Isomorphic Clathrate Crystals of Isomeric Host Compounds Based on Thieno[3,2-*b*]thiophene and Thieno[2,3-*b*]thiophene

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Two isomeric host compounds **1** and **2**, which are similar in shape and size to each other, afford crystalline host–guest inclusion complexes in different host : guest ratios with only an exception for Me_2SO, a guest compound with strong hydrogen-bonding ability, to form isomorphic crystals of [**1**][Me_2SO]$_2$ and [**2**][Me_2SO]$_2$.

Crystalline host–guest inclusion complexes, generally known as clathrate crystals,[1] afford isomorphic host lattices for different guest molecules,[2] since change of the guest component, especially of the non-polar guest compounds, causes only slight perturbation of the whole host–guest crystal. However, for different hosts, isomorphic crystals have rarely been encountered, even incorporating common guest species. This may be because lattices depend mainly on the host structure, usually larger than the guest component, so perturbation to the crystal packing induced by the host is more pronounced. Structurally similar host compounds are as yet unexamined. This communication describes a unique example of isomorphous crystals of the host–guest clathrates driven by strong host–guest intermolecular hydrogen bonding.

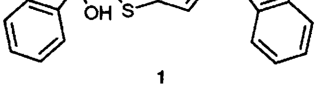
2,5-Bis(9-hydroxyfluoren-9-yl)thieno[3,2-*b*]thiophene **1** and its homologous series of compounds, all of which are composed of condensed thiophene rings as a rigid backbone and fluorenyl groups as highly bulky substituents, have been exploited as new host species for crystalline inclusion complexes.[3,4] 2,5-Bis(9-hydroxyfluoren-9-yl)thieno[2,3-*b*]thiophene **2** was prepared as an isomeric host compound of **1**, as the two are similar in shape and size. Recrystallization of **1** and **2** from solutions of various solvents yielded the clathrate crystals, as given in Table 1, with different host : guest stoichiometric ratios. The inclusion complexes obtained from host **1** have a 1 : 2 host-to-guest ratio, with only one exception for benzene, whereas host **2** shows no discernible trend in the host : guest ratio. Only for Me_2SO and *n*-propyl alcohol, did both hosts yield the same host : guest ratio of 1 : 2.

The X-ray crystal structures were determined for Me_2SO and benzene clathrates, the former being capable of strong hydrogen bonding and the latter having only weak intermolecular interactions. The crystal structures of [**1**][Me_2SO]$_2$ and [**2**][Me_2SO]$_2$ are shown in Fig. 1,† with the cell parameters† shown in Table 2; they are isomorphous. Differences in their crystal structures are the occurence of an inversion disorder of the thienothiophene plane and a locational disorder of the guest Me_2SO in [**2**][Me_2SO]$_2$. In both crystals there are two crystallographically independent [host][Me_2SO]$_2$ units. In each unit, two OH groups located on opposite sides of the molecular framework adopt an *anti* orientation so that each is individually hydrogen bonded to a Me_2SO molecule. Such an *anti* orientation is associated with the conformational preference of the SC–CO bonds in [**1**][Me_2SO]$_2$.[3] The attractive electrostatic S···O interactions have been recognized with respect to the conformation of the SC–CO bonds to bring about a *gauche* conformation close to the *eclipsed* one.[5] Now, in [**2**][Me_2SO]$_2$, the two C–OH bonds of host **2** are arranged in *anti* conformation at the expense of the conformational preference of the SC–CO bonds, leading the whole unit of [**2**][Me_2SO]$_2$ to the structure as same as [**1**][Me_2SO]$_2$. The close-packing principle predicts that structures with inversion

Table 1 Host : guest ratio of crystalline inclusion complexes of hosts 1 and 2

	1	2
acetone	1 : 2	4 : 1
benzene	3 : 4	1 : 1
DMF	1 : 2	*a*
Me_2SO	1 : 2	1 : 2
dioxane	1 : 2	1 : 1
CH_2Cl_2	*a*	2 : 1
EtOH	1 : 2	2 : 1
Pr^nOH	1 : 2	1 : 2

[a] No complexation was observed.



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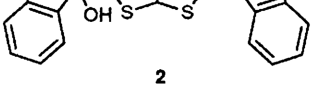

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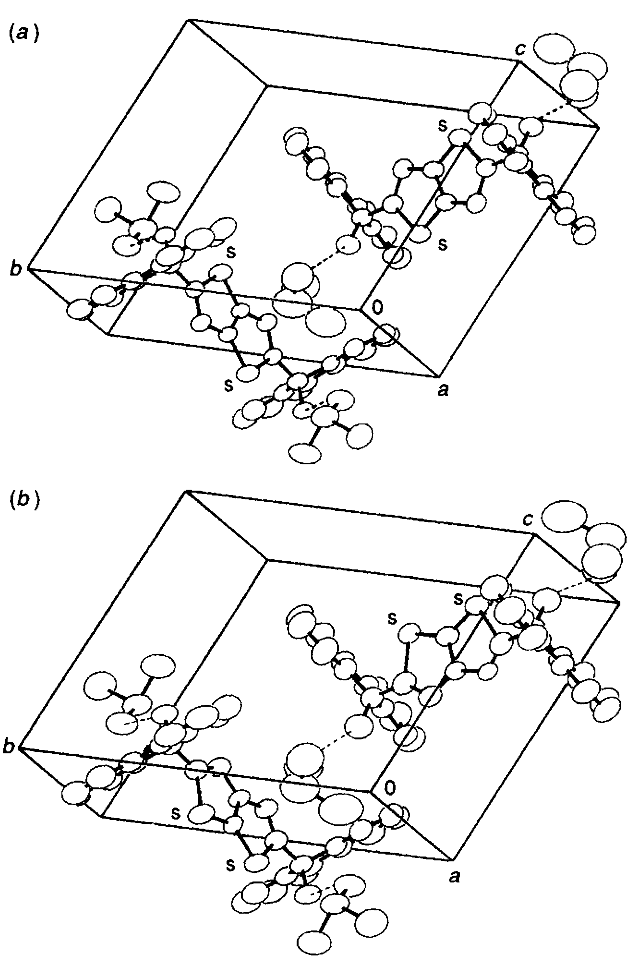

