

Mesomorphic Behavior of Bent-shaped Molecules with Non-aromatic Central Core Based on Bis(*p*-hydroxyphenyl)methane

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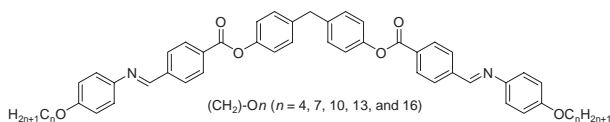
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New homologous series of bent-shaped molecules with non-aromatic central core based on bis(*p*-hydroxyphenyl)methane were studied comparing with the conventional bent-shaped molecules with aromatic central core.

Since discovery by Watanabe et al. for the first time,¹ bent-shaped molecules (so-called banana molecules) have attracted great attention in the field of innovative liquid crystal research. Their unique properties of spontaneous chiral symmetry breaking and decoupling of polar and tilt order have been extensively studied for the last decade.^{2–4} A number of bent-shaped molecules have been synthesized and characterized, and at least eight different phases have been identified.⁵ Particularly, the structure–property relationship in bent-shaped molecules is a very important factor for the development of polar order and chirality, and it can cause considerable interlayer interaction, influencing the constitution for the *B_n* phases.^{5,6} For this reason, many approaches have been made to vary the chemical structure, especially the central bent core position. Nevertheless, most bent-shaped molecules are usually designed by using 1,3-disubstituted aromatics or heteroaromatic units, or by joining two rod-like molecules by noncyclic spacers with an odd number of atoms. However, the introduction of non-aromatic central core units has been rarely reported. Thus, we have synthesized a new homologous series of bent-shaped molecules [(CH₂)_{*n*}-O*n*, see Scheme 1] with non-aromatic central core based on bis(*p*-hydroxyphenyl)methane and side wings containing Schiff base moieties.¹⁰ Electro-optical and X-ray diffraction measurements have been utilized for the investigation of their mesomorphic properties and phase structures.

All the compounds exhibited enantiotropic transitions, and their mesophase behavior was different from each other in accordance with the length of terminal alkyl chain. The mesomorphic transition temperature and enthalpy change for the final products were collected from DSC in conjunction with POM. They are listed in Table 1.

On cooling from the isotropic liquid compound (CH₂)₄-O4 formed a fan-shaped texture along with a mosaic pattern in some regions (Figure 1a). This fan-shaped texture was sensitive to change in applied electric field. Optical birefringence in fan-shaped textures suddenly increased and a smooth texture was obtained (Figure 1b). However, the texture remained unchanged



Scheme 1.

Table 1. Phase-transition temperature (°C) and enthalpies (ΔH , kJ mol⁻¹) for the (CH₂)_{*n*}-O*n* series (on cooling at a rate of 10 °C min⁻¹)

<i>n</i>	Transition temperature (enthalpy)
4	Iso 253.1 (14.5) B1 _{rev} 208.9 (52.3) Cr ₁
7	Iso 241.5 (21.9) B7 184.0 (51.9) Cr ₁
10	Iso 228.8 (20.6) B7 175.8 (47.7) Cr ₂ 127.4 (1.88) Cr ₁
13	Iso 220.5 (18.4) B7 168.6 (43.7) Cr ₂ 135.3 (10.7) Cr ₁
16	Iso 216.5 (26.0) B7 164.0 (63.1) Cr ₂ 138.3 (13.2) Cr ₁

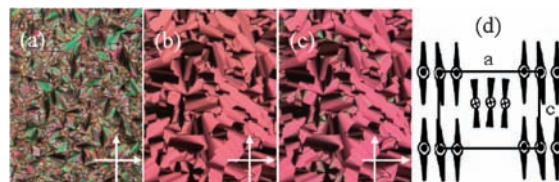


Figure 1. Photomicrographs of the frustrated smectic phases observed for compound (CH₂)₄-O4. (a) B1_{rev} phase obtained on cooling the liquid isotropic phase, (b) B1_{rev} phase during the DC field (7.8 V/μm) application, and (c) B1_{rev} phase observed upon the off-state of the field. White arrows indicate polarizer directions. (d) Proposed schematic representation.

after terminating the electric field with only a small decrease of the birefringence (Figure 1c). Both field-on and field-off states had the same extinction directions, which means that the field-induced texture change is irreversible and the principal axes of the optical dielectric tensor do not change after the electric field is applied. However, polarization reversal current was not found at this phase for field lower than 30 V/μm. The X-ray diffraction pattern was obtained using X-ray beam perpendicular to cells sandwiched between thin glasses. Two sharp inner reflections and a broad outer reflection were observed, indicating intralayer liquid-like order. These characteristics of the diffraction come from the two-dimensional (2D) frustrated smectic phase structure, and the original and additional peaks correspond to (002) and (101), respectively. Thus, this diffraction geometry of the frustrated phase can be explained nicely by 2D lattice of the non-tilted B1_{rev} phase with *a* = 44.7 Å and *c* = 40.6 Å (Figure 1d) in which 2D density modulations are in a plane perpendicular to the spontaneous polarization vector.⁷ The molecular length (40.5 Å) calculated by Spartan'02 program is consistent with the layer spacing by X-ray diffraction experiment (40.6 Å).

