An Even–Odd Effect in Inclusion Properties and Crystal Structures of a New Host Series Based on Linearly Condensed Polythiophenes

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For a new host series **1a–4c** the host–guest (Me_2SO) composition and the conformation of the host molecule in the crystalline inclusion compounds are dependent on whether the number of condensed thiophene rings in the host compound is even or odd.

A rigid backbone and bulky groups are usually required in the design of host moelcules for crystalline inclusion compounds,[1] for example, 1,1,6,6-tetraphenyl-2,4-hexadiyn-1,6-diol, as explored by Toda.[2] The 2,4-hexadiyne part forms a rigid, linear backbone and both its terminal carbons bear the bulky phenyl groups. Thus, this host molecule could be regarded as a 'wheel and axle' structure. We have designed a new host series, using linearly condensed thiophenes[3] as an 'axle' part, and have synthesized a series of compounds **1a–4c**. The rigid belt-like structure of condensed thiophenes is expected to provide a range of inclusion capacities and cavities in the crystals depending on the length of the belt, and hence on the number of the condensed thiophene rings. We demonstrate here a novel correlation between the length of the host molecules and the solid-state conformation in the host molecule, which is also associated with the host–guest stoichiometric ratio.

The host compounds were prepared by dilithiation of the precursor condensed thiophenes[3] followed by treatment with cyclohexylketone, benzophenone and fluorenone, respectively, and were obtained in 75–97% yields.[4] Upon recrystallization from various solvents these compounds showed broad

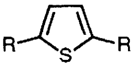
Table 1 Formation of crystalline inclusion compounds of the host **1a**–**4c** and their guest : host ratios. Numbers specify molar ratios to the host compounds

Guest	1a	1b	1c	2a	2b	2c	3a	3b	3c	4c
Ethanol	0	0	0	2	0	2	2	0	1	*a*
Acetone	0	1	0	0	2	2	1	1	1	*a*
Me_2SO	1	1	1	2	2	2	2	1	1	2
DMF	1	1	2	2	2	2	2	1	2	0
Dioxane	1	2	1	2	1	2	1	2	1	2
Benzene	1	0	0	0	0	4/3	1	2	0	*a*

[a] Not determined as the guest molecules are immediately lost.

Table 2 The S–C–C–O dihedral angles (θ) in the host molecule

Compound	θ/°
1c·(Me_2SO)	+32, −41, +33, −41
2c·$(Me_2SO)_2$	+19, −19, +40, −40
3c·(Me_2SO)	+29, −39
4c·$(Me_2SO)_2$	+34, −34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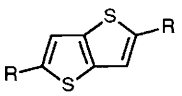
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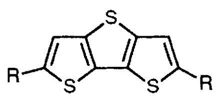
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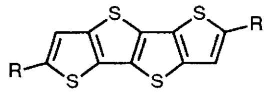
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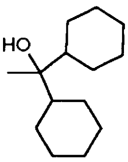

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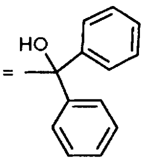

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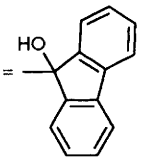

inclusion properties (Table 1). The host–guest stoichiometric ratios were determined by means of NMR integration, HPLC analysis and microanalysis.†

The host compounds with an even number of thiophene rings have a tendency to give 1:2 stoichiometry, whereas those with an odd number tend to give 1:1. A typical example is seen in the fluorenyl host series **c** including Me_2SO as the guest; for Me_2SO the inclusion crystal **1c**·(Me_2SO), **2c**·$(Me_2SO)_2$, **3c**·(Me_2SO) and **4c**·$(Me_2SO)_2$ is formed, respectively, from the corresponding host compound.

