

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

The role of a liquid crystal oligomer in stabilizing blue phases

Atsushi Yoshizawa^a; Hirotochi Iwamochi^a; Shinpei Segawa^a; Masatada Sato^a

^a Department of Frontier Materials Chemistry, Faculty of Science and Technology, Hirosaki University, Hirosaki 036-8561, Japan

To cite this Article Yoshizawa, Atsushi, Iwamochi, Hirotochi, Segawa, Shinpei and Sato, Masatada(2007) 'The role of a liquid crystal oligomer in stabilizing blue phases', *Liquid Crystals*, 34: 9, 1039 – 1044

To link to this Article: DOI: 10.1080/02678290701565867

URL: <http://dx.doi.org/10.1080/02678290701565867>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

The role of a liquid crystal oligomer in stabilizing blue phases

ATSUSHI YOSHIKAWA*, HIROTOSHI IWAMOCCHI, SHINPEI SEGAWA and MASATADA SATO

Department of Frontier Materials Chemistry, Faculty of Science and Technology, Hirosaki University,
3 Bunkyo-cho, Hirosaki 036-8561, Japan

(Received 22 May 2007; accepted 1 July 2007)

A novel liquid crystal oligomer, 4-(4-cyanophenyl)phenyl 4-octyloxy-2-{7-[4-[4-(4-hexylphenyl)-2,3-difluorophenyl]phenoxy]heptanoyloxy}benzoate, was prepared and found to exhibit a wide temperature range of a nematic phase in spite of being far from a rod-like structure. Furthermore, the compound induced blue phases in the mixture with a chiral smectic liquid crystal. The molecular shape and its 2,3-difluorophenyl unit play a role in stabilizing the blue phases.

1. Introduction

Blue phases are of particular interest because they have a fluid lattice, the structure of which is stabilized by lattice defects. They are believed to consist of a double twist cylinder, so are classified into three categories depending on packing structure of double twist cylinder, i.e. blue phase I (BPI), blue phase II (BPII) and blue phase III (BPIII) [1–4]. The packing structure of BPI is bcc and BPII has a simple cubic structure [5, 6]. On the other hand, theoretical insights have revealed that BPIII and the isotropic phase have the same symmetry [7]. It can be expected that BPIII consists of double twist cylinders with arbitrary orientation [5, 8, 9]. Usually, blue phases are found in a very narrow temperature range (~1 K) between the isotropic liquid (I) and the chiral nematic (N*) phase of a compound of sufficiently short pitch. Blue phases have potential applications as fast light modulators or tunable photonic crystals, but their narrow temperature range is a critical problem. Therefore, stabilizing the blue phases has attracted much attention [10–14]. Recently, Coles and Pivnenko reported that mixtures composed of several dimesogenic compounds containing fluorine atoms and a chiral additive show a wide temperature range of BPI [15].

We report here the molecular design of a host nematic liquid crystal for stabilizing the blue phases. Supermolecular liquid-crystalline materials in which several mesogenic units are organized in a single molecule are current topics in the design of self-assembly systems. We designed a new liquid crystal oligomer in which a mesogenic molecule possessing a

terminal cyano group and a mesogenic molecule possessing lateral fluorine atoms are connected via a flexible spacer. The newly prepared compound was found to show an enantiotropic nematic phase with a wide temperature range. Furthermore, mixtures of the compound and a chiral smectic liquid crystal exhibited blue phases. We discuss oligomeric effects of the host nematic liquid crystal on stabilizing the blue phases.

2. Experimental

2.1. Preparation of materials

4-(4-Hexylphenyl)-1-(4-hydroxyphenyl)-2,3-difluorobenzene was obtained from Midori Kagaku Co., Ltd. A chiral smectic liquid crystal, (*S*)-4-(1-methyl)heptyloxycarbonylphenyl 4-hexyloxybenzoate (**S811**), was obtained from Merck Co., Ltd.

