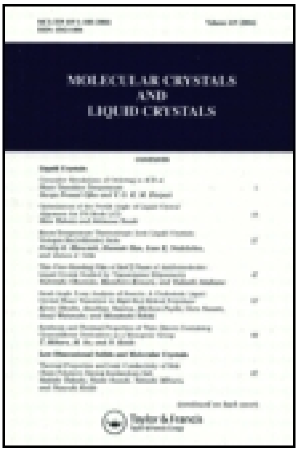

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Pre-Organization Effects on Chirality, Polarity and Biaxiality in Liquid Crystals: Novel Laterally Connected Mesogens showing Anomalous Properties

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Pre-Organization Effects on Chirality, Polarity and Biaxiality in Liquid Crystals: Novel Laterally Connected Mesogens showing Anomalous Properties

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*Pre-organization effects are investigated for the laterally-connected liquid crystals possessing a biphenyl connecting group. The homeotropic texture of the N phase of a free-standing film sample was found to change into the other "*Schlieren*" texture on cooling even in the N phase, which then changes into the "*Schlieren*" texture of the SmC phase on further cooling. The possibility of the emergence of biaxiality in the N phase is discussed.*

1. Introduction

Organization in liquid crystal phases is constructed by the molecular recognition among the constituting molecules. "Supermolecular liquid crystals" [1] are therefore the products based on the sophisticated soft materials design. "Pre-organization" is one of the most important concepts for producing supermolecular liquid crystals[2,3]. So far, the effects of pre-organization on the chirality- or polarity-dependant structural and electrical[2,4], and optical[5] properties have been intensively investigated. For example, the introduction of chiral moieties at both ends of the twin molecular configuration (see Fig. 1(a)) is a simple pre-organization but is a promising molecular design for producing special chiral effects. If such molecules form a smectic layered structure as shown in Fig. 1 (b), then the chiral moieties aggregate between the layer surfaces, producing a strong chiral interaction among the molecules.

The structure and position of chiral centres are important for the design of the pre-organization based on the concept shown in Fig. 1. Fig. 2 shows some examples highlighting the effect. Introduction of 1-methylheptyl chiral groups at the peripheral ends (Fig. 2 (a)) produces a complex molecular assembly of the ferrielectric phase[6], which is not observed for the other materials possessing related structures (Fig. 2 (b)[7] and (c)[8]).

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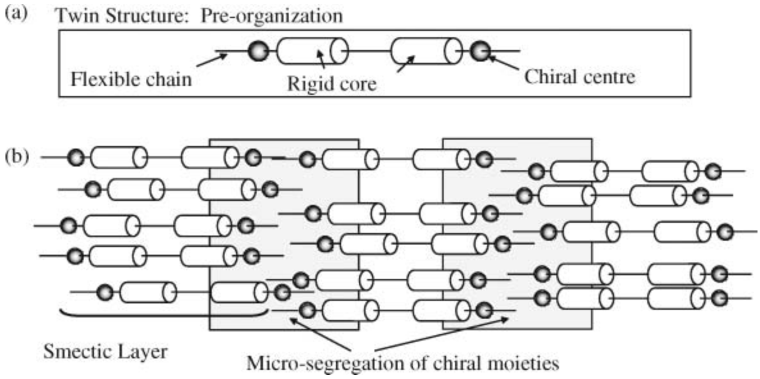

Figure 1. (a) Twin structure as an example of the pre-organization, and (b) expected molecular assembly of the pre-organized molecules.

The importance of the style and structure of the linking part has also been emphasized by the systematic investigation, in which the identical chiral centres are introduced in the same position of the molecular structure (i.e., peripheral ends), on the correlation between the pre-organization styles and the resulting liquid crystal phases (Fig. 3).

