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Helical Assembly Formed by Chiral [11]Thiaheterohelicene Molecules in Crystals. Architecture with Triple Helix

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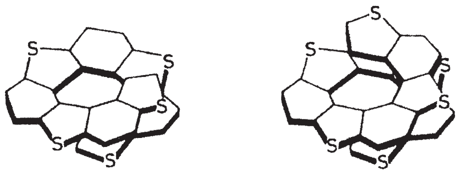
Projection of the crystal structure of a *P* enantiomer of [11]thiaheterohelicene (11TH) with a helical structure of one and a half turns along the *a* axis revealed huge helical assemblies, in which three crystallographically independent molecules formed a smaller right-handed helix, no similar helical assembly being observed for the crystal structures of an 11TH racemate and a [9]thiaheterohelicene enantiomer.

In the field of supramolecular chemistry, the self-assembly of building blocks into a huge architecture possessing structural similarity is an attractive phenomenon.[1] So far, many investigations have been carried out on the crystal structures of carbohelicene[2] and heterohelicene,[3] in particular, from the standpoint of chiral habit in the stacks of molecules. One can imagine that helicene molecules with the same winding manner are one-dimensionally stacked upon each other in crystals to form a huge helix. One can imagine also that a string is passed through the central hole of the stacked homochiral helicene molecules. However, to our knowledge, no one has reported the crystal structures of the helicene family with such molecular stacking. We describe herein the unique molecular assembly of enantiomeric [11]thiaheterohelicene (11TH)[4] composed of alternating thiophene and benzene rings, and compare it with the assembly of the racemic 11TH.



9TH 11TH

Scheme 1.

Figure 1 shows the crystal structure of a right-handed (*P*) enantiomer[5] of 11TH in a unit cell, as projected on a *bc* plane.[6] One can recognize two huge helixes lying in a zigzag fashion almost along the *c* axis in parallel to each other. Twelve molecules are involved in the unit cell in the space group of $P2_12_12_1$, which implies the existence of three kinds of mutually independent molecules (A, B, and C) with different conformations; for example, the dihedral angles between the terminal rings in a molecule are 9.23, 10.48, and 7.69° for A, B and C molecules, respectively. As illustrated in the simplified scheme of Figure 1, the centers of these three molecules are aligned forward to and backward from the plane on the page in the order of A, B and C molecules, thereby drawing an arc of a right–handed screw. Since these arcs appear to be linked to each other, the huge zigzag helixes appear when viewed downward from the direction along the *a* axis.

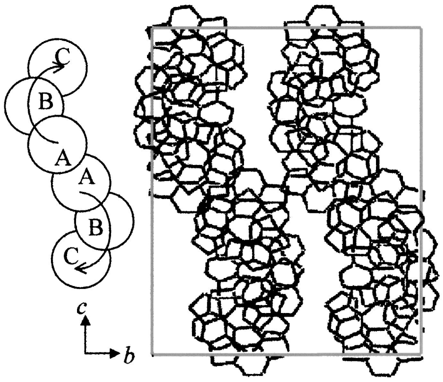


Figure 1. Crystal structure of (*P*)11TH projected on the *bc* plane (right) and the schematic drawing (left).

The projection of these three independent molecules on the *ac* plane revealed that they are situated in the positions facing the mutual terminal thiophene rings of A and B, and of B and C molecules, respectively (Figure 2(a)). Although the central molecule (B) crystallographically lost an intramolecular C_2 axis, its pseudo C_2 axis is approximately parallel to the *b* axis. Therefore, the relative locations of A and C molecules are roughly correlated by turning around the pseudo C_2 axis of B molecule. The intermolecular dihedral angle between the nearby terminal rings of A and B molecules is 144° and that of B and C molecules is 147°. The shortest nonbonding atomic distance between those