2.1.1. 2-Hydroxy-4-octyloxybenzoic acid. To a solution of 2,4-dihydroxybenzoic acid (15.0 g, 100 mmol) and 1-bromooctane (20.7 g, 106 mmol) in ethanol (140 ml) was added a solution of KOH (21 g, 3.9 mol) in water (80 ml). The mixture was stirred under reflux for 9 h. After the solvent was removed, the residue was acidified with 2M of aq. HCl (160 ml). The solution was extracted with diethyl ether (3 × 100 ml). The organic layers were combined, dried over anhydrous magnesium sulfate, filtered and evaporated. Recrystallization from ethanol gave the desired compound; yield 2.52 g (9%); m.p. 35°C. ¹H NMR (500 MHz, solvent CDCl₃, standard TMS) δ_H/ppm: 10.64 (s, 1H, Ar-COOH), 7.81 (d, 1H, Ar-H, *J*=8.6 Hz), 6.49–6.44 (m, 2H, Ar-H), 3.99 (t, 2H, -O-CH₂-, *J*=6.6 Hz), 1.82–1.74 (m, 2H, -OCH₂-CH₂-), 1.48–1.29 (m, 10H, aliphatic), 0.89 (t, 3H, -CH₃, *J*=6.9 Hz). IR (KBr) ν_{max}/cm⁻¹: 3141, 2929, 2855, 1675, 1621, 1249, 1152.

*Corresponding author. Email: ayoshiza@cc.hirosaki-u.ac.jp

2.1.2. 4-(4-Cyanophenyl)phenyl 2-hydroxy-4-octyloxybenzoate. To a solution of 2-hydroxy-4-octyloxybenzoic acid (1.3 g, 5.0 mmol) and 4-(4-cyanophenyl)phenol (0.98 g, 5.0 mmol) in dichloromethane (30 ml), *N,N*-dicyclohexylcarbodiimide (1.0 g, 5.0 mmol) and 4-(*N,N*-dimethylamino)pyridine (0.061 g, 0.05 mmol) were added. The resulting solution was stirred at room temperature for 24 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified by recrystallization from ethanol to give desired compound; yield 0.84 g (38%); m.p. 107°C. ¹H NMR (500 MHz, solvent CDCl₃, standard TMS) δ_H/ppm: 10.62 (s, 1H, Ar-OH), 7.98 (d, 1H, Ar-H, *J*=9.2 Hz), 7.75 (d, 2H, Ar-H, *J*=8.6 Hz), 7.69 (d, 2H, Ar-H, *J*=8.6 Hz), 7.66 (d, 2H, Ar-H, *J*=8.6 Hz), 7.33 (d, 2H, Ar-H, *J*=8.6 Hz), 6.53 (dd, 1H, Ar-H, *J*=2.6, 8.9 Hz), 6.50 (d, 1H, Ar-H, *J*=2.3 Hz), 4.02 (t, 2H, -O-CH₂-, *J*=6.6 Hz), 1.84–1.79 (m, 2H, -OCH₂-CH₂-), 1.47–1.30 (m, 10H, aliphatic), 0.90 (t, 3H, -CH₃, *J*=6.9 Hz). IR (KBr) ν_{max}/cm⁻¹: 3262, 2920, 2850, 2225, 1678, 1619, 1248, 1198.

2.1.3. Ethyl 7-{4-[4-(4-hexylphenyl)-2,3-difluorophenyl]phenyloxy}heptanoate. Potassium carbonate (0.83 g, 6.0 mmol) was added to a solution of 4-(4-hexylphenyl)-1-(4-hydroxyphenyl)-2,3-difluorobenzene (2.2 g, 6.0 mmol) and ethyl 7-bromoheptanoate (1.3 g, 6.0 mmol) in cyclohexanone (20 ml). The reaction mixture was stirred under reflux for 9 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a toluene/ethyl acetate (9/1) mixture to give the desired compound; yield 1.8 g (60%); m.p. 128°C. ¹H NMR (500 MHz, solvent CDCl₃, standard TMS) δ_H/ppm: 7.52 (d, 2H, Ar-H, *J*=8.6 Hz), 7.50 (d, 2H, Ar-H, *J*=8.8 Hz), 7.28 (d, 2H, Ar-H, *J*=8.0 Hz), 7.25–7.20 (m, 2H, Ar-H), 6.98 (d, 2H, Ar-H, *J*=8.6 Hz), 4.16–4.11 (q, 2H, -COO-CH₂-, *J*=7.1 Hz), 4.01 (t, 2H, -O-CH₂-, *J*=6.6 Hz), 2.66 (t, 2H, Ar-CH₂-, *J*=7.7 Hz), 2.32 (t, 2H, -OC-CH₂-, *J*=7.4 Hz), 1.85–1.30 (m, 16H, aliphatic), 1.26 (t, 3H, -COOCH₂-CH₃, *J*=7.2 Hz), 0.90 (t, 3H, -CH₃, *J*=7.2 Hz). IR (KBr) ν_{max}/cm⁻¹: 2955, 2922, 1713, 1457, 1248, 1184.