The host–guest composition observed for Me_2SO as the guest is also associated with the crystal structures of the inclusion compounds; we have investigated the crystal structures by X-ray diffraction for **1c**·(Me_2SO), **2c**·$(Me_2SO)_2$, **3c**·(Me_2SO) and **4c**·$(Me_2SO)_2$.‡

The most remarkable structural features in the host molecules are seen in the conformation of the 'wheel' part. Two C–OH bonds in the host molecule take a *gauche* conformation close to the eclipsed one with respect to the C–S bonds of the terminal thiophene rings. This means that in **1c**·(Me_2SO) and **3c**·(Me_2SO), two C–OH groups on both ends of the 'axle' are directed to the same side as each other (*syn*), whereas, in the host having an even number of thiophene rings **2c**·$(Me_2SO)_2$ and **4c**·$(Me_2SO)_2$, the C–OH groups are directed to opposite sides to each other (*anti*). Consequently, the two bulky fluorenyl groups are arranged on the same side for **1c**·(Me_2SO) and **3c**·(Me_2SO) and on opposite sides for the **2c**·$(Me_2SO)_2$ and **4c**·$(Me_2SO)_2$. The dihedral angles between the C–S and the C–O bonds are summarized in Table 2.

All of the guest Me_2SO molecules are hydrogen bonded to the OH groups in the host molecules. In **2c**·$(Me_2SO)_2$ and **4c**·$(Me_2SO)_2$, two OH groups adapt an *anti* orientation so that each of the two hydroxy groups of the host molecule is individually hydrogen bonded to a Me_2SO molecule, resulting in a host : guest ratio of 1:2 [Fig. 1(*b*) and (*d*)]. The O–H···O(S) distances are 2.66 and 2.73 Å for **2c**·$(Me_2SO)_2$ and 2.63 Å for **4c**·$(Me_2SO)_2$, respectively. On the other hand, the host composed with an odd number of thiophene rings has its two hydroxy groups in the *syn* alignment, thereby making a cyclic dimer by face-to-face intermolecular hydrogen bonds. Two guest molecules participate to link these two host molecules, therefore, leading to the 1:1 ratio. Thus, in **1c**·(Me_2SO), the sulfoxide group as a proton acceptor links the hydroxy groups of two host molecules with the O–H···O(S) distances of 2.91 and 2.78 Å [Fig. 1(*a*)]. In **3c**·(Me_2SO), the face-to-face intermolecular hydrogen bonds (O–H···O: 2.86 Å) make a dimeric cycle and a Me_2SO molecule is involved as an acceptor at one of the hydrogen-bonding sites [O–H···O(S): 2.68 Å] of the two host molecules [Fig. 1(*c*)].

Guest-free crystals of **2c** maintain no lattice for inclusion cavities and adopt a close-packed structure. Upon inclusion of the guest, this pattern is fundamentally maintained in the inclusion complexes.§ Thus, the 'wheel' of the host molecule is faced to the 'axle' of the neighbouring host molecules.

A host series **1c**–**4c** with guest Me_2SO as the hydrogen-bond acceptor may provide a typical case for the even–odd effect; several of the inclusion compounds, *e.g.* hosts **3a** and **3b** and guest dioxane, do not show so good a correlation as for the host–guest ratio. These may be ascribable to conformational flexibilities of the 'wheel' part, which are considered to be in the order of **a** (dicyclohexyl) > **b** (diphenyl) > **c** (fluorenyl)

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† Satisfactory analytical data were obtained for all new host compounds and complexes.

‡ X-Ray data were collected with Mo-Kα graphite monochromated radiation (λ = 0.71069 Å) on a Rigaku AFC-5R four-circle diffractometer at 25 °C. The structures were solved by the direct method using SAPI85; least-squares refinement with anisotropic temperature factors on all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms were employed.