In this study, a novel strategy of the pre-organization is introduced, which is related to the lateral connection of the mesogenic parts, instead of the previously mentioned linear connection. This pre-organization is expected to enhance the molecular biaxiallity and sometimes to produce the molecular chirality. Among the molecular designs for the pre-organization, a special attention has been paid in the structure of the connecting group. Three related molecular architectures of the laterally-connected systems, in which the connecting group is systematically varied, are compared in Fig. 4. A "binaphthyl" connecting group (Fig. 4 (a)) is famous as the origin of axis-chirality, as such the resulting laterally-connected compound can be optically active. However, a "phenyl" connecting group (Fig. 4 (c)) possesses no axis in the connection structure, and thus no axis-chirality appears. As such, the binaphthyl derivatives (Fig. 4 (a)) could possess both molecular biaxility and chirality but the phenyl derivatives (Fig. 4 (c)) can exhibit only the molecular biaxiality. A "biphenyl" connecting group (Fig. 4 (b)) possesses an intermediate character among them. The biphenyl

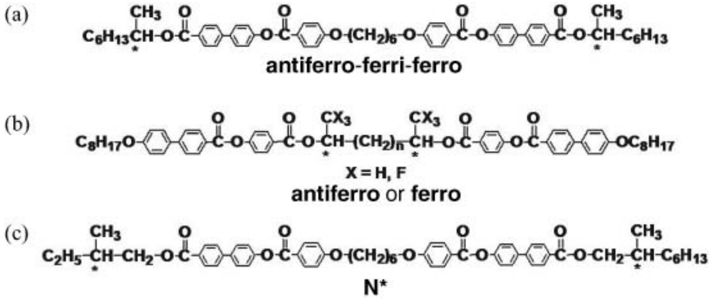

Figure 2. Effect of the structure and position of chiral centres in three related chiral liquid crystal compounds on the liquid crystal phase: (a) 1-methylheptyl chiral groups at the peripheral ends[6], (b) 1-methyl (or 1-trifluoromethyl) heptyl groups located in central region[7], and (c) 2-methybutyl chiral groups at the peripheral ends[8].

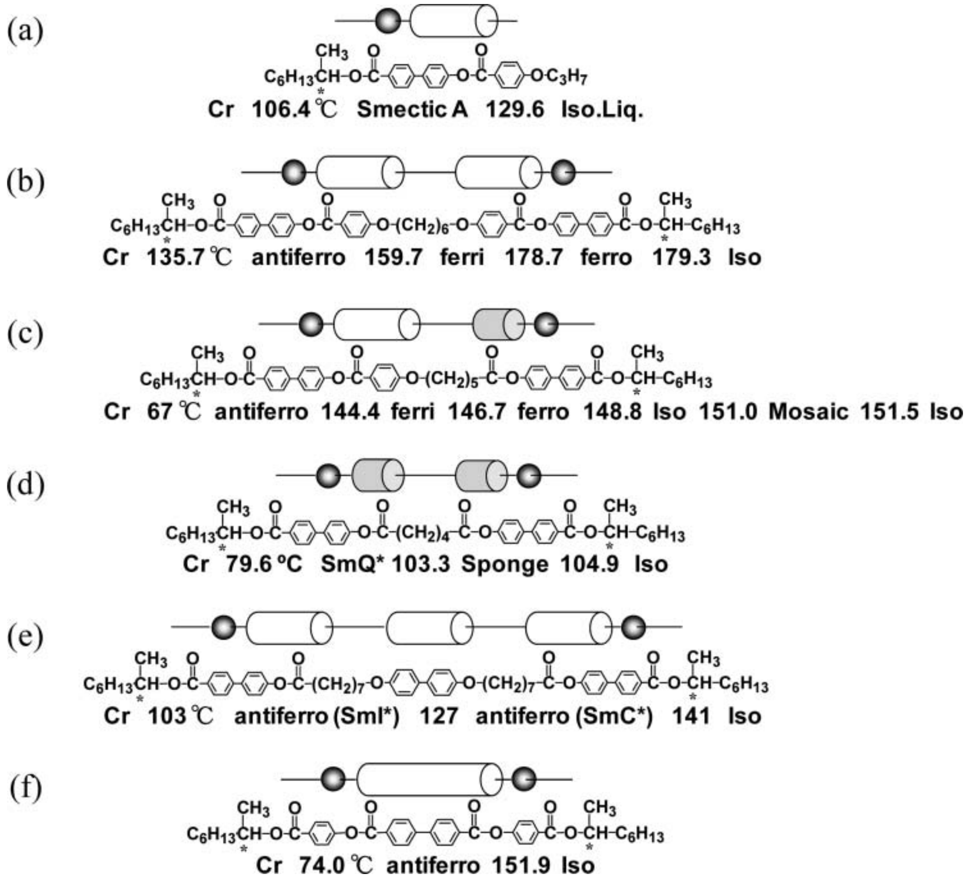

Figure 3. A variety of chiral liquid crystal phases observed in systematically pre-organized systems: (a) chiral monomeric compound as a component of pre-organization, (b) symmetric twin[6], (c) non-symmetric twin[9], (d) symmetric twin showing a thermotropic sponge phase[10]. (e) trimer[11], and (f) dichiral compound possessing a rigid core[12].

