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## Synthesis and mesomorphic properties of bent-shaped molecule with low bent-angle central core and long alkylthio tail

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## Abstract

Two homologous series of bent-shaped molecules composed of low bent-angle naphthalene central core and long alkoxy tail or alkylthio tail, N(1,7)-n-OPIMB and N(1,7)-n-SPIMB (n = 20, 22), respectively, were synthesized. The mesomorphic properties were investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XRD). Compared to the direct transition from the isotropic phase to the chiral B4 phase examined in N(1,7)-n-OPIMB, N(1,7)-n-SPIMB exhibited a rare Iso– $N_{col}$ –Col<sub>h</sub>–B4 phase sequence. The combination of the asymmetric low bent-angle 1,7-naphathalene central core and the flexible long alkylthio tail is considered to play an important role in the formation of such a novel phase sequence.  $\bigcirc$  2011 Mao Sheng Zhan. Published by Elsevier B.V. on behalf of Chinese Chemical Society. All rights reserved.

Keywords: Bent-shaped; Liquid crystal; Alkylthio tail; Mesomorphic behaviour

Since the spontaneous formation of smectic phases with unique polarity and microscopic chirality in bent-shaped liquid crystals was discovered [1,2], extensive attention has been attracted in this intriguing area for the last decades. To clarify the structure-property relationship is one of the major research targets in this area. Though a variety of bent-shaped molecules have been synthesized, the alkoxy tail and a central core such as 1,3-dioxybenzene or 2,7-dioxynaphthalene unit are mostly often used [3,4]. In these molecules, the bent-angle is approximately 120° although some angular variation is allowed through the rotation of the linkage group to the side wings. Li *et al.* prepared liquid crystalline copolymers based on 1,4-, 1,5- and 2,7-dioxynaphthalene rings and discussed their morphological features [5–7]. The introduction of side wings at different positions of the central dioxynaphthalene core have opened up new areas of molecular structure design in bent-shaped liquid crystal field.

Lee *et al.* prepared molecules composed of a 1,7-naphthalene central core and schiff-base side chain with alkoxy tail, N(1,7)-*n*-OPIMB (n = 4, 8, 12, 16), which forms chiral B4 phase irrespective of their low bent angle of approximately 60°. And no switchable banana phases have been found [8]. Recently, we have synthesized bent-shaped molecules with 1,7-naphthalene central core and alkylthio tail, N(1,7)-*n*-SPIMB (n = 8, 12, 14, 16). Interestingly, the introduction of the alkylthio tail in place of the alkoxy tail induces a new type of switchable hexagonal columnar phase (Col<sub>n</sub>), with a phase sequence of Iso–Col<sub>h</sub>–B4 [9]. However, none of the previous research touches upon the compounds with longer tail ( $n \ge 20$ ), which might cause considerable molecular interlayer interactions. Therefore, a

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Scheme 1. Synthetic route of 1,7-naphthalene-bis[4-(4-alkylthiophenyliminomethyl)]benzoate, N(1,7)-n-SPIMB.

continuing effort has been carried out which focused on the synthesis and characterization of bent-shaped molecules with low bent-angle 1,7-naphthalene central core and longer tail, N(1,7)-*n*-SPIMB and N(1,7)-*n*-OPIMB (n = 20, 22).

N(1,7)-*n*-SPIMB was prepared according to the synthetic route shown in Scheme 1. A solution of 4-alkylthioanline and bisaldehyde in chloroform was heated under reflux for 6 h. The reaction mixture was concentrated and recrystallized from chloroform–ethanol to give yellow crystals. The preparation of the bisaldehyde was performed by using procedures described in our previous report [9]. N(1,7)-*n*-OPIMB was prepared with similar methods. All compounds were characterized by NMR and elemental analysis [10].

