# Self-assembly of (*P*)-heterohelicenediol into a four-leaf clover motif

**Kazuhiko Tanaka*† and Yoshinori Kitahara**

*Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8224, Japan*

**(*P*)-2,13-Bis(hydroxymethyl)heterohelicenediol [(*P*)-1] self-assembles through a right-handed helical network of hydrogen bonds to form a four-leaf clover motif; a full turn of the helix comprises four chiral subunits which associate in a *left-handed* helical manner with a $4_3$ screw axis.**

The construction of highly ordered supramolecular structures has important implications not only for the developement of new materials such as nanoscale molecular devices,[1–4] but also for the synthesis of artificial systems that can mimic biological functions.[5] Among the self-assembled supramolecular architectures, such as tapes,[6] capsules,[7] spheres,[8] squares,[9] cylinders[5] and helices,[10,11] helical arrangements[12,13] are characterized by chirality based on the screw sense [right-handed (*P*) or left-handed (*M*) helicity], and hence the helicoselective (or enantioselective) synthesis of helical motifs is an active field of research in supramolecular chemistry.[14] Here we report the first example of construction of a four-leaf clover motif from optically active (*P*)-2,13-bis(hydroxymethyl)dithieno[3,2-*e*:3′,2′-*e*′]benzo[1,2-*b*:4,3-*b*′]bis[1]benzothiophene [(*P*)-**1**] (Fig. 1).[15]

Crystals suitable for X-ray crystallographic analysis were grown from a solution of (*P*)-**1** in $CH_2Cl_2$–acetone.‡ The stereoview of the crystal structure (Fig. 2) clearly shows that (*P*)-**1** self-assembles through a right-handed helical network of hydrogen bonds. A full turn of the helix comprises four chiral helicenediols and the pitch of the helix is 15.49 Å. The most remarkable feature of (*P*)-**1** is that the right-handed helicenediols arrange in a *left-handed* helical manner and the cloverleaf motif repeats by the $4_3$ screw axis. In the supramolecular structure, one of the hydroxy functionalities of (*P*)-**1** forms an intramolecular bridge to the other hydroxy group of the same molecule and also forms an intermolecular hydrogen bond to one of the hydroxy groups of an adjacent molecule (Fig. 3). The interplanar angle between the terminal thiophene rings of (*P*)-**1** is 33.83° (Table 1). This is in contrast with the guest-free racemic heterohelicenediol (*PM*)-**1** which self-assembles to form an alternate-leaf motif (Fig. 4).§ In the crystal of (*PM*)-**1**, the two stacking columns, consisting of helicenediols of the same helicity, are aligned along the *c* axis. Since each hydroxy group of (*PM*)-**1** interacts with one of the hydroxy functions of an adjacent molecule *via* an intermolecular hydrogen bond, the interplanar angle between the terminal thiophene rings increases to 44.70° (Table 1). This represents an increase of