Crystal data for **1c**·(Me_2SO): $C_{32}H_{26}S_2O_3$, $M = 522.676$, triclinic, space group $P\bar{1}$, $a = 14.469(5)$, $b = 21.208(5)$, $c = 8.741(4)$ Å, $\alpha = 90.92(2)$, $\beta = 99.13(3)$, $\gamma = 94.56(2)°$, $V = 2639(2)$ Å^3, $Z = 4$, $D_x = 1.316$ g cm^{-3}, $\mu = 2.235$ cm^{-1}. A total of 13 171 unique data were collected in the scan range $3 < 2\theta < 55$, with 7440 of $F > 3\sigma(F)$. Refinement of 876 parameters converged to $R = 0.067$ and $R_w = 0.086$.

Crystal data for **2c**·$(Me_2SO)_2$: $C_{36}H_{32}S_4O_4$, $M = 656.886$, triclinic, $P\bar{1}$, $a = 12.618(1)$, $b = 13.161(2)$, $c = 11.615(3)$ Å, $\alpha = 115.41(2)$, $\beta = 97.04(2)$, $\gamma = 103.41(1)°$, $V = 1640(1)$ Å^3, $Z = 2$, $D_x = 1.329$ g cm^{-3}, $\mu = 3.138$ cm^{-1}. A total of 6346 unique data were collected in the scan range $3 < 2\theta < 55$, with 5075 of $F > 2.5\sigma(F)$. Refinement of 526 parameters converged to $R = 0.10$. Half of the Me_2SO molecules showed large thermal motion. All attempts to locate two or more discrete positions for any of these guest molecules were unsuccessful.

Crystal data for **3c**·(Me_2SO): $C_{36}H_{26}S_4O_3$, $M = 634.840$, monoclinic, $P2_1/n$, $a = 17.942(3)$, $b = 14.831(1)$, $c = 11.487(1)$ Å, $\beta = 102.42(1)°$, $V = 2985(1)$ Å^3, $Z = 4$, $D_x = 1.413$ g cm^{-3}, $\mu = 3.406$ cm^{-1}. A total of 6898 unique data were collected in the scan range $3 < 2\theta < 55$, with 1860 of $F > 2.5\sigma(F)$. Owing to crystallographic difficulties resulting from an irregularly shaped crystal the various refinements converged only at $R = 0.12$ for 485 parameters.

Crystal data for **4c**·$(DMSO)_2$: $C_{40}H_{32}S_6O_4$, $M = 769.050$, monoclinic, $P2_1/n$, $a = 10.875(3)$, $b = 17.385(2)$, $c = 10.455(2)$ Å, $\beta = 109.43(2)°$, $V = 1864(1)$ Å^3, $Z = 2$, $D_x = 1.369$ g cm^{-3}, $\mu = 3.907$ cm^{-1}. A total of 4764 unique data were collected in the scan range $3 < 2\theta < 55$, with 3408 of $F > 2.5\sigma(F)$. Refinement of 311 parameters converged to $R = 0.046$ and $R_w = 0.059$.

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

§ X-Ray crystal structure analysis was undertaken for the guest-free host crystals of **2c** and the dihedral angle was found to be 57°. These results and the crystal structure analysis on other inclusion complexes that are currently underway will be reported elsewhere.

