

Complexation with Helical Molecules: Helical Crystal Structure of Bis(hydroxymethyl)[7]thiaheterohelicene-Ethanol Clathrate

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Bis(hydroxymethyl)[7]thiaheterohelicene affords a crystalline host-guest inclusion complex with ethanol having a 1:1 host-guest ratio self-assembled through a helical network of hydrogen bonds.

The design and synthesis of the crystalline host-guest inclusion complexes (clathrates) has attracted considerable attention from the viewpoints of chemical separations,¹ topochemical reactions,² or development of new solid materials.³ Polyfunctionalized molecules such as disubstituted 1,1'-binaphthyls,⁴ bis-(hydroxy)thienothiophenes,⁵ tartaric acid derivatives,⁶ and *trans*-1,2-cyclohexanediol⁷ constitute effective clathrate host compounds towards alcohols, amines, ketones, and dipolar aprotic compounds or aromatic hydrocarbons. However, little is known about crystalline inclusion complexes derived from helical host molecules.⁸ In this communication, we report the first example of crystalline inclusion complex self-assembled through a helical network of intermolecular hydrogen bonds between a bifunctionalized [7]heterohelicene possessing C₂-symmetry and ethanol.

When racemic 2,13-bis(hydroxymethyl)dithieno[3,2-*e*:3',2'-*e'*]benzo[1,2-*b*:4,3-*b'*]bis[1]benzothiophene⁹ **1** was recrystallized from ethanol, a yellow inclusion complex was obtained, which contained ethanol with a 1:1 host-guest ratio (NMR integration). The complex is remarkably stable at room temperature, and releases the guest at 100 °C and decomposes at 178–183 °C. The inclusion of ethanol was also confirmed by the X-ray structure analysis[‡] which unambiguously showed highly organized supramolecular structure (Fig. 1).

Thus, the host molecules of same chirality are aligned in a stacking column along the crystallographic *b* direction by intermolecular hydrogen bonds. Two stacking columns of same helicity are interlocked by the guest molecules through hydrogen bonds, giving either a right-handed strand of [(*P*)-**1**][EtOH] or a left-handed strand of [(*M*)-**1**][EtOH]. The central benzene ring of (*P*)-helicenediol in a strand and that of (*M*)-enantiomer in a neighbouring strand are displaced by an average

distance of 4.33 Å in the direction of the molecular axis as shown in Fig. 2, indicating the presence of comparatively weaker π interaction between them, so that the helical network is completely rigid.

Within the host molecule itself, four thiophene rings and three benzene rings constitute a full turn of the helix and the terminal thiophene rings are spread away with an interplanar angle of 38°. The distortion from planarity influences double bond character and thus bond lengths. The C–C distances of the outer rings [C(4)–C(5), C(9)–C(10), C(14)–C(15)] shown in Fig. 3] are shortened to 1.36 Å and the inner bonds [C(20)–C(21), C(22)–C(23), C(24)–C(25)] are lengthened to 1.42–1.44 Å, compared with the bond length (1.39 Å) in benzene. The inner C–C bond lengths in the thiophene rings are lengthened to 1.46 from 1.42 Å of the C(3)–C(4) bond length of thiophene.¹⁰ The angles between two adjacent planes vary from –9.33 to +11.63° (Table 1), which indicates that the strain seems mainly to be

