating nitrobenzene and aniline.[8] On the other hand, for different hosts, isomorphous crystals have rarely been encountered, even if common guest species are incorporated. This may be because the lattices depend mainly on the host structure, so the perturbation to the crystal packing induced by the host is more pronounced. Furthermore, host compounds with structural similarity have not been explored thus far. In this paper we describe the inclusion properties of hosts **1** and **2**, focusing on the similarity and difference of the X-ray crystal structures of their clathrate crystals. Two

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(2) Hayashi, N.; Mazaki, Y.; Kobayashi, K. *J. Chem. Soc., Chem. Commun.* **1994**, 2351.

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Table 1. Crystalline Inclusion Compounds of 1 and 2: Host-to-Guest Stoichiometric Ratios

guest	host 1	host 2
acetone	1:2	4:1
benzene	3:4	1:1
DMF	1:2	*b*
DMSO	1:2	1:2
dioxane	1:2	1:1
CH_2Cl_2	*a*	2:1
EtOH	1:2	2:1
^nPrOH	1:2	1:2

[a] No complexation was observed. [b] Difficult to crystallize.

guest species, benzene and dimethyl sulfoxide (DMSO), were used as guest species providing two extreme cases of intermolecular interactions, the former having only weak intermolecular interactions and the latter being capable of strong hydrogen bonding.

Results and Discussion

Inclusion Properties of 1 and 2. Recrystallization of **1** and **2** from various solvents yielded the clathrate crystals, as given in Table 1. Both act as efficient host compounds.[2,6] However, in spite of the structural similarity, **1** and **2** gave rather different host-to-guest stoichiometric ratios for each guest compound. The inclusion complexes obtained from host **1** have a 1:2 host-to-guest ratio with only one exception for benzene, whereas host **2** does not show any trend in host-to-guest ratios. Hydrogen bonding between the diol host and the guest may play a principal role in host **1** leading to the preferential enclathration with a 1:2 stoichiometry. Benzene cannot be involved in hydrogen bonding, and therefore, lattice-controlled cocrystallization might be responsible for the rather unusual host-to-guest stoichiometry of 3:4. As there are no particular trends in the inclusion properties of host **2** which is also a diol host, the molecular packing may depend on various factors, including the hydrogen bonding, the electrostatic S···O interactions, and the close-packing principle of the structure with the inversion center.

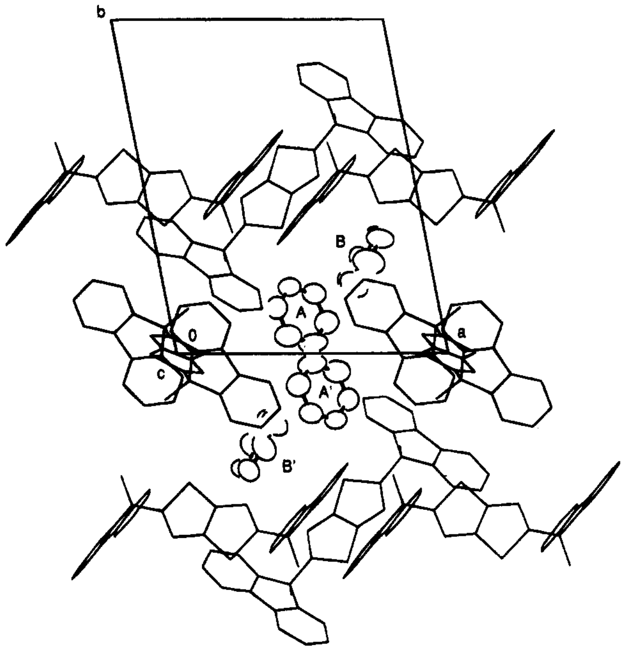

Figure 1. Packing arrangements of $(\mathbf{1})_3(\text{benzene})_4$ viewed down the *c* axis. The host molecules are represented by sticks, the atoms in guest molecules are in thermal elipsoids.