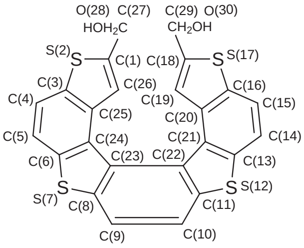

**Fig. 1** Numbering scheme of heterohelicenediol

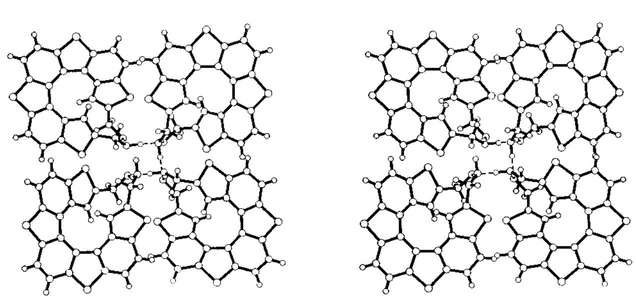

**Fig. 2** A stereoview of the four-leaf clover motif of (*P*)-heterohelicenediol assembled along the *c* axis

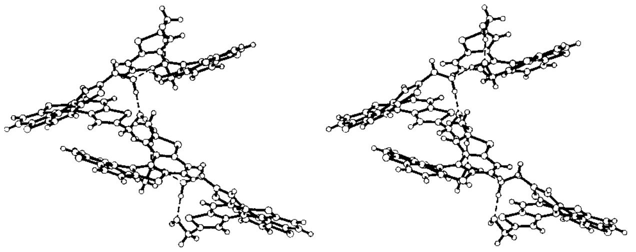

**Fig. 3** Stereoview of (*P*)-heterohelicenediol from the crystallographic *b* axis

**Table 1** Interplanar angles between the adjacent rings and the terminal thiophene rings (°)

| | (*P*)-**1** | (*PM*)-**1** | (*PM*)-**1**·EtOH[a] |
|---|---|---|---|
| ring(1)–ring(2) | 8.40 | 5.82 | 8.29 |
| ring(2)–ring(3) | 6.92 | 7.70 | 8.29 |
| ring(3)–ring(4) | 9.73 | 10.46 | 11.63 |
| ring(4)–ring(5) | 9.35 | 12.72 | 9.33 |
| ring(5)–ring(6) | 8.73 | 9.84 | 7.10 |
| ring(6)–ring(7) | 6.33 | 6.61 | 7.30 |
| ring(1)–ring(7) | 33.83 | 44.70 | 37.96 |

[a] Ref. 16.

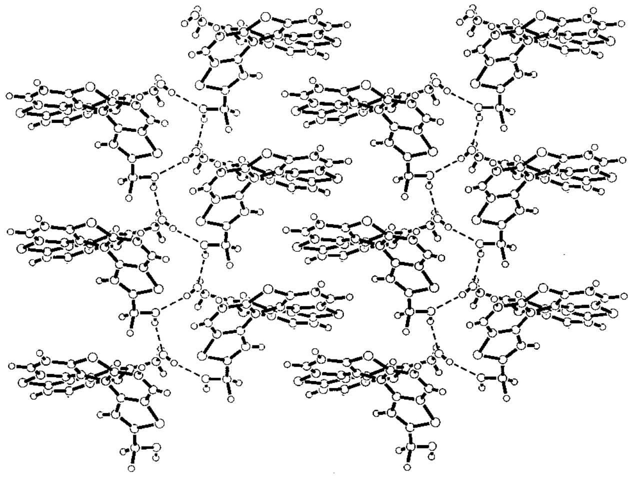

**Fig. 4** Side view of the hydrogen-bonding network showing an alternate-leaf motif of racemic heterohelicenediol

10.87° or 32.1%. When the racemic heterohelicenediol (*PM*)-**1** forms an inclusion complex with EtOH through helical hydrogen-bonding, the interplanar angle decreases to 37.96°.[16] These results clearly indicate that the helicene framework exhibits significant elasticity by changing its dihedral angle. The distortion from planarity locates on the central aromatic rings of the helical framework, and therefore the dihedral angles between two adjacent rings range from 8.73 to 9.73 for (*P*)-**1** and from 9.84 to 12.72° for (*PM*)-**1**. However, the double bond character of two helicenediols are unchanged. Thus, the carbon–carbon bond distances of the outer rings range from 1.33 to 1.36 Å in the case of (*P*)-**1** and from 1.33 to 1.37 Å in (*PM*)-**1**, and the inner carbon–carbon bond distances [C(20)–C(21), C(22)–C(23) and C(24)–C(25)] are 1.42 Å for (*P*)-**1**, and in a range of 1.41 to 1.43 Å for (*PM*)-**1**. The inner carbon–carbon bond lengths in the thiophene rings [C(19)–C(20), C(21)–C(22) and C(25)–C(26)] range from 1.43 to 1.47 Å for both (*P*)-**1** and (*PM*)-**1**. The common feature of these helical geometry is that the carbon–sulfur bond distances in the thiophene rings of (*P*)-**1**, (*PM*)-**1** and (*PM*)- **1**·EtOH are uniformly lengthened from 1.71 to 1.73 Å.