group itself does not show the axis-chirality in most cases, which can however be induced if the rotational barrier around the biphenyl axis is enhanced by any means, e.g., by the intra- and/or intermolecular interactions of the mesogenic parts attached to the phenyl ring.

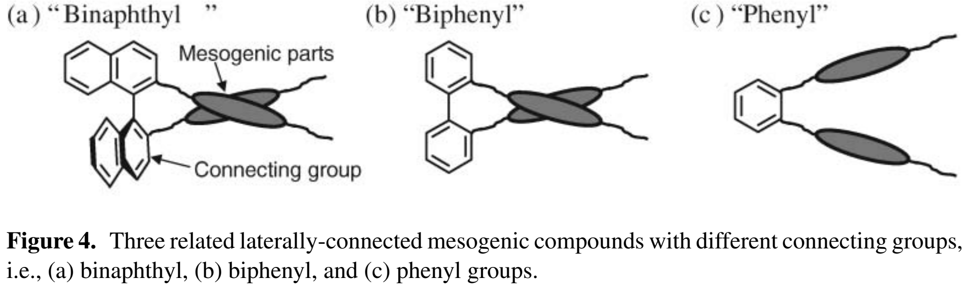

Figure 4. Three related laterally-connected mesogenic compounds with different connecting groups, i.e., (a) binaphthyl, (b) biphenyl, and (c) phenyl groups.

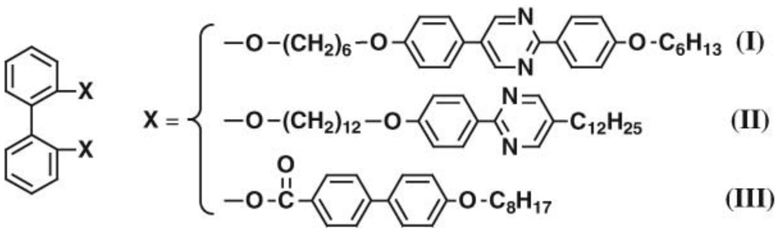

Figure 5. Laterally-connected mesogenic compounds studied based on the new pre-organization strategy.

This delicate nature with respect to the axis-chirality, as well as expected large molecular biaxial nature than the phenyl analogue, is attractive as the design for the pre-organization. Therefore, in this study, the biphenyl connecting group has been selected as the target and the effect of the pre-organization investigated. The structures studied are shown in Fig. 5.

2. Experimental

Characterisation of Materials

The purification of the final compound (**I**) was carried out using column chromatography over silica gel (70-230 mesh) (Sigma-Aldrich Co.) using dichloromethane-hexane mixture as the eluent, followed by the recrystallization from ethylacetate. The purities of all of the final compounds were checked by reverse-phase (ZORBAX, Eclipse XDB-C8) and normal-phase (CLC-SIL(M), Shimadzu) high-performance liquid chromatography. Elemental analyses were performed using an ELEMENTAR varioEL system. The structures of the materials were elucidated by infrared (IR) spectroscopy (Shimadzu FTIR-8100A infrared spectrophotometer), proton nuclear magnetic resonance (1H NMR) spectrometry (Bruker DRX-500 (500 MHz) nuclear magnetic resonance spectrometer), and mass (MS) spectrometry using an FD-MS (JEOL, JMS-700) method. The analyses of the structures of the products and intermediates by spectroscopic methods were found to be consistent with the predicted structures.