The isomorphous crystals should be found in the clathrates of the same host-to-guest stoichiometric ratios for **1** and **2**. As revealed by our previous X-ray analyses, $(\mathbf{1})(\text{DMSO})_2$ and $(\mathbf{2})(\text{DMSO})_2$ were isomorphous to each other.[6] We believe that the same stoichiometric ratio and the isostructural packing are attributable to the strong hydrogen bonding ability of DMSO,[9] as discussed later.

The Crystal Structures of $(\mathbf{1})_3(\text{benzene})_4$ and $(\mathbf{2})(\text{benzene})$ Including Pairwise Benzenes. Crystal data are given in Table 2. The structural diagram of $(\mathbf{1})_3(\text{benzene})_4$ is shown in Figure 1. In crystals $(\mathbf{1})_3(\text{benzene})_4$ there are three crystallographically independent host molecules. These host molecules adopt almost the same conformation: the C−O(H) bonds are situated close to the eclipsed conformation with respect to the C−S bond of the thiophene ring. Thus, in $(\mathbf{1})_3(\text{benzene})_4$, the

Table 2. Crystal Data, Experimental Parameters, and Selected Details of the Refinement Calculations (esds Are in Parentheses)

	$(\mathbf{1})(\text{DMSO})_2$	$(\mathbf{2})(\text{DMSO})_2$	$(\mathbf{1})_3(\text{benzene})_4$	$(\mathbf{2})(\text{benzene})$
formula	$(C_{32}H_{20}O_2S_2)(C_2H_6SO)_2$	$(C_{32}H_{20}O_2S_2)(C_2H_6SO)_2$	$(C_{32}H_{20}O_2S_2)_3(C_6H_6)_4$	$(C_{32}H_{20}O_2S_2)(C_6H_6)$
M_w	656.91	656.91	1814.39	578.71
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	12.618(1)	12.613(1)	13.940(5)	12.427(4)
b/Å	13.161(2)	13.383(3)	15.537(2)	13.041(4)
c/Å	11.615(3)	11.601(2)	13.040(4)	10.733(2)
α/deg	115.41(2)	115.49(1)	104.13(2)	92.97(2)
β/deg	97.04(2)	97.28(1)	119.91(2)	104.79(2)
γ/deg	103.41(1)	104.60(1)	92.24(2)	117.10(1)
cell volume/Å^3	1639.7(6)	1647.3(5)	2330(1)	1468.2(7)
Z	2	2	1	2
D_c/g cm^{-3}	1.331	1.324	1.293	1.309
crystal dimens/mm	0.50 × 0.40 × 0.40	0.60 × 0.40 × 0.30	0.40 × 0.40 × 0.40	0.45 × 0.35 × 0.20
scan range [scan mode]	4 − 55 [$\omega - 2\theta$ scan]	4 − 40 [ω scan] 40 − 55 [$\omega - 2\theta$ scan]	3 − 55 [ω scan]	4 − 45 [ω scan] 45 − 55 [$\omega - 2\theta$ scan]
N_{obs}	7809	7993	10194	7199
$N_{ref}[\lvert F_o\rvert > 3\sigma(\lvert F_o\rvert)]$	4552	4290	7855	5158
no. of variables refined	380	461	716	484
direct methods	SAPI-85	SHELXS 86	SHELXS 86	SHELXS 86
R value	0.10	0.0951	0.0478	0.0481
R_w value[a]	0.0741	0.0903	0.0582	0.0449
weights	$g = 0.001$[b]	unit weight	$g = 0.005$[b]	unit weight

[a] $R_w = [\sum w\lvert\Delta F\rvert^2/\sum w\lvert F_o\rvert^2]^{1/2}$. [b] $w^{-1} = \sigma(\lvert F_o\rvert)^2 + g\lvert F_o\rvert^2$.