As shown in Figures 2a–2c, a variety of texture variants to the B7 phase was observed in compounds (CH₂)₇-O7 and (CH₂)₁₀-O10 when the cell was slowly cooled from the isotropic phase. Spiral, myelinic-like, banana-leaf-like, oval-like, and

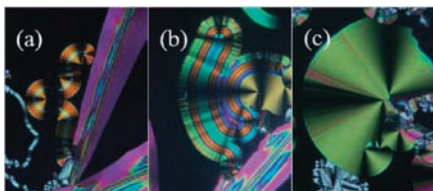


Figure 2. Typical photomicrographic textures observed in the B7 phase: (a) spiral and banana-leaf-like, (b) two-dimensional periodic pattern domains, and (c) fan-shaped domain.

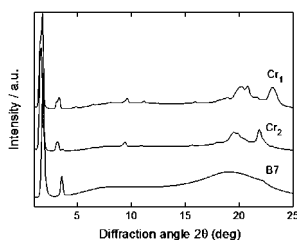


Figure 3. X-ray intensity profiles of compound (CH₂)-O10.

circular domain textures were observed. One can also observe fan-shaped textures with different colors, in which the brushes of the extinction cross are parallel to the polarizer and analyzer directions. This mesophase was not switchable despite little change in birefringence. No switching current peak was recorded even at high voltage. X-ray diffraction measurement was also performed, as shown in Figure 3. A diffuse scattering in the wide angle region is observed indicating a liquid-like order within the smectic layer as in the B2 phase and sharp reflections are detected in the small angle region.

In compound (CH₂)-O10, on slowly cooling from the B7 phase, all domains appeared to be broken with sudden birefringent change. This phase shows no distinct difference between this intermediate phase and the lower temperature crystal phase although a transition peak is clearly observed by DSC. Thus, this phase can be characterized to be crystalline phase (Cr₂ phase) and the two crystal phases existing at the lower temperature region below the B7 phase. On continuous cooling to the lower-temperature-crystalline phase (Cr₁ phase), only a little change in birefringence was observed without significant change in the photomicrograph. X-ray patterns and layer spacing (Cr₂ and Cr₁ phase are 58.9 and 58.1 Å, respectively) were also almost the same.

(CH₂)-O13 and (CH₂)-O16 also show a similar phase transition to (CH₂)-O10. But the B7 phase shows quite different domain. From the isotropic melt, spherulitic domains slowly appeared and coalesced to fan-shaped domains. X-ray diffraction data for this phase supported the B7 phase with layer spacings of 53.3 and 61.5 Å. This B7 phase was also unswitchable despite little change of birefringence observed. On cooling from the B7 phase, a somewhat broken circular shape texture of Cr₂ phase was also observed as well as Cr₁ phase.

As mentioned in the introduction section, the variation of the central bent core is very important for interlayer interaction, which is related to the constitution of specific B_n mesophase. In this study, we used the non-aromatic –CH₂– unit for central bent core instead of aromatic ones. This central core makes the bent angle between side wings smaller compared with the aromatic one. This assumption was confirmed by molecular simu-

lations by Spartan'02 program. It was shown that replacement of phenyls with –CH₂– reduce the angle between side wings by about 7°. Moreover, the band linkage between –CH₂– core and phenyl can make rotation somewhat free in the lowest energy conformation, thus the twist angle of the phenyl becomes 90°.⁸ Therefore more flexible conformations are allowed in the liquid crystalline region, which leads to essentially different mesophases from that based on the aromatic central core. In fact, all of our molecules shows mesophase at a temperature region below the isotropic melt different from that of the conventional phenyl central core molecules, P-*n*-O-PIMB, despite that the chemical structure is almost the same except in the central core.⁹ For example, most of the conventional phenyl central core molecules show the B2 phase at a temperature region below the isotropic melt, but our molecules show the B7 phase on cooling from the isotropic liquid. Another difference is that our molecules do not show the chiral segregated domains as was observed in the chiral blue phase. Thus, these results indicate that the modification of central bent core plays a major role for the emergence of mesophase structures. Especially the formation of the B7 phase may be more advantageous in non-aromatic central core molecules. We are now proceeding with a decisive study of the properties of the B7 phase in non-aromatic central core systems and more comprehensive results will be reported in due course.

In summary, the mesomorphic behavior of new homologous series of bent-shaped molecules with non-aromatic central core based on bis(*p*-hydroxyphenyl)methane has been studied. All compounds exhibited the well-defined fluid smectic mesophase, B1_{rev} or B7 phase, depending on the length of alkyl terminal chain. However, the phase sequence is totally different from the conventional aromatic central core molecules. This difference may attribute to the structural properties of central bent-core; the free rotation and somewhat smaller bent angle between the side wings.

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- 10 Supporting Information is also available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chemlett/index.html>.