Mesomorphic properties of N(1,7)-*n*-OPIMB and N(1,7)-*n*-SPIMB (n = 20, 22) were examined under a polarizing optical microscope(POM) equipped with a hot stage. Transition temperatures and associated enthalpy changes obtained by DSC are listed in Table 1. N(1,7)-20-OPIMB and N(1,7)-22-OPIMB exhibited a direct transition from the isotropic phase to the chiral B4 phase, which is the same with compounds composed of shorter tail (n = 4, 8, 12, 16). However, N(1,7)-*n*-SPIMB (n = 20, 22) showed a rare Iso– $N_{col}$ –Col<sub>h</sub>–B4 phase sequence. The DSC thermo-gram of N(1,7)-20-SPIMB is shown in Fig. 1. On cooling from the isotropic liquid between glass plates, a marble texture appears from the isotropic melt, which gradually changes to the dark homeotropic texture (Fig. 2a). Then Col<sub>h</sub> phase appears as a smooth fan-shaped texture, characteristic of hexagonal molecular arrangement. In some areas, the textures also include optically isotropic zone which indicates columns align perpendicularly to the substrate (Fig. 2b). With further cooling to the B4 phase, all areas change to a dark blue texture with a low birefringence (Fig. 2c). There exist two types of optically active domain with opposite chirality. And the brightness of each domain is interchanged under the positive or negative rotation of the polarizer from the cross position (Fig. 2d).

To elucidate more detailed mesomorphic structure for N(1,7)-*n*-SPIMB (n = 20, 22), powder X-ray investigations were carried out with samples kept in glass capillary tubes. For N(1,7)-20-SPIMB, the X-ray diffraction shows only one inner reflection in  $N_{col}$  phase with a layer spacing of 65.6 Å (Fig. 3). The outer broad diffuse scattering of 4.6 Å corresponds to the liquid-like lateral packing of the molecules. In Col<sub>h</sub> phase, the inner three diffraction peaks reflect layer spacings of 65.1 Å, 37.2 Å and 32.5 Å, which can be nicely indexed as the (1 0 0), (1 1 0), and (2 0 0) reflections of a hexagonal columnar phase [11]. The hexagonal lattice edge was calculated as 75.2 Å. The lowest-temperature B4 phase shows only one inner layer reflection, which is 44.9 Å. It should be noted that the layer spacing of  $N_{col}$  phase, 65.6 Å, is close to the mean distance between columns in Col<sub>h</sub> phase, 65.1 Å, and larger than the molecular length (51.7 Å calculated by Spartan 08 with the most stable conformation). Thus, the molecules in  $N_{col}$  phase are assumed to

Table 1 Transition temperatures and enthalpies of N(1,7)-*n*-SPIMB and N(1,7)-*n*-OPIMB (n = 20, 22).

Compound	Transition temperature <sup>a</sup> (°C) (enthalpy/kJ mol <sup><math>-1</math></sup> )
N(1,7)-20-SPIMB	B4 118.6 (38.4) Col <sub>h</sub> 143.5 (2.4) N <sub>col</sub> 150.1 (5.2) Iso
N(1,7)-22-SPIMB	B4 117.9 (39.8) Col <sub>h</sub> 146.0 (2.1) N <sub>col</sub> 151.8 (6.5) Iso
N(1,7)-20-OPIMB	B4 147.5 (31.2) Iso
N(1,7)-22-OPIMB	B4 146.4 (28.6) Iso

<sup>a</sup> Based on cooling data of DSC.



Fig. 1. DSC thermo grams of N(1,7)-20-SPIMB.



Fig. 2. Photomicrographs of (a) N<sub>col</sub> phase (b) Col<sub>h</sub> phase (c) (d) B4 phase for N(1,7)-20-SPIMB (arrows indicate directions of polarizers).



Fig. 3. X-ray diffraction patterns of (a)  $N_{col}$  phase (b) Col<sub>h</sub> phase and (c) B4 phase for N(1,7)-20-SPIMB.

stack in columns that possess no long range lateral positional order. Consequently, the Col<sub>h</sub> to  $N_{col}$  transition could be interpreted as the melting of the 2D hexagonal lattice, without complete destruction of the columns [12]. The particularly low barriers of long alkylthio terminal chain might enable the compound to change conformations more easily, which would affect the mesophase properties [13].