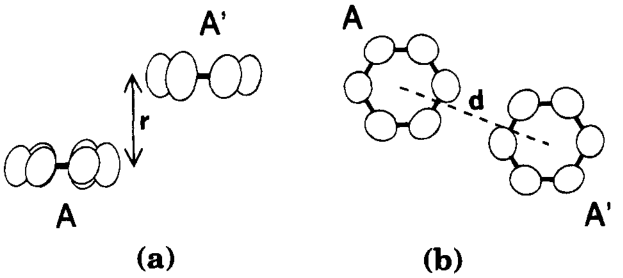

Figure 2. Geometry of the parallelwise benzene molecules of A···A' in $(\mathbf{1})_3(\text{benzene})_4$: (a) side views; (b) face-on view; the interplanar distance $r = 2.73$ Å. The offset distance $d = 4.81$ Å.

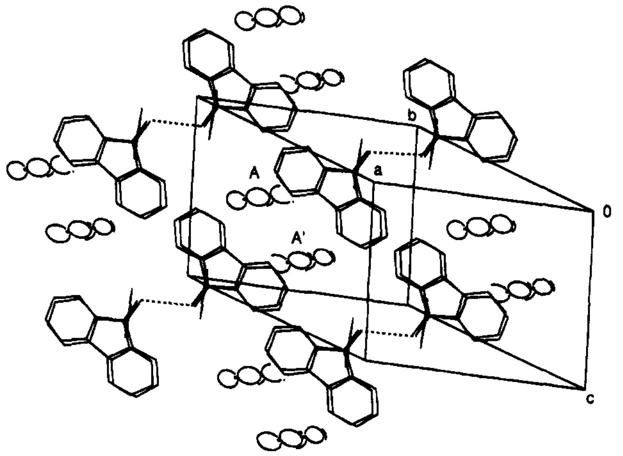

Figure 3. Packing arrangements of (**2**)(benzene). The dotted lines indicate the relations linked by the hydrogen bonds. See also Figure 4.

two hydroxyl groups in each host molecule are directed on the opposite side of the molecular framework (*anti* orientation). The torsional angles of the OC–CS bonds of the host compounds of $(\mathbf{1})_3(\text{benzene})_4$ are 48°, 43°, and 56°. There are no hydrogen bonds linking the host **1** molecules.

Two crystallographically independent benzene molecules (A and B) are arranged to make centrosymmetrically related pairs of each (A···A' and B···B'). These four guest molecules are enclosed in the cages, which are surrounded by the flat π-fragments of a total of eight host molecules. Therefore, the complex $(\mathbf{1})_3(\text{benzene})_4$ is regarded as a *true clathrate*.[10] Among four benzene molecules, the two benzene molecules in the A···A' pair are positioned close to each other in parallel orientation. The mode of orientation in the pairwise benzene molecules is shown in Figure 2. The center-to-center separation is 5.53 Å, and the interplanar distance formed by the two parallel benzenes is 2.73 Å. Thus, the benzene rings are not directly overlapped.

The crystal structure of (**2**)(benzene) is shown in Figure 3. In contrast to $(\mathbf{1})_3(\text{benzene})_4$, the C–O(H) bonds in (**2**)(benzene) crystals are arranged on the same side (*syn* orientation). The dihedral angles are 31° and 33°. Two neighboring host molecules make a hydrogen-bonded cyclic dimer with an O···O distance of 2.86 Å.[11] An inclusion cavity is produced inside the dimeric structure (Figure 4), in which two benzene molecules are located as parallel pairs at a center of inversion. The interplanar distance of pairwise benzene molecules is 3.53 Å and the center-to-center separation is 4.08 Å, as seen in Figure 5 which shows the overlapping motif. The orientation associated with the $\pi-\pi$ interactions is thought to be electrostatic in origin, and therefore, intense $\pi-\pi$ interactions have been suggested to occur in offset stacked and edge-to-face orientations.[12] More recent calculations favor a parallel-displaced structure as the most stable one.[13] The parallel-displaced geometry realized in the benzene dimer in (**2**)(benzene) is considered to be in the range of the most stable $\pi-\pi$ interaction.[13]