Preparation of 5-{4-(6-bromohexyl)}phenyl-2-(4-hexyloxyphenyl)pyrimidine (I-a)

Potassium carbonate (0.59 g, 4.3 mmol) was added to a solution of 5-(4-hydroxy)phenyl-2-(4-hexyloxyphenyl)pyrimidine (1.50 g, 4.3 mmol) (purchased from Midori Kagaku Co. Ltd., Japan) and 1,6-dibromohexane (1.58 g, 4.0 mmol) in cyclohexanone (30 ml). The reaction mixture was stirred at 95°C overnight. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the product was purified by column chromatography over silica gel using a mixture of dichloromethane/hexane (1:1) as the eluent, to give an intermediate bromo-compound. Yield = 1.26 g, (57%).

Preparation of 2,2′-Bis{6-[4-(2-(4-hexyloxyphenyl)pyrimidine-5-yl) phenyloxy]hexyloxy}biphenyl (I)

Potassium carbonate (0.25 g, 1.8 mmol) was added to a solution of the obtained bromo-intermediate, 5-{4-(6-bromohexyl)}phenyl-2-(4-hexyloxyphenyl)pyrimidine (**I-a**), (0.95 g, 1.9 mmol) and 2,2′-dihydroxybipheny (0.17 g, 0.91 mmol) in cyclohexanone (10 ml). The reaction mixture was stirred at 130°C overnight. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the product was purified by column chromatography over silica gel using a mixture of dichloromethane/hexane (2:1) as the eluent, and the resulting product was recrystallized from ethylacetate (80 ml), to give a colorless solid. Yield = 0.55 g, (57%). Elemental analysis found; C% 77.9, H% 7.6, N% 5.2, calculated for $C_{68}H_{78}O_6N4$; C% 78.0, H% 7.5, N% 5.3. δH (500MHz, $CDCl_3$, TMS); 8.91 (s, 4H, Ar-H), 8.40 (m, 4H, Ar-H), 7.52 (m, 4H, Ar-H), 7.26 ((m, 4H, Ar-H), 7.00 (m, 12H, Ar-H), 4.03 (t, 4H, Ar-O-C**H**$_2$-, $J = 6.6$ Hz), 3.93 (two overlapping triplets, 8H, Ar-O-C**H**$_2$-), 1.82-1.36 (m, 32H, aliphatic-H), 0.92 (t, 6H, -CH_2-C**H**$_3$, $J = 5.0$ Hz). ν/cm-1 (KBr); 2941, 2869 (C-H str.), 1607 (C-C str.), 830 (1, 4-disub. C-H o.o.p.d). *m/z*; 1046 (M^+). HPLC purity; Normal phase Si column: 99.8%, Reverse Phase C8 column: 100%.

Preparation of 5-(12-bromododecyl)-2-(4-dodecyloxyphenyl)pyrimidine (II-a)

Potassium carbonate (0.81 g, 5.9 mmol) was added to a solution of 5-dodecyl-2-(4-hydroxyphenyl)pyrimidine (2.00 g, 5.9 mmol) (purchased from Midori Kagaku Co. Ltd., Japan) and 1,12-dibromododecane (2.89 g, 8.82 mmol) in cyclohexanone (15 ml). The reaction mixture was stirred at 80°C overnight. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the product was purified by column chromatography over silica gel using a mixture of dichloromethane/hexane (1:1) as the eluent, to give an intermediate bromo-compound. Yield = 2.21 g, (64%).

Preparation of 2,2′-Bis{12-[4-(5-dodecylpyrimidin-2-yl)phenyloxy] dodecyloxy}biphenyl (II)

Potassium carbonate (0.24 g, 1.7 mmol) was added to a solution of the obtained bromo-intermediate, 5-(12-bromododecyl)-2-(4-dodecyloxyphenyl)pyrimidine (**II-a**), (1.01 g, 1.7 mmol) and 2,2′-dihydroxybipheny (0.16 g, 0.9 mmol) in cyclohexanone (8 ml). The reaction mixture was stirred at 130°C overnight. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the product was purified by column chromatography over silica gel using dichloromethane as the eluent, and the resulting product was recrystallized from a mixture of ethanol/ethylacetate (2:3) (25 ml), to give a colorless solid. Yield = 0.47 g, (46%). Elemental analysis found; C% 79.9, H% 10.4, N% 4.5, calculated for $C_{78}H_{118}O_4N_4$; C% 79.7, H% 10.1, N% 4.8. δH (500MHz, $CDCl_3$, TMS); 8.57 (s, 4H, Ar-H), 8.34 (m, 4H, Ar-H), 7.25 ((m, 4H, Ar-H), 6.99 (m, 12H, Ar-H), 4.02 (t, 4H, Ar-O-C**H**$_2$-), 3.89 (t, 4H, Ar-O-C**H**$_2$-), 2.59 (t, 4H, Ar- C**H**$_2$-), 1.82-1.26 (m, 80H, aliphatic-H), 0.89 (t, 6H, -CH_2-C**H**$_3$). ν/cm-1 (KBr); 2918, 2851 (C-H str.), 1609 (C-C str.), 843 (1, 4-disub. C-H o.o.p.d). *m/z*; 1198 (M^+). HPLC purity; Normal phase Si column: 99.9%, Reverse Phase C8 column: 99.6%.

