Peculiar Crystal Structure of a Thiophene/Phenylene Co-oligomer of 2,5-Bis(4′-methoxybiphenyl-4-yl)thiophene

Shu Hotta,*[1] Midori Goto,[2] and Reiko Azumi[3]
[1]*Kyoto Institute of Technology, Department of Macromolecular Science and Engineering, Matsugasaki, Sakyo-ku, Kyoto 606-8585*
[2]*Technical Service Center, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565*
[3]*Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Tsukuba Central 5, 1-1-1 Higashi, Tsukuba 305-8565*

(Received October 10, 2006; CL-061190; E-mail: hotta@kit.ac.jp)

The crystal structure of a thiophene/phenylene co-oligomer of 2,5-bis(4′-methoxybiphenyl-4-yl)thiophene has been investigated. The crystals are orthorhombic with space group $Cmc2_1$. The crystal structure is characterized by that the molecular long axis is rigorously perpendicular to the bottom crystal plane (the *bc*-plane).

A large number of molecular semiconductors have been proposed and synthesized during the past decades. Of these, a variety of oligophenylenes and oligothiophenes are potentially useful as functional materials that can be applied to optoelectronic devices such as thin-film transistors (TFTs) and light-emitting diodes.[1–3] More recently a particular class of materials including both thiophenes and phenylenes as building blocks are developed and known as thiophene/phenylene co-oligomers (TPCOs).[4] These crystals show high carrier mobility[5] and peculiar emission properties such as the laser oscillation[6,7] and amplified spontaneous emission (ASE).[8]

The TPCOs are characterized by the following aspects in light of the molecular and crystal design: (i) Various molecular shapes bent, zigzag, pseudo-straight, etc. are readily accessible by appropriately arranging the pentagonal thiophenes and hexagonal phenylenes in the molecule. (ii) Such nonstraight molecules produce a unique crystallographic structure where a tilt of the molecular long axis is very small against the bottom crystal plane (the *ab*-plane in most cases). For instance, the tilt angle between the molecular long axis and the normal of the *ab*-plane is no larger than ca. 2.6° for the oligothiophenes (up to tetramer) with biphenylyl wings on either molecular terminals.[9] This is in sharp contrast with crystals of (pseudo)-straight molecules such as oligophenylenes and oligothiophenes; the corresponding tilt angles are around 20° for them.[10] How small we can make the tilt angle will be a central question when we apply the functional materials to the devices. The reasons are as follows: Since the charge transport predominates through the face-to-face packed molecular array, the most favorable performance is expected regarding the thin-film devices laterally designed when the above tilt angle is 0°.[1] The tilt angle of 0° causes the transition dipoles to stand perpendicular to the bottom crystal plane. This configuration produces a large optical gain along that plane.[9a]

From the point of view of crystallographic symmetry, however, the crystals of TPCOs investigated so far belong to virtually the same monoclinic space group of $P2_1/c$ (or $P2_1/n$).[9] Because of this symmetry the tilt angle of the molecular long axis mentioned above usually differs from 0°. In the present studies, we have investigated the crystal structure of 2,5-bis(4′-methoxybiphenyl-4-yl)thiophene (**BP1T-OMe**);[11] see the structural formula in Figure 1a. The compound is one of the oligothiophene analogues with biphenylyl wings on either molecular terminal, but that substituted with methoxy groups at the para-positions of the terminal phenyls. We define in Figure 1a the molecular long axis as the line connecting the two oxygens. The crystals are orthorhombic with space group $Cmc2_1$. In the crystals the molecular long axis is perpendicular to the bottom crystal plane (the *bc*-plane); the tilt angle of the molecular long axis is rigorously 0°. We report here an unusual feature of this crystal structure.[12,13]

Figure 1b depicts the ORTEP diagram of **BP1T-OMe** that represents the actual molecular structure. Molecules are bent and twisted relative to the planar thiophene ring so that the molecules can hold the mirror symmetry with respect to the plane vertically intersecting the thiophene ring. The deviation from the symmetry of C_{2v}, however, is relatively small. The dihedral angle between the two least-squares planes of thiophene and the adjacent phenylene is 9.3°. That between the two phenylenes within the same biphenylyl is 4.3°.