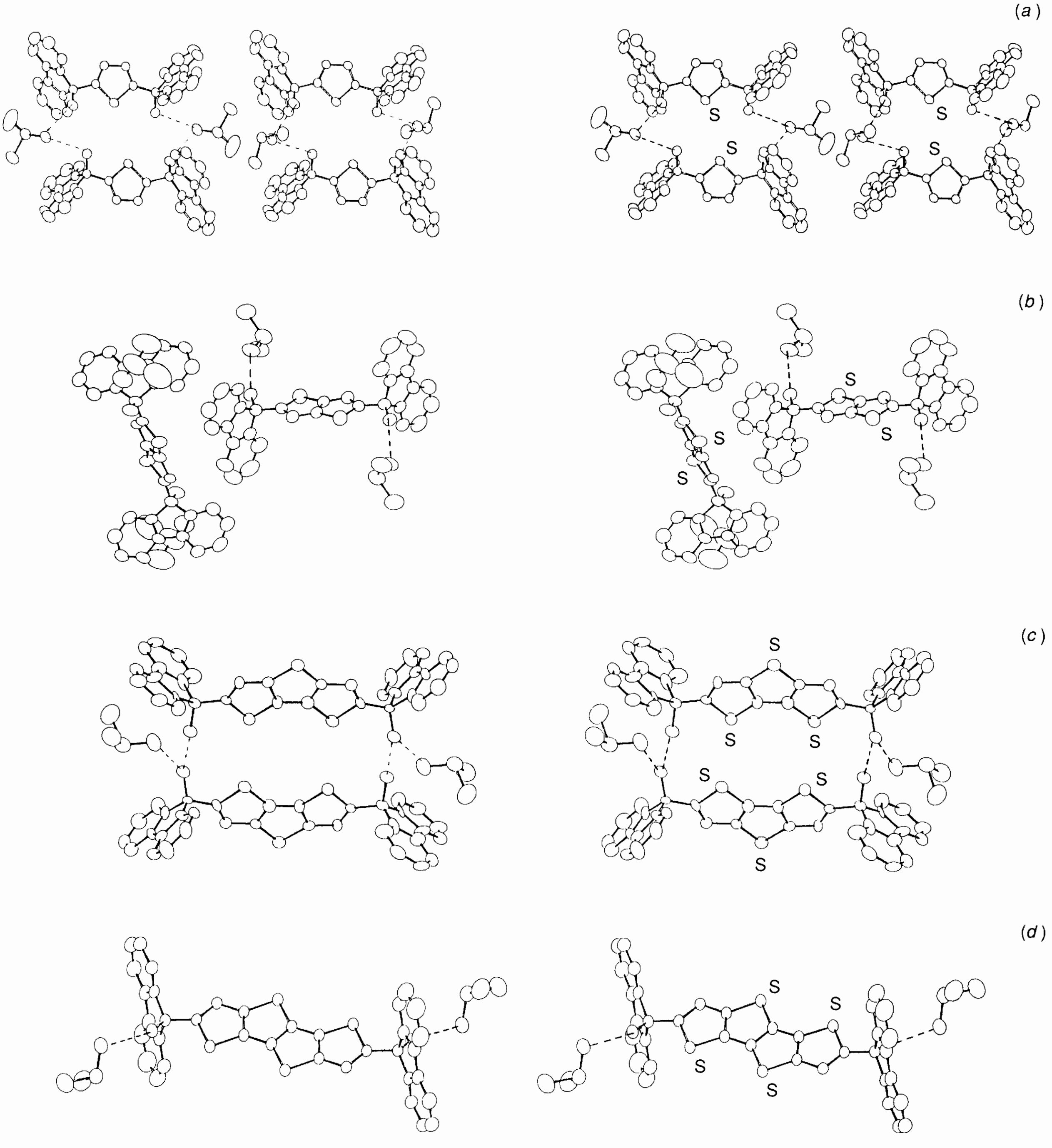

Fig. 1 Stereoviews of the Me_2SO inclusion complexes, (*a*) **1c**·(Me_2SO), (*b*) **2c**·(Me_2SO)$_2$, (*c*) **3c**·(Me_2SO) and (*d*) **4c**·(Me_2SO)$_2$. Crystallographically non-equivalent host and guest molecules are all shown except for **3c**·(Me_2SO)$_2$, wherein a dimeric pair of crystallographically equivalent two host and two guest molecules are depicted.

and the size and hydrogen-bond character (donor or acceptor) of the guest molecules.

In conclusion, we have demonstrated the interesting conformational changes of the 'wheel' in the host molecules depending on the length of the 'axle', that is, the number of condensed thiophene rings, which results in the control of the direction of the hydrogen bonds and, hence, is responsible for the host : guest stoichiometry.

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