Preparation of 2,2′-Bis{4-oxtyloxy-4′-carbonyloxybipheny}biphenyl (III)

4-(4-Octyloxyphenyl) beozoicacid (0.84 g, 2.5 mmol), 2,2′-dihydroxybipheny (0.24 g, 1.3 mmol), and DMAP (0.03 g, 0.3 mmol) were added to dry dichloromethane (13 ml). DCC (0.80 g, 3.9 mmol) was then added and the resulting mixture was stirred at room temperature for one day. Precipitated materials were removed by filtration. After removal of the solvent by evaporation under reduced pressure, the product was purified by column chromatography over silica gel using a mixture of dichloromethane/hexane (1:1) as the eluent, and the resulting product was recrystallized from a mixture of ethanol/ethylacetate (3:1) (40 ml), to give a colorless solid. Yield = 0.62 g, (60%). Elemental analysis found; C% 80.7, H% 7.4, calculated for $C_{54}H_{58}O_6$; C% 80.8, H% 7.2. δH (500MHz, $CDCl_3$, TMS); 8.01 (m, 4H, Ar-H), 7.57 (m, 8H, Ar-H), 7.40-7.28 (m, 4H, Ar-H), 6.98 (m, 4H, Ar-H), 4.00 (t, 4H, Ar-O-C**H**$_2$-, $J = 6.5$ Hz), 1.81-1.30 (m, 24H, aliphatic-H), 0.89 (t, 6H, -CH_2-C**H**$_3$, $J = 5.9$ Hz). ν/cm-1 (KBr); 2926, 2855 (C-H str.), 1740 (C = O str.), 1605 (C-C str.), 830 (1, 4-disub. C-H o.o.p.d). *m/z*; 802 (M^+). HPLC purity; Normal phase Si column: 99.9%, Reverse Phase C8 column: 99.4%.

Liquid-Crystalline and Physical Property Measurements

The initial phase assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using an Nikon Optiphot-pol polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit. The heating and cooling rates were 2°C min^{-1}. Free-standing films were made for textural observation by spreading the sample across a small hole (1∼2 mm diameter) in a metal plate. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a MAC Science MTC1000S calorimeter. The materials were studied at a scanning rate of 5°C min^{-1}, after being encapsulated in aluminium pans. The X-ray scattering experiment was performed by real-time X-ray diffractometer (Bruker AXS D8 Discover). The monochromatic X-ray beam (CuKαline) was generated by 1.6 kW X-ray tube and Göbel mirror optics. The 2D position sensitive detector has 1024 × 1024 pixels in a 5 cm × 5 cm beryllium window. A sample was introduced in a thin glass capillary (diameter 1.0 mm), which was placed in a custom-made temperature stabilized holder (stability within ± 0.1°C). The X-ray diffraction measurement and the textural observation by the polarized light microscopy using a CCD camera were performed simultaneously on the sample in the glass capillary tube.

3. Results and Discussion

Phase transition temperatures of the compounds studied are as follows:

Compound (**I**) Isotropic liquid 173.8°C N 162.2 SmC 90 recryst. (mp = 143°C),
Compound (**II**) Isotropic liquid 71.4 SmA 65 recryst. (mp = 97), and
Compound (**III**) Isotropic liquid 72 recryst. (mp = 120).