The mirror planes are identical to the (100)- and (200)-planes as represented with the arrows in Figure 2. In virtue of this mirror symmetry the molecular long axis stands rigorously upright against the *bc*-plane. This is the most outstanding feature of the present crystals. Notice that this is not a consequence of the orthorhombic crystals alone. The condition of the upright

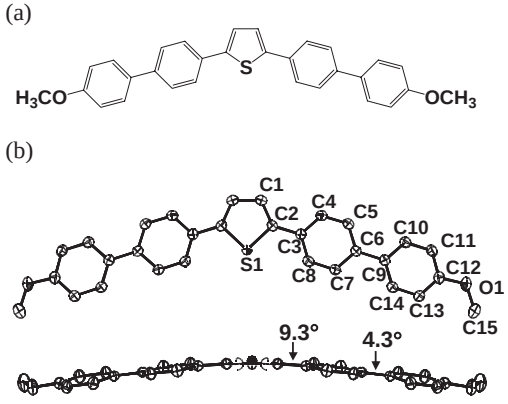

Figure 1. (a) Structural formula and (b) ORTEP diagram of **BP1T-OMe**. Numerals denote dihedral angles (see text).

Copyright © 2007 The Chemical Society of Japan

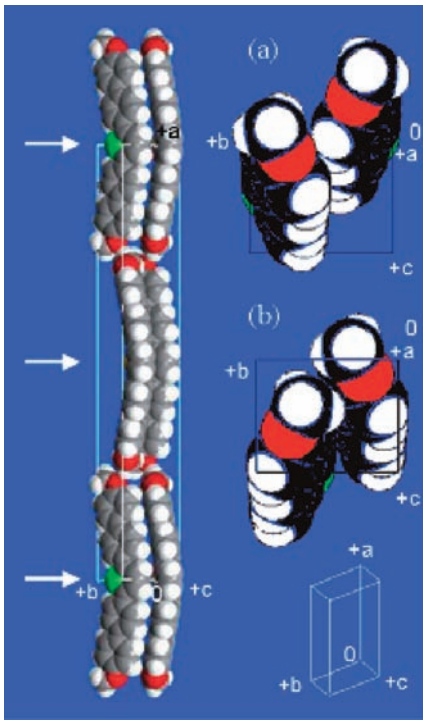

Figure 2. Molecular packing in the crystal. Two distinct packing schemes viewed along the *a*-axis are depicted as (a) and (b). Arrows denote mirror planes.

molecular axis is more severe. The upright configuration of the molecules is indeed a consequence of the presence of the mirror symmetry in combination with the orthorhombic crystals. The methoxy groups are likely to play a role in stabilizing the orthorhombic form of the crystals.[10a] It is worthy of note that the **BP1T-OMe** crystals lack the center of symmetry, seeing that many of organic crystals possess it.[9,10]

The crystals are characterized by the presence of the molecular layered structure in which the molecules form the well-known herringbone structure laterally spreading along the *bc*-plane. We have estimated the herringbone angles between the nearest-neighbor thiophenes at 47.4°, being related to those of other crystals with the related herringbone structure.[10] This structural feature is also advantageous to the device applications of the molecular semiconductors.[10c] Two distinct molecular packing schemes are observed, even though in both the cases the molecules nestle close to each other. One is the upper (or equivalently bottom) pair in Figure 2 [see also inset (a)]. Another is the central pair [inset (b)]. This difference is recognized in that the methyl groups are turned aside (the former case) or turned in (the latter case). The corresponding separation between the two methyl-carbons (oxygen) in the nearest-neighbor molecules is either 5.755(2) [4.592(2)] Å or 3.846(2) [4.884(2)] Å.

In summary we have demonstrated the crystallographic features of **BP1T-OMe** as an illustration among the newly occurring class of molecular semiconductors of TPCOs that may be promising in optoelectronic device applications. The material **BP1T-OMe** is expected to supply us with a good opportunity to survey the structure/property relationship. It will therefore be of high interest and importance to determine the crystal structure of related co-oligomers.