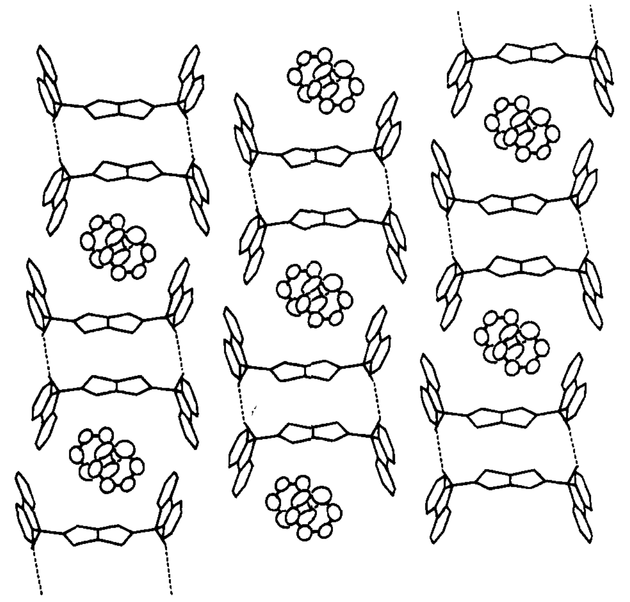

Figure 4. Perspective view of the inclusion cavity of (**2**)(benzene).

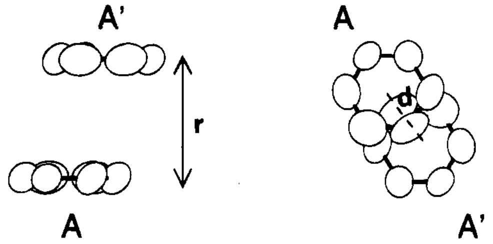

Figure 5. Molecular overlappings of the pairwise benzenes in (**2**)(benzene): (a) side view; (b) face-on view; the interplanar distance $r = 3.53$ Å. The offset distance $d = 2.05$ Å.

In the clathrate crystals of benzene, all the OC–CS bonds in the host molecules adopt a preferentially gauche conformation close to the eclipsed one with respect to the C–S and C–O bonds, as summarized in Table 3. These results could be attributed to the attractive electrostatic S···O interaction.[14] Thus, the two hydroxyl groups of host **1** are directed opposite each other (*anti*), and those of host **2** are in a *syn* orientation according to the geometry of the C–S bonds in the thieno[3,2-*b*]thiophene and thieno[2,3-*b*]thiophene backbone. Benzene cannot be involved in hydrogen bonding, and therefore, the electrostatic

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(10) Weber, E. In ref 1b; Vol. 140, p 1.

(11) Following the current consensus for OH···O hydrogen bonding, we consider the O···O distance of 2.4–3.0 Å as proof of existence of hydrogen bonding.

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Table 3. Torsional Angles $|\chi|$ of the OC–CS Bonds of the Host Molecules

compd	$|\chi|$ (deg)			
$(\mathbf{1})_3$(benzene)$_4$	48	43	56	
(**2**)(benzene)	31	33		
(**1**)(DMSO)$_2$	41	20		
(**2**)(DMSO)$_2$	11	172	143	38

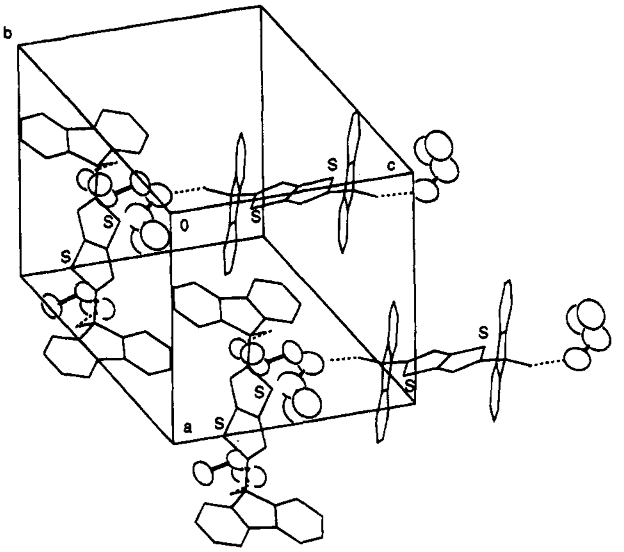

Figure 6. Packing arrangements of (**1**)(DMSO)$_2$.