Compound (**II**) shows the usual homeotropic and fan-shaped textures in the vertically and homogenously aligned regions, respectively, which is typical for the SmA phase. However, Compound (**I**) shows rather an anomalous textural change at the SmC-N phase transition as shown in Fig. 6. Fig. 6 (a) shows the *Schlieren* texture observed for the SmC phase of Compound (**I**). On heating, the texture changes at the SmC-N phase transition (Fig. 6 (c)), resulting in the other *Schlieren* texture of the N phase (Fig. 6 (e)). Since the inner surfaces of the glass plates had been treated as vertical alignment, the appearance of the *Schlieren* texture in the SmC is reasonable. However, the appearance of the *Schlieren* texture in the N phase is anomalous, because the N phase of the vertical alignment sample is expected to show the homeotropic texture; the *Schlieren* texture is usually observed for the N phase with the planar alignment. There are two possibilities for this anomalous *Schlieren-Schlieren* textural change at the SmC-N transition: (1) the occurrence of the director change at the SmC-N transition, e.g. change in the molecular axis direction from pseudo-homeotropic

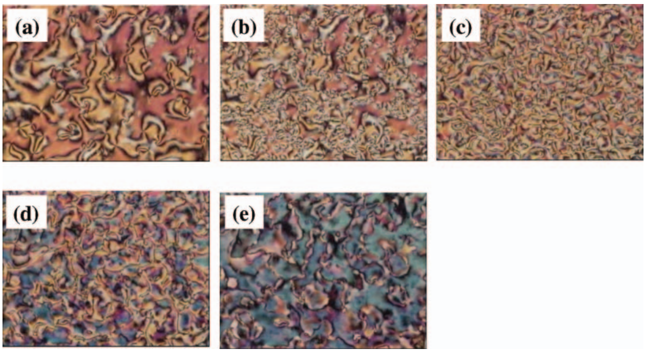

Figure 6. Textural changes at the SmC-N transition of Compound (**I**) on heating: (a) 162.0°C (SmC), (b) 162.1°C (SmC), (c) 162.2°C (SmC-N transition), (d) 162.3°C (N), and (e) 162.5°C (N).

to planar or molecular tilting in a certain portion of the sample, and (2) the emergence of biaxiality in the N phase[13].

The apparent biaxiality is produced even in the vertically aligned nematic sample if a part of the molecules tilts with respect to the normal to the substrates. In order to reduce the tendency of undesirable tilting of the molecules, free-standing films of the Compound (**I**) have been made and the textural change at the SmC-N phase transition observed. Air is known to produce a strong vertical anchoring to the liquid crystal molecules at the air-liquid crystal interface. Figure 7 shows the textural change of the free-standing film of the Compound (**I**), in which the *Schlieren-Schlieren* textural change, same as observed for the sandwiched sample between glass plates, is observed (see Fig. 7 (b)).

The textural observation was also made in the cooling process for the nematic phase of the free-standing film sample of Compound (**I**). The N phase shows a typical homeotropic texture as shown in Fig. 8(a). On further cooling, the *Schlieren* texture gradually appears even in the N phase (Fig. 8 (b)), which becomes clear on further cooling (Fig. 8 (c)). The appearance of the *Schlieren* texture is not resulted from the phase transition to the SmC phase, because the *Schlieren* texture shown in Fig. 8 (c) again changes into the other *Schlieren* texture of the SmC phase on further cooling.

These results on the textural change suggest a possibility of the emergence of the biaxial N phase in Compound (**I**). If this is the case, the homeotropic texture (Fig. 8 (a)) indicates the usual uniaxial N phase, whereas the *Schlieren* texture (Fig. 8 (b) and (c)) is produced

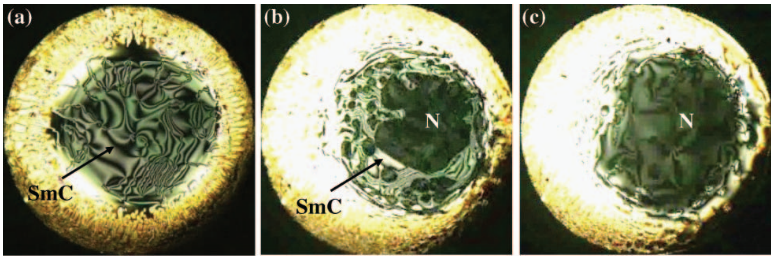

Figure 7. Textural changes at the SmC-N transition observed on heating, for the free-standing film sample of Compound (**I**): (a) a *Schlieren* texture of the SmC, (b) coexistence of two *Schlieren* textures of the SmC and N at the SmC-N phase transition, and (c) a *Schlieren* texture of the N.