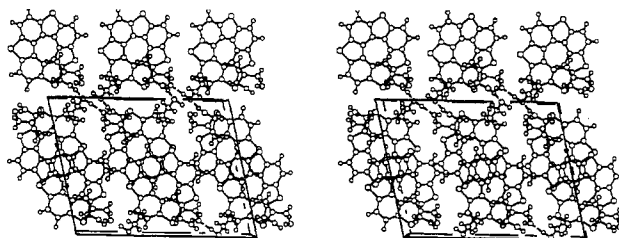


Fig 2 Stereoview of 1-EtOH crystal as viewed along the *b* axis

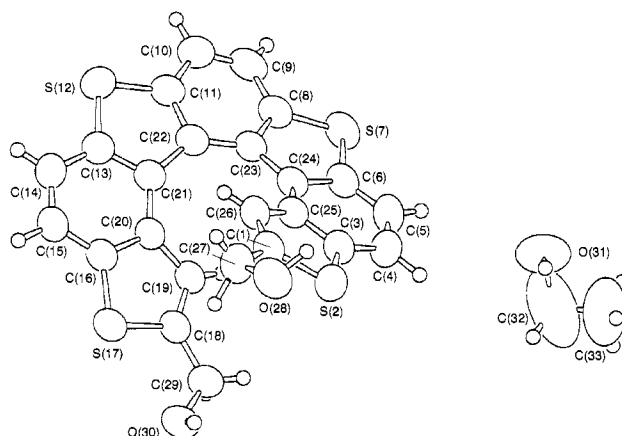


Fig. 3 Numbering scheme for the crystal structure of 1-EtOH

Table 1 Dihedral angles between planes (°)

Plane	1	2	3	4	5	6
2	8.29					
3	15.32	8.29				
4	24.76	19.50	11.63			
5	146.38	151.19	159.07	170.67		
6	143.10	146.57	153.80	165.18	7.10	
7	142.04	143.86	150.03	160.32	13.97	7.30

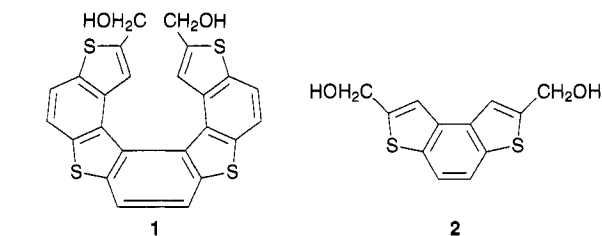


Fig. 1 Stereoview of 1-EtOH crystal showing the relation linked by the hydrogen-bonding between (*P*)-helicenediol and the guest

localized in the inner aromatic rings, giving rise to an irregular screw of the helicene. The longest nonbonded C...C distance is 4.73 Å of C(27)...C(29) and two oxygen atoms [O(28)...O(30)] are separated by 5.70 Å. The deviation from planarity in the solid state is also confirmed by ¹H NMR spectroscopy in dichloromethane solution. Thus, the resonance of protons (δ 6.60) on C(15) and C(20) shown in Fig. 3 is at higher field than a proton (δ 7.55) on C(3) of 2,5-bis(hydroxymethyl)benzo[1,2-b:4,3-b']dithiophene **2**. This upfield shift indicates that these protons experience the shielding of the terminal overlapping thiophene rings.

The above results suggest that inclusion of guest molecules within a helical network is possible. Since optically pure **1** can be prepared by lipase-catalysed transesterification,⁹ there is also a potential for chiral recognition of racemic guests based on helicity. Further investigation on molecular recognition are in progress and will be reported in due course.

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Footnotes

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‡ Crystal data: C₂₆H₂₀S₄O₃, *M* = 508.68, crystal size 0.20 × 0.10 × 0.60 mm, crystal system, monoclinic, space group *P*2₁/*c* (No. 14), *a* = 15.028(2), *b* = 8.046(2), *c* = 19.369(2) Å, β = 102.779°, *V* = 2284.0(5) Å³, *Z* = 4, *D*_c = 1.479 g cm⁻³. The crystal data were collected on a Rigaku AFC7R diffractometer using Cu-Kα radiation and a 12 kW rotating anode generator at a temperature of 20 ± 1° using the ω-2θ scan technique to a maximum 2θ value of 120.1°. The structure was solved by direct methods using SAPI91¹¹ and expanded Fourier techniques (DIRDIF92).¹² The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms refined isotopically, and the rest were included in fixed positions. The final cycle of full-matrix least-squares refinement was based on 2792 observed reflections

and 347 variable parameters and converged with unweighted and weighted agreement factors of *R* = 0.046 and *R*_w = 0.055, respectively. 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.

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