O···S interactions are considered to be most significant in the molecular packing which depends on the position of the sulfur in the molecular periphery.

Isostructural Crystal Packing of (1)(DMSO)$_2$ and (2)(DMSO)$_2$. The crystal data of both clathrates are compared in Table 2. The X-ray crystal analyses of (**1**)(DMSO)$_2$ and (**2**)(DMSO)$_2$ have been described previously.[2] In (**1**)(DMSO)$_2$ crystals there are two crystallographically independent (host)(guest)$_2$ units, as illustrated in Figure 6. In each unit two OH groups adopt an *anti* orientation so that each of the two OH groups is individually hydrogen-bonded to a DMSO molecule with O···O distances of 2.65 and 2.73 Å. Thus, the (host)(guest)$_2$ units constitute a "wheel and axle" with the thienothiophene as the axle part and the fluorenyl groups, together with the DMSO-linked OH groups, as two wheel parts.[15] The wheel of one (host)(guest)$_2$ unit is closely located in the voids made by another (host)(guest)$_2$ unit.

The crystal structure of (**2**)(DMSO)$_2$ is shown in Figure 7. The crystal is isomorphous with (**1**)(DMSO)$_2$. Both crystallize as $P\bar{1}$. The unit cell parameters of the two crystals are quite similar (see Table 2), and the packing motifs are essentially the same. The remarkable difference in the crystal structures is the occurrence of a flip-flop disorder in the thieno[2,3-*b*]thiophene ring of (**2**)(DMSO)$_2$. This disorder could be ascribed to the similarity of dimensions of the C–S–C and C=CH–C groups of the thiophene moiety.

Two bonds connecting the wheel moieties at the 2 and 5 positions of the thieno[2,3-*b*]thiophene rings of **2** are extrapolated to intersect by 3°. The flip-flop disorder in the molecule of such a noncentrosymmetric structure would require more space occupied by the host and guest units as compared with crystal structures containing no disorder. Thus, the (**2**)(DMSO)$_2$ crystal seems to pack less closely and to be less stable than (**1**)(DMSO)$_2$. The slight difference in the density of the crystals is consistent with the structures; the calculated density of (**1**)(DMSO)$_2$ is 1.331 g cm^{-3}, higher than 1.324 g cm^{-3} for (**2**)(DMSO)$_2$. Furthermore, the (**2**)(DMSO)$_2$ crystal loses guest molecules much easier than (**1**)(DMSO)$_2$, as described later.

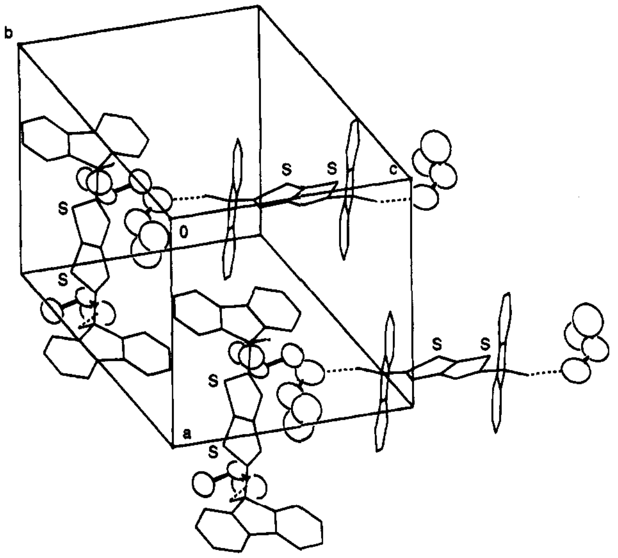

Figure 7. Packing arrangements of (**2**)(DMSO)$_2$.