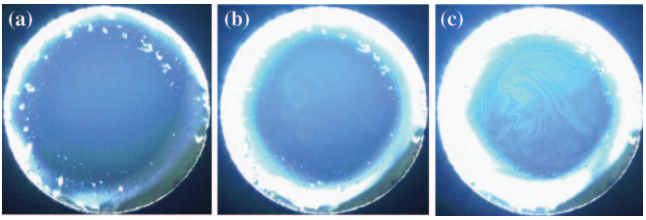

Figure 8. Textural changes in the N on cooling, for the free-standing film sample of Compound (**I**): (a) a *Schlieren* texture of the N, (b) gradual appearance of the *Schlieren* textures on cooling from (a), and (c) a *Schlieren* texture of the N in the lower temperature region.

by the biaxiality of the N phase. A possible uniaxial-biaxial phase transition was tried to be detected by the thermal study. However, no additional peak appears, corresponding the biaxial-uniaxial transition in the N phase (Fig. 9). This may be because the transition is second order in nature or two DSC peaks with respect to the SmC-N and the uniaxial-biaxial phase are too close to be separated.

Layer spacing of Compound (**I**) is calculated from the position of the X-ray diffraction peak at the small angle region, which is shown in Fig. 10, together with the amplitude of the diffraction.

The molecular length of Compound (**I**) in the *cisoid*, i.e., the molecular configuration shown in Fig. 4 (b) or Fig. 5, is estimated to be c.a. 30 Å, which well corresponds to the obtained layer spacing that is smaller value than the estimation due to the tilt in the SmC phase. The molecules have a tendency to form *cisoid* also in the nematic phase, which is suggested by the position of the weak x-ray diffraction in the small angle region. Thus, Compound (**I**) are expected to possess board-like molecular configuration of *cisoid* in the N phase, which makes molecular biaxiality larger.

A free-standing film of Compound (**I**) exhibits that a normal homeotorpic texture of the N phase changes into the "*Schlieren*" texture on cooling even in the lower temperature region of the N phase, which shows, on further cooling, the other "*Schlieren-Schlieren*" textural change at the N-SmC phase transition. The lower temperature range of the N phase

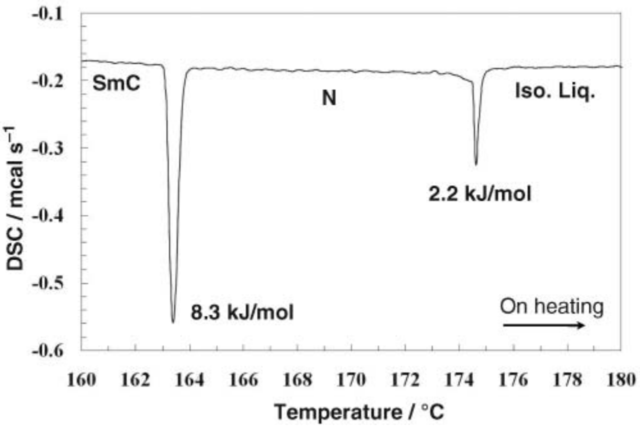

Figure 9. DSC chart of Compound (**I**) measured on heating, in which two DSC peaks appear corresponding to the SmC-N and the N-Iso.Liq. phase transitions, respectively.

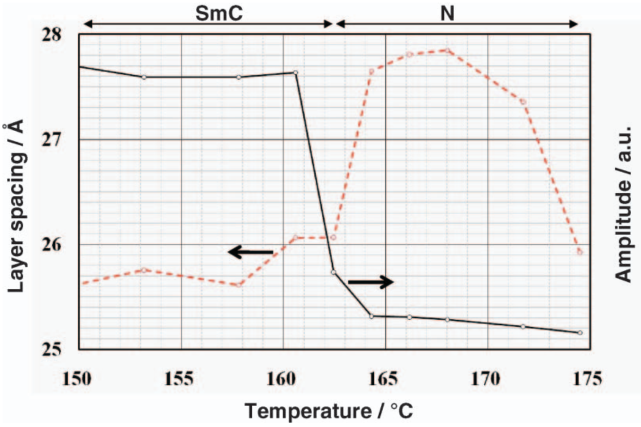

Figure 10. Layer spacing calculated from the position of the X-ray diffraction peak at the small angle region and the amplitude of the diffraction as a function of temperature, for Compound (**I**).