In conclusion, all the target bent-shaped molecules with low bent-angle central core and long tail exhibit enantiotropic transitions. N(1,7)-n-OPIMB (n = 20, 22) exhibited an Iso-B4 phase transition behavior. In contrast, N(1,7)-n-SPIMB (n = 20, 22) showed a rare Iso- $N_{col}$ -Col<sub>h</sub>-B4 phase sequence. The combination of the asymmetric low bent-angle 1,7-naphathalene central core and the flexible long alkylthio tail is considered to play an important role in the formation of such a novel phase sequence.

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- [10] Analytical and secroscopic data for the target compounds. N(1,7)-20-SPIMB, yield 51.8%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.88 (t, 6H, J = 6.8 Hz), 1.25–1.75 (m, 72H), 2.94 (t, 4H, J = 6.4 Hz), 7.19–8.09 (m, 18H), 8.29 (d, 2H, J = 8.4 Hz), 8.40 (d, 2H, J = 8.4 Hz), 8.56 (s, 1H), 8.58 (s, 1H). Elemental analysis: calcd. for C<sub>78</sub>H<sub>106</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C 78.08, H 8.90, N 2.33, O 5.33, S 5.34; found: C 77.87, H 8.72, N 2.31, O(+S) 11.10. N(1,7)-22-SPIMB, yield 56.2%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.88 (t, 6H, J = 6.8 Hz), 1.25–1.75 (m, 80H), 2.94 (t, 4H, J = 6.4 Hz), 7.19–8.09 (m, 18H), 8.29 (d, 2H, J = 8.4 Hz), 8.40 (d, 2H, J = 8.4 Hz), 8.56 (s, 1H), 8.58 (s, 1H). Elemental analysis: calcd. for C<sub>82</sub>H<sub>114</sub>N<sub>2</sub>O<sub>4</sub>S<sub>2</sub>: C 78.42, H 9.15, N 2.23, O 5.10, S 5.11; found: C 78.27, H 9.07, N 2.34, O(+S) 10.32. N(1,7)-20-OPIMB, yield 68.3%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.87 (t, 6H, J = 7.2 Hz), 1.25–1.75 (m, 72H), 3.98 (t, 4H, J = 7.3 Hz), 7.19–8.09 (m, 18H), 8.29 (d, 2H, J = 8.4 Hz), 8.42 (d, 2H, J = 8.4 Hz), 8.55 (s, 1H), 8.57 (s, 1H). Elemental analysis: calcd. for C<sub>78</sub>H<sub>106</sub>N<sub>2</sub>O<sub>6</sub>: C 80.23, H 9.15, N 2.40, O 8.22; found: C 80.37, H 9.11, N 2.42, O 8.10. N(1,7)-22-OPIMB, yield 60.7%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.87 (t, 6H, J = 7.2 Hz), 1.25–1.75 (m, 80H), 3.98 (t, 4H, J = 7.3 Hz), 7.19–8.09 (m, 18H), 8.57 (s, 1H). Elemental analysis: calcd. for C<sub>78</sub>H<sub>106</sub>N<sub>2</sub>O<sub>6</sub>: C 80.23, H 9.15, N 2.40, O 8.22; found: C 80.37, H 9.11, N 2.42, O 8.10. N(1,7)-22-OPIMB, yield 60.7%, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.87 (t, 6H, J = 7.2 Hz), 1.25–1.75 (m, 80H), 3.98 (t, 4H, J = 7.3 Hz), 7.19–8.09 (m, 18H), 8.29 (d, 2H, J = 8.4 Hz), 8.42 (d, 2H, J = 7.3 Hz), 7.19–8.09 (m, 18H), 8.29 (d, 2H, J = 8.4 Hz), 8.42 (d, 2H, J = 7.3 Hz), 7.19–8.09 (m, 18H), 8.29 (d, 2H, J = 8.4 Hz), 8.42 (d, 2H, J = 7.3 Hz), 7.19–8.09 (m, 18H), 8.29 (d, 2H, J = 8.4 Hz), 8.42 (d, 2H, J = 7.3 Hz), 7.19–8.09 (m, 18H), 8.29 (d, 2H, J = 8.4 Hz), 8.42 (d, 2H, J = 8.4 Hz), 8.55 (s, 1H), 8.57 (s, 1H). Elemental analysis: calcd. for C<sub>82</sub>H<sub>114</sub>N<sub>2</sub>O<sub>6</sub>:
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