Upon enclathration of DMSO the packing scheme is not dependent on the mode of fusion of the thiophene units in these isomeric molecules. Thus, the similarity of the molecular geometry, rather than location of the sulfur atoms in the molecular framework, is the important factor in determining the crystal structure. In (**1**)(DMSO)$_2$, two C–O(H) bonds in the host adopt a gauche conformation close to the eclipsed one with respect to the C–S bonds of the thienothiophene rings. However, in (**2**)(DMSO)$_2$, one of the two C–OH bonds results in an *anti* conformation at the expense of the attractive electrostatic interaction between the C–O and C–S bonds.[14] These observations may be rationalized in terms of the stabilization brought about by the strong hydrogen bonding to the guest DMSO molecules. The whole unit of (**2**)(DMSO)$_2$, which has strong hydrogen bonding, prefers the structure with the inversion center for close packing in the solid state. This factor would overcome other weak interactions such as the electrostatic O···S attractive forces, and therefore, the difference in the geometry of the C–S bonds is considered to have little effect on the molecular packing.

The crystal structures of the guest-free hosts **1** and **2** themselves should be investigated. Do they produce isomorphous crystals? Unfortunately, we could not obtain an appropriate single crystal of **2** for an X-ray crystallographical study. In the IR spectra of **1** and **2**, however, there were clear differences: **1** shows free OH absorptions, whereas **2** exhibits the presence of the hydrogen bonding seen in the solid state. Thus, **1** and **2** constitute no isostructural crystals, indicating that the position of the sulfur atoms is a rather important factor in determining their crystal structures.

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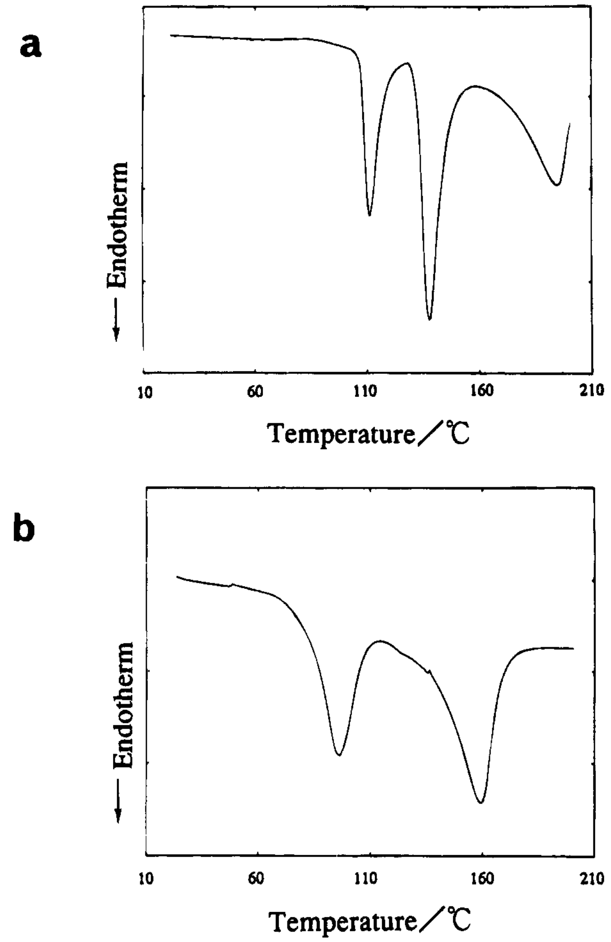

Figure 8. DSC traces: (a) (**1**)(DMSO)$_2$, (b) (**2**)(DMSO)$_2$. The peak at around 200 °C in (a) is due to melting of guest-free **1**.