thus exhibits a "biaxial" nature. One possible reason for the appearance of the biaxiality is the emergence of the biaxial N phase. The other possibilities, however, e.g., the tilt of the molecules, cannot be completely ruled out at this stage of work. Further analyses of the molecular organization and alignment of the free-standing film sample of Compound (**I**) are now in progress.

References

[1] I. Saez and J. W. Goodby, "Supermolecular liquid crystals", *J. Mater. Chem.*, 2005, **15**, 26–40.
[2] I. Nishiyama, "Remarkable effect of pre-organization on the self assembly in chiral liquid crystals", *The Chemical Record*, 2009, **9**, 340–355.
[3] A. Yoshizawa, "Unconventional liquid crystal oligomers with a hierarchical structure", *J. Mater. Chem.*, 2008, **18**, 2877–2889.
[4] I. Nishiyama, J. Yamamoto, J.W. Goodby and H. Yokoyama, "Chiral Smectics: Molecular Design and Superstructures", *Mol. Cryst. Liq. Cryst.*, 2005, **443**, 25–41.
[5] J. Yamamoto, I. Nishiyama, M. Inoue and H. Yokoyama, "Optical isotropy and iridescence in a smectic 'blue phase'", *Nature*, 2005, **437**, 525–528.
[6] I. Nishiyama, J. Yamamoto, J.W. Goodby and H. Yokoyama, "A symmetric chiral liquid-crystalline twin exhibiting stable ferrielectric and antiferroelectric phases and a chirality-induced isotropic-isotropic liquid transition", *J. Mater. Chem.*, 2001, **11**, 2690–2693.
[7] Y. Suzuki, T. Isozaki, T. Kusumoto and T. Hiyama, "Synthesis and properties of dimeric antiferroelectric liquid crystals", *Chem. Lett.*, 1995, 719; Y. Suzuki, T. Isozaki, S. Hashimoto, T. Kusumoto, T. Hiyama, Y. Takanishi, H. Takezoe and A. Fukuda, "Stability of the antiferroelectric phase in dimeric liquid crystals having two chiral centres with CF3 or CH3 groups; evaluation of conformational and electric interactions", J. Mater. Chem., 1996, 6, 753.
[8] E-J. Choi *et al.* , *Bull. Korean Chem. Soc.*, "Dimesogenic Compounds with Chiral Tails: Synthesis and Liquid Crystalline Properties of a Homologous Series of α,ω-Bis[4-(4'-(S)-(-)-2-methylbutoxycarbonylbiphenyl-4-oxycarbonyl)phenoxy]alkanes", 2000, **21**, 110–117.
[9] I. Nishiyama, J. Yamamoto, J.W. Goodby and H. Yokoyama "Novel non-symmetric chiral twin liquid crystals possessing two identical chiral moieties at both peripheral ends: highly chirality-sensitive phases appeared between smectic and isotropic liquid phases", *J. Mater. Chem.*, 2002, **12**, 1709–1716.
[10] I. Nishiyama, J. Yamamoto, J.W. Goodby and H. Yokoyama, "Novel chiral effects on the molecular organization in the liquid-crystalline phases", *Chem. Mater.*, 2004, **16**, 3213–3214.

[11] I. Nishiyama, J. Yamamoto, J.W. Goodby and H. Yokoyama “Liquid crystal trimer showing stable anticlinic structures in smectic C and I phases”, *J. Mater. Chem.*, 2003, **13**, 2429–2435.

[12] I. Nishiyama, J. Yamamoto, J.W. Goodby and H. Yokoyama, “Chirality-induced liquid-crystalline nano-structures and their properties”, *Proc. of SPIE*, 2004, **5518**, 201–210.

[13] L. A. Madsen, T. J. Dingemans, M. Nakata, and E.T. Samulski, “Thermotropic Biaxial Nematic Liquid Crystals”, *Phys. Rev. Lett.*, 2004, **92**, 145505-1-145505-4.