The present results reveal for the first time that the helical conjugated π-electron framework of helicenediol **1** acts as a helical spring due to the pattern of hydrogen bonds.

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas 'Organic Nonlinear Optics' (No. 09222212) from the Japanese Ministry of Education, Science, Culture and Sports.

## Notes and References

† E-mail: tanaka@kuchem.kyoto-u.ac.jp

‡ *Crystal data* for (*P*)-**1**: $C_{24}H_{14}O_2S_4$, $M$ = 462.61, crystal size 0.40 × 0.26 × 0.40 mm, crystal system, tetragonal, space group $P4_3$, $a$ = 11.4866(9), $c$ = 15.493(3) Å, $V$ = 2044.1(4) Å$^3$, $Z$ = 4, $D_c$ = 1.503 g cm$^{-3}$. The final cycle of full-matrix least-squares refinement was based on 1538 observed reflections and 271 variable parameters and converged with unweighted and weighted agreement factors of $R$ = 0.032 and $R_w$ = 0.050, respectively.

§ *Crystal data* for (*PM*)-**1**: $C_{24}H_{14}O_2S_4$, $M$ = 462.61, crystal 0.25 × 0.75 × 0.01 mm, crystal system, orthorhombic, space group *Pccn*, $a$ = 15.217(6), $b$ = 33.919(9), $c$ = 7.85(1) Å, $V$ = 4051(7) Å$^3$, $Z$ = 8, $D_c$ = 1.517 g cm$^{-3}$. The final cycle of full-matrix least-squares refinement was based on 1588 observed reflections and 328 variable parameters and converged with unweighted and weighted agreement factors of $R$ = 0.069 and $R_w$ = 0.077, respectively. The crystal data were collected on a Rigaku AFC7R diffractometer using Cu-K$\alpha$ radiation and a 12 kW rotating anode generator at a temperature of 20 °C using the $\omega$–2$\theta$ scan technique. CCDC 182/860.

1 J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304.
2 G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2311.
3 C. Piguet, J.-C. Bünzli, G. Bernardinelli, G. Hopfgartner, S. Petoud and O. Schaad, *J. Am. Chem. Soc.*, 1996, **118**, 6681.
4 D. B. Amabilino and J. F. Soddart, *Chem. Ber.*, 1995, **95**, 2725.
5 M. R. Ghadiri, J. R. Granja and L. K. Buehler, *Nature*, 1994, **369**, 301.
6 J. C. MacDonald and G. M. Whitesides, *Chem. Rev.*, 1994, **94**, 2383.
7 M. M. Conn and J. Rebeck, Jr., *Chem. Ber.*, 1997, **97**, 1647.
8 M. Fugita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **378**, 469.
9 J. Manna, J. C. Kuel, J. A. Whiteford, P. J. Stang, D. C. Muddiman, S. A. Hofstadler and R. D. Smith, *J. Am. Chem. Soc.*, 1997, **119**, 11 611.
10 D. M. Bassani, J.-M. Lehn, G. Baum and D. Fenske, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1845.
11 P. N. W. Baxter, H. Sleiman, J.-M. Lehn and K. Rissanen, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 1297.
12 Y. Hamuro, S. J. Geib and A. D. Hamilton, *J. Am. Chem. Soc.*, 1997, **119**, 10 587.
13 A. Williams, *Chem. Eur. J.*, 1997, **3**, 15.
14 C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005.
15 K. Tanaka, H. Osuga, H. Suzuki, Y. Shogase and Y. Kitahara, *J. Chem. Soc., Perkin Trans. 1*, 1998, 935.
16 K. Tanaka, Y. Shogase, H. Osuga, H. Suzuki, W. Nakanishi, N. Nakamura and Y. Kawai, *J. Chem. Soc., Chem. Commun.*, 1995, 1873.

*Received in Cambridge, UK, 27th February 1998; 8/01650J*