Thermal Behavior of the Clathrates Including DMSO and Benzene. Thermal analysis of the clathrate crystals of **1** and **2** including DMSO and benzene was carried out. The (**1**)$_3$(benzene)$_4$ crystals are not stable enough to carry out differential scanning calorimetry (DSC) analysis: on standing at ambient temperature the guest molecules were immediately lost. Such instability can be ascribed to the true clathrate nature of (**1**)$_3$(benzene)$_4$ crystals. On the other hand, the DSC trace of (**2**)(benzene) showed a sharp endothermic peak at 128 °C, which is ca. 48 °C higher than the intrinsic boiling point of benzene. As shown in the crystal structure of (**2**)(benzene), the guest molecules are packed closely and surrounded by the rigid walls of the π-planes of the hydrogen-bonded dimeric host molecules (Figure 3). Furthermore, the $\pi-\pi$ interactions between the offset stacked dimeric benzenes may make guest extrusion difficult.

We are particularly interested in the thermal behavior of (**1**)(DMSO)$_2$ and (**2**)(DMSO)$_2$, since isomorphous forms provide a unique opportunity for the investigation of the structure-properties relationship. In spite of the isostructural crystal packing, their thermal behavior is rather different. In both crystals two endothermic peaks due to the stepwise release of the guest DMSO molecules were observed (Figure 8) at 111 and 138 °C for (**1**)(DMSO)$_2$ and at 96 and 159 °C for (**2**)(DMSO)$_2$. The first peak corresponding to the release of the DMSO molecule from (**2**)(DMSO)$_2$ crystals is at 15 °C lower than that of (**1**)(DMSO)$_2$. These results could be attributed to the less close packing of (**2**)(DMSO)$_2$ as a result of the flip-flop disorder noted above. Furthermore, the disorder in (**2**)(DMSO)$_2$ is accompanied by unfavorable conformation of the O−C bonds, that is, not being in the eclipsed conformation to the C−S bonds, therefore, the electrostatic attractive interactions between the C−S and C−O bonds exert less effect, resulting in the thermal instability of (**2**)(DMSO)$_2$.

Conclusions

We have demonstrated a unique example of isomorphous crystals of the host−guest clathrate type in which the molecular shape of the host component is quite similar. The guest-free hosts **1** and **2** crystallize with different packing from each other; nevertheless, the two-component crystals including **1** or **2** along with the common guest component produced the isostructural crystals. This phenomenon is interpreted in terms of the strong hydrogen bonding involving the guest component, in this instance, DMSO. In contrast, weakly interacting guest compounds such as benzene are enclathrated differently. In such clathrates, a variety of intermolecular interactions, including van der Waals forces, $\pi-\pi$ interactions, and electrostatic O···S attractions could compete as packing forces in cocrystallization. Thus, the crystal structure might be sensitive to a slight difference in the molecular structures of the isomeric host compounds. Furthermore, we found that benzene shows a tendency to be incorporated pairwise in both **1** and **2**.