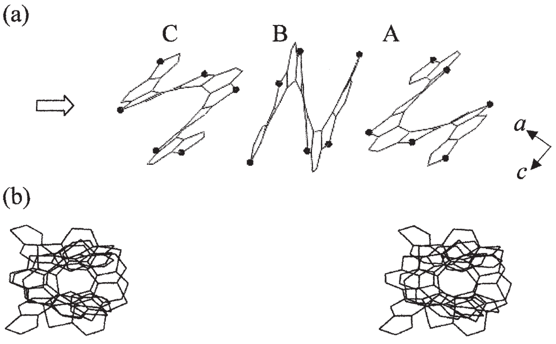


Figure 2. (a) Projection of three independent molecules (A, B and C) on the *ac* plane. (b) Stereodiagram of their overlapping holes by viewing them from the direction as indicated by an arrow in (a). Sulfur atoms are represented by black circles.

terminal rings is 3.50 Å for A and B molecules, and 3.53 Å for B and C molecules. From the similarity between these corresponding values, it is understandable that these three molecules, on the whole, form a larger right-handed helix. One can inspect the overlapping of the central holes of the three molecular helixes by viewing them from the [1 0 0.5] direction as indicated by an arrow in Figure 2(a). Figure 2(b) demonstrates the stereodiagram of the overlapping holes of the larger helix produced by stacking the three molecules. The structures of individual 11TH molecules possessing one and a half turns of the right-handed helix retain the characteristics of the helicene family, as previously reported.[7] The structural differences among the three independent molecules were found to be rather small: the rough diameters of the molecular skeleton are in the range of 7.9–8.0 Å and the approximate pitches of the helix, 3.9–4.0 Å.

In order to infer the origin of the huge helix formation, the crystal structures of racemic 11TH and enantiomeric [9]thiaheterohelicene (9TH)[8] were examined. The packing diagram of 11TH racemate[9] is illustrated in Figure 3(a) as projected on the *bc* plane, and shows quite large differences from that of the enantiomer. A unit cell is comprised of four molecules, that is, two independent molecules and their corresponding enantiomers. A pair of enantiomers is stacked with the closest nonbonding atomic distance of 3.37 Å. No helical assembly of the molecules was observed at all, regardless of the viewing direction of the crystal lattice. Furthermore, Figure 3(b) shows the crystal structure of a right-handed (*P*) enantiomer of 9TH,[10] a lower homolog of 11TH, as projected on the *bc* plane. Orthogonal approaches between neighboring molecules were recognized at once, and no formation of a helix larger than that of a molecule could be found. The crystallographic C_2 axis is maintained through the central thiophene ring in a molecule. This axis is parallel to the *a* axis, thereby resulting in such a packing fashion in the unit cell.

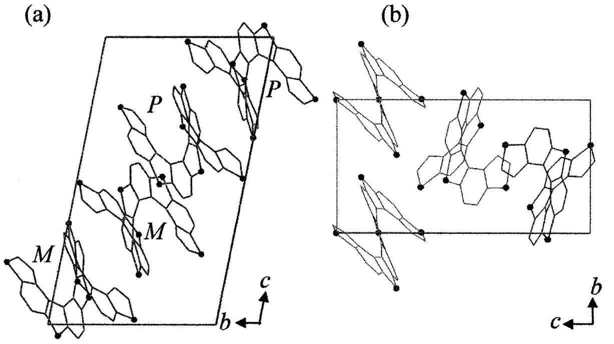


Figure 3. (a) Crystal structure of racemic 11TH projected on the *bc* plane. (b) Crystal structure of (*P*)9TH projected on the *bc* plane. Sulfur atoms are represented by black circles.

The origin of the helical assembly in the crystal structure of enantiomeric 11TH remains uncertain, and it may be inadvertently formed. However, the number of independent molecules in the unit cell might provide a clue to solving this problem. The number of enantiomeric 11TH is three, which is the largest value among the carbohelicene and heterohelicene series reported thus far.[11] This suggests the diversity of the stable or metastable states taken by the molecules with different conformations of similar energies, namely, between these molecules, a weak interaction such as the van der Waals attraction may be anticipated, in order to select the helical array as their most stable arrangement in crystals.