This work was partly supported by a Grant-in-Aid for Scientific Research B (No. 15350115) from the Ministry of Education, Culture, Sports, Science and Technology, Japan. This work was also partly supported by a Grant-in-Aid for Science Research in a Priority Area "Super-Hierarchical Structures" (No. 17067009) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 S. Hotta, Y. Ichino, Y. Yoshida, in *Electronic and Optical Properties of Conjugated Molecular Systems in Condensed Phases*, ed. by S. Hotta, Research Signpost, Trivandrum, **2003**, Chap. 24, pp. 615–635.
2 S. Hotta, in *Handbook of Organic Conductive Molecules and Polymers*, ed. by H. S. Nalwa, John Wiley & Sons, Chichester, **1997**, Vol. 2, Chap. 8, pp. 309–387.
3 H. Yanagi, S. Okamoto, *Appl. Phys. Lett.* **1997**, *71*, 2563.
4 a) S. Hotta, H. Kimura, S. A. Lee, T. Tamaki, *J. Heterocycl. Chem.* **2000**, *37*, 281. b) S. Hotta, S. A. Lee, T. Tamaki, *J. Heterocycl. Chem.* **2000**, *37*, 25. c) S. Hotta, T. Katagiri, *J. Heterocycl. Chem.* **2003**, *40*, 845.
5 M. Ichikawa, H. Yanagi, Y. Shimizu, S. Hotta, N. Suganuma, T. Koyama, Y. Taniguchi, *Adv. Mater.* **2002**, *14*, 1272.
6 M. Ichikawa, R. Hibino, M. Inoue, T. Haritani, S. Hotta, K. Araki, T. Koyama, Y. Taniguchi, *Adv. Mater.* **2005**, *17*, 2073.
7 K. Shimizu, Y. Mori, S. Hotta, *J. Appl. Phys.* **2006**, *99*, 063505.
8 M. Nagawa, R. Hibino, S. Hotta, H. Yanagi, M. Ichikawa, T. Koyama, Y. Taniguchi, *Appl. Phys. Lett.* **2002**, *80*, 544.
9 a) S. Hotta, M. Goto, R. Azumi, M. Inoue, M. Ichikawa, Y. Taniguchi, *Chem. Mater.* **2004**, *16*, 237. b) S. Hotta, M. Goto, *Adv. Mater.* **2002**, *14*, 498. c) T. J. Dingemans, N. S. Murthy, E. T. Samulski, *J. Phys. Chem. B* **2001**, *105*, 8845.
10 a) J. Bernstein, J. A. R. P. Sarma, A. Gavezzotti, *Chem. Phys. Lett.* **1990**, *174*, 361. b) K. N. Baker, A. V. Fratini, T. Resch, H. C. Knachel, W. W. Adams, E. P. Socci, B. L. Farmer, *Polymer* **1993**, *34*, 1571. c) S. Hotta, K. Waragai, *J. Mater. Chem.* **1991**, *1*, 835. d) G. Horowitz, B. Bachet, A. Yassar, P. Lang, F. Demanze, J.-L. Fave, F. Garnier, *Chem. Mater.* **1995**, *7*, 1337. e) D. Fichou, B. Bachet, F. Demanze, I. Billy, G. Horowitz, F. Garnier, *Adv. Mater.* **1996**, *8*, 500.
11 T. Katagiri, S. Hotta, *J. Heterocycl. Chem.*, to be published.
12 Intensity data from a Bruker SMART-CCD diffractometer (Mo Kα). Crystallographic data for **BP1T-OMe**; $C_{30}H_{24}O_2S$, MW 448.55, orthorhombic, $Cmc2_1$, $a = 49.638(10)$, $b = 7.4290(15)$, $c = 5.8779(12)$, $V = 2167.5(8)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.375$ g cm^{-3}, $T = 223$ K. 6692 reflections measured, 2363 unique reflections [R(int) = 0.0167]. $R1 = 0.0306$ [$I \geq 2.0\sigma(I)$], $wR2 = 0.0827$ (all data), GOF = 1.049 Crystallographic data reported in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-630600. Copies of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
13 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

Published on the web (Advance View) January 18, 2007; doi:10.1246/cl.2007.270