Experimental Section

Materials. 2,5-Bis(9-hydroxyfluoren-9-yl)thieno[3,2-*b*]thiophene (**1**) was prepared in almost quantitative yield by lithiation of 2,5-dibromothieno[3,2-*b*]thiophene with n-BuLi, followed by treatment with 9-fluorenone. **1**: colorless prisms; mp 203 °C dec; ν_{max} (Nujol) 3540 cm^{-1}; UV−vis (CH_2Cl_2, nm) λ_{max} (log ϵ) 282 (4.68); δ_H (270 MHz, $CDCl_3$) 7.7−7.2 (m, 16H, ArH), 6.81 (s, 2H, ArH), 2.62 (s, 2H, OH); δ_C (68 MHz, $CDCl_3$) 149.63, 148.86, 139.10, 137.73, 129.41, 128.33, 124.80, 120.14, 116.35, 82.30; MS (*m/z*) 500 [M$^+$]. Anal. Calcd for $C_{32}H_{20}O_2S_2$: C, 76.77; H, 4.03; S, 12.81. Found: C, 76.69; H, 4.11; S, 12.66. 2,5-Bis(9-hydroxyfluoren-9-yl)thieno[2,3-*b*]thiophene (**2**) was prepared in a similar procedure employed for the preparation of **1**, using 2,5-dibromothieno[2,3-*b*]thiophene as a precursor. **2**: colorless prisms; mp 203 °C dec; ν_{max} (Nujol) 3270 cm^{-1}; UV−vis (CH_2Cl_2, nm) λ_{max} (log ϵ) 282 (4.68); δ_H (270 MHz, $CDCl_3$) 7.7−7.2 (m, 16H, ArH), 6.64 (s, 2H, ArH), 2.63 (s, 2H, OH); δ_C (126 MHz, $CDCl_3$) 151.55, 149.73, 138.63, 136.68, 128.90, 128.01, 124.64, 120.21, 115.71, 81.20; MS (*m/z*) 500 [M$^+$]. Anal. Calcd for $C_{32}H_{20}O_2S_2$: C, 76.77; H, 4.03; S, 12.81. Found: C, 76.63; H, 3.99; S, 12.68. Crystalline inclusion complexes were grown by slow evaporation of the solvent from a solution of **1** and **2** dissolved in a minimum amount of the respective solvent. The host:guest ratios were determined by means of the ^{1}H-NMR integrations and/or X-ray analysis.

Crystal Structure Determination. Crystals of (**1**)$_3$(benzene)$_4$, (**2**)(benzene), (**1**)(DMSO)$_2$, and (**2**)(DMSO)$_2$, suitable for X-ray diffraction, were grown from solutions of the host compounds **1** and **2** in the corresponding solvents. In order to prevent solvent evaporation during X-ray data collection, the crystal of (**1**)$_3$(benzene)$_4$ was carefully coated by an epoxy adhesive. All the other clathrate crystals were stable during X-ray data collection.

X-ray diffraction data were collected on a RIGAKU AFC-5 four-circle diffractometer with a graphite monochromator, using Mo−Kα (λ = 0.710 69 Å) radiation and the ω and/or $\omega - 2\theta$ scan technique at room temperature. Final refinements were based only on those observations that satisfied the conditions $|F_o| \rangle 3\sigma(|F_o|)$ for all compounds. Crystal data, details of data collection, and structural refinement are listed in Table 2. The structures were solved by direct methods using the program package SAPI-85[16] for (**1**)(DMSO)$_2$ and SHELXS-86[17] for (**1**)$_3$(benzene)$_4$, (**2**)(benzene), and (**2**)(DMSO)$_2$. All non-hydrogen atom positions of all crystals were obtained by a Fourier technique except for the atoms of C(A16), C(A17), C(B16), and C(B17) in (**2**)(DMSO)$_2$, which were calculated because of the disorder as noted in the text. For (**1**)(DMSO)$_2$, all hydrogen atoms were readily seen in the difference Fourier map; for others, hydrogen atoms were found at calculated positions.

The structures were refined by the block-diagonal least-squares method using UNICS-III.[18] Non-hydrogen atoms were refined anisotropically. Hydrogen atoms obtained from Fourier maps were refined isotropically, and those positioned by calculation were not refined. The final R and R_w values are also listed in Table 2. The occupancies in the flip-flop disorder of the thieno[2,3-*b*]thiophene moiety in (**2**)(DMSO)$_2$ crystal were estimated from the peak heights of Fourier-map to be 0.5:0.5 and were fixed. The positional disorder of DMSO molecules in (**2**)(DMSO)$_2$ was refined to give an occupancy factor of 0.77:0.23.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.[19]

Thermal Analysis. Differential scanning calorimetry (DSC) was performed on a Seiko SSC-5220 DSC system. The temperature ranges were from ambient to approximately the melting point of the host compounds at a heating rate of 10 °C min^{-1} for *ca.* 10 mg of sample in each case.

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