References and Notes

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2 For example: R. Kuroda, *J. Chem. Soc., Perkin Trans. 2*, **1982**, 789; S. Ramdas and J. M. Thomas, *J. Phys. Chem.*, **85**, 2421 (1981); B. S. Green and M. Knossow, *Science*, **214**, 795 (1981); G. Le Bas, A. Navaza, M. Knossow, and C. de Rango, *Cryst. Struct. Commun.*, **5**, 713 (1976).

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4 IUPAC Name: bisthieno[3″,2″ : 4′,5′][1]benzothieno-[3′,2′ : 4,5]benzo[1,2-b : 4,3-b’]di[1]benzothiophene. Synthesis: K. Yamada, S. Ogashiwa, H. Tanaka, H. Nakagawa, and H. Kawazura, *Chem. Lett.*, **1981**, 343; Optical resolution: H. Nakagawa, S. Ogashiwa, H. Tanaka, K. Yamada, and H. Kawazura, *Bull. Chem. Soc. Jpn.*, **54**, 1903 (1981).

5 Chirality of the heterohelicenes used here was determined by measurements of CD spectra. K. Yamada, H. Tanaka, H. Nakagawa, S. Ogashiwa, and H. Kawazura, *Bull. Chem. Soc. Jpn.*, **55**, 500 (1982).

6 Crystal data for (*P*)11TH: $C_{34}H_{14}S_6$, $M_r = 614.84$, $P2_12_12_1$, $a = 13.9701(3)$, $b = 20.8322(3)$, $c = 26.5249(4)$ Å, $V = 7719.5(2)$ Å^3, $D_{calcd} = 1.587$ gcm^{-3}, $Z = 12$, 9575 unique reflections. λ(Mo Kα) = 0.7107 Å, 9094 observed, $I > 2\sigma(I)$, 1124 parameters, $R_1 = 0.033$, $wR_2 = 0.031$, Flack parameter = 0.00(5).

7 R. H. Martin, *Angew. Chem., Int. Ed. Engl.*, **13**, 649 (1974).

8 IUPAC Name: bis[1]benzothieno[5′,4′ : 2,3]thieno[3,2-*e* : 4,5-e′]di[1]benzothiophene. The references for synthesis and optical resolution are the same as ref. 4.

9 Crystal data for 11TH racemate: $C_{34}H_{14}S_6$, $M_r = 614.84$, triclinic, $P\bar{1}$, $a = 11.4098(4)$, $b = 11.5070(4)$, $c = 20.1448(9)$ Å, $\alpha = 78.753(1)$, $\beta = 89.665(2)$, $\gamma = 87.862(3)°$, $V = 2592.3(2)$ Å^3, $D_{calcd} = 1.575$ g cm^{-3}, $Z = 4$, 1256 unique reflections. λ(Mo Kα) = 0.7107 Å, 9444 observed, $I > 2\sigma(I)$, 749 parameters, $R_1 = 0.050$, $wR_2 = 0.096$.

10 Crystal data for (*P*)9TH: $C_{28}H_{12}S_5$, $M_r = 508.70$, $P3_221$, $a = 10.4663(5)$, $c = 17.1426(7)$ Å, $V = 1626.3(1)$ Å^3, $D_{calcd} = 1.558$ gcm^{-3}, $Z = 3$, 1441 unique reflections. λ(Mo Kα) = 0.7107 Å, 1582 observed, $I > 1\sigma(I)$, 156 parameters, $R_1 = 0.030$, $wR_2 = 0.038$, Flack parameter = $-0.0(1)$. Crystallographic data have been deposited with Cambridge Crystallographic Data Center as supplementary publication no.: (*P*)11TH CCDC-185521, 11TH racemate CCDC-185523 and (*P*)9TH CCDC-185522.

11 The number of three has been reported for [7]helicene, which gives no helical assembly in crystals. Th. E. M. van den Hark and P. T. Beurskens, *Cryst. Struct. Commun.*, **5**, 247 (1976).