Fig. 1 (*a*) View of [**1**][Me_2SO]$_2$ crystal and (*b*) [**2**][Me_2SO]$_2$ crystal showing the relation linked by the hydrogen bonding between the host and the guest. [The O···O distances are (*a*) 2.66 and 2.73, (*b*) 2.65 and 2.74 Å].

Table 2 Crystal data for clathrates [**1**][Me_2SO]$_2$[a] and [**2**][Me_2SO]$_2$

	[**1**][Me_2SO]$_2$	[**2**][Me_2SO]$_2$
	triclinic $P\bar{1}$	triclinic $P\bar{1}$
a/Å	12.618(1)	12.613(1)
b	13.161(2)	13.383(3)
c	11.615(3)	11.601(2)
α/°	115.41(2)	115.49(1)
β	97.04(2)	97.28(1)
γ	103.41(1)	104.60(1)
D_{calc}/g cm^{-3}	1.331	1.324
U/Å^3	1639.7(6)	1647.3(5)
Z	2	2

[a] See ref. 3.

centres pack more efficiently than those without. Thus, the advantage of the strong hydrogen bonding and the resulting centrosymmetric packing could overcome other weak interactions such as the electrostatic S···O one to bring about the isomorphic packing of [**2**][Me_2SO]$_2$.

In contrast to the enclathration of Me_2SO, for benzene, where no strong molecular interactons exist, the electrostatic S···O interactions dominate, leading to different inclusion properties depending on the position of the sulfur atoms at the periphery of the host compounds. Thus, all the C–OH bonds in [**1**]$_3$[benzene]$_4$ and [**2**][benzene] crystal† are now directed close to the C–S bonds: in [**1**]$_3$[benzene]$_4$, the C–OH bonds of two hydroxy groups in each host molecule are located on the opposite side of the molecular framework, whereas in [**2**][benzene] these are on the same side. These inclusion complexes with benzene should be regarded as true clathrates.[1a] The guest-free host compounds **1** and **2** also crystallize in different packing motifs.‡

The existence of isomorphic forms provides a unique opportunity for the investigation of structure–properties relationships. The thermal behaviour of [**1**][Me_2SO]$_2$ and [**2**][Me_2SO]$_2$ in DSC measurements are different; the guest Me_2SO molecules are released stepwise from [**1**][Me_2SO]$_2$ at 111.2 and 137.7 °C. However, the first step of the guest release in [**2**][Me_2SO]$_2$ takes place at the lower temperature of 96.2 °C. We attribute these results to the presence of disorder in [**2**][Me_2SO]$_2$ crystals.

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Footnotes

† *Crystal data* for [**2**][Me_2SO]$_2$ are listed in Table 2, along with those for [**1**][Me_2SO]$_2$, which have previously been reported.[3] [**1**]$_3$[benzene]$_4$: M = 1814.39, triclinic, $P1$, a = 13.940(5), b = 15.537(2), c = 13.040(4) Å, α = 104.13(2), β = 119.91(2), γ = 92.24(2)°, D_c = 1.293 g cm^{-3}, U = 2330(1) Å^3, Z = 1. [**2**][benzene]: M = 578.71, triclinic, $P1$, a = 12.427(4), b = 13.041(4), c = 10.733(2) Å, α = 92.97(2), β = 104.79(2), γ = 117.10(1)°, D_c = 1.309 g cm^{-3}, U = 1468.2(7) Å^3, Z = 2. In each analysis intensity data were collected on a Rigaku AFC-5 diffractometer at ambient temperature using graphite monochromated Mo-Kα radiations (λ = 0.7107 Å) and the ω-2θ or ω mode. The structures were solved by the direct methods using the program systems SHELXS 86[6] and refined by the block-diagonal least square methods using UNICS-III.[7] Non hydrogen atoms were refined anisotropically. Hydrogen atoms obtained by differential Fourier-map were refined isotropically and hydrogen atoms positioned by calculation were not refined. The occupancy of the inversion disorder in [**2**][Me_2SO]$_2$ was estimated from the peak heights of Fourier-map to be 0.5 : 0.5 and was fixed. The positional disorder of Me_2SO molecules in [**2**][Me_2SO]$_2$ was refined to give an occupancy factor of 0.77 : 0.23. The final conversions were at reflections over 4000 [$F_o > 3(F_o)$] converged at R = 0.0951, R_w = 0.0903 for [**2**][Me_2SO]$_2$, R = 0.0478, R_w = 0.0582 for [**1**]$_3$[benzene]$_4$, and R = 0.0481, R_w = 0.0449 for [**2**][benzene]. The details on the crystal structures of the benzene clathrates will be reported elsewhere.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

‡ Although we could not obtain an appropriate single crystal of guest-free **2** for an X-ray analysis, the IR spectra indicate that the **1** and **2** crystals are not isomorphic, since the hydrogen bonding is observed in **2**, but not in **1**.

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