2.1.4. 7-{4-[4-(4-Hexylphenyl)-2,3-difluorophenyl]phenyloxy}heptanoic acid. Ethyl 7-{4-[4-(4-hexylphenyl)-2,3-difluorophenyl]phenyloxy}heptanoate (1.5 g, 2.9 mmol) was added to a solution of KOH (0.43 g, 8.0 mmol) in an ethanol/water (3/1) mixture. The resulting solution was stirred under reflux for 4 h. After removal of the ethanol by evaporation, the residue was acidified with aq. HCl. The solution was extracted with

dichloromethane. The organic layers were combined, dried over anhydrous magnesium sulfate, filtered and evaporated. The desired compound was obtained; yield: 0.79 g (57%); m.p. 71°C. ¹H NMR (500 MHz, solvent CDCl₃, standard TMS) δ_H/ppm: 7.52 (d, 2H, Ar-H, *J*=8.6 Hz), 7.50 (d, 2H, Ar-H, *J*=8.6 Hz), 7.28 (d, 2H, Ar-H, *J*=8.1 Hz), 7.25–7.20 (m, 2H, Ar-H), 6.99 (d, 2H, Ar-H, *J*=8.6 Hz), 4.02 (t, 2H, -OCH₂-, *J*=6.3 Hz), 2.66 (t, 2H, Ar-CH₂-, *J*=7.8 Hz), 2.39 (t, 2H, -OC-CH₂-, *J*=7.5 Hz), 1.86–1.26 (m, 16H, aliphatic), 0.90 (t, 3H, -CH₃, *J*=7.2 Hz). IR (KBr) ν_{max}/cm⁻¹: 2927, 2856, 1733, 1459, 1252, 1180.

2.1.5. 4-(4-Cyanophenyl)phenyl 4-octyloxy-2-{7-[4-[4-(4-hexylphenyl)-2,3-difluorophenyl]phenyloxy}heptanoxy}benzoate (1). To a solution of 7-{4-[4-(4-hexylphenyl)-2,3-difluorophenyl]phenyloxy}heptanoic acid (0.38 g, 0.8 mmol) and 4-(4-cyanophenyl)phenyl 2-hydroxy-4-octyloxybenzoate (0.35 g, 0.8 mmol) in dichloromethane (12 ml), *N,N*-dicyclohexylcarbodiimide (0.17 g, 0.8 mmol) and 4-(*N,N*-dimethylamino)pyridine (0.01 g, 0.08 mmol) were added. The resulting solution was stirred at room temperature for 24 h. Precipitated materials were removed by filtration. After removal of the solvent by evaporation, the residue was purified by column chromatography on silica gel with a dichloromethane/hexane (9/1) mixture. Recrystallization from ethanol gave the final compound; yield 0.37 g (51%). ¹H NMR (400 MHz, solvent CDCl₃, standard TMS) δ_H/ppm: 8.18 (d, 1H, Ar-H, *J*=8.8 Hz), 7.71 (d, 2H, Ar-H, *J*=8.3 Hz), 7.66 (d, 2H, Ar-H, *J*=8.8 Hz), 7.62 (d, 2H, Ar-H, *J*=8.8 Hz), 7.51–7.48 (m, 4H, Ar-H), 7.29–7.27 (m, 4H, Ar-H), 7.23–7.20 (m, 2H, Ar-H), 6.95 (d, 2H, Ar-H, *J*=8.8 Hz), 6.88 (dd, 1H, Ar-H, *J*=2.4, 8.8 Hz), 6.66 (d, 1H, Ar-H, *J*=2.4 Hz), 4.04 (t, 2H, Ar-OCH₂-, *J*=6.6 Hz), 3.97 (t, 2H, Ar-OCH₂-, *J*=6.6 Hz), 2.66 (t, 2H, Ar-CH₂-, *J*=7.8 Hz), 2.63 (t, 2H, -OCOCH₂-, *J*=7.6 Hz), 1.85–1.24 (m, 28H, aliphatic), 0.90 (t, 6H, -CH₃, *J*=6.3 Hz). IR (KBr) ν_{max}/cm⁻¹: 2928, 2856, 2227, 1756, 1732, 1611, 1259, 1125.

2.2. Physical properties

The initial assignments and corresponding transition temperatures for the final product and its mixtures were determined by thermal optical microscopy using a polarizing optical microscope (Olympus BX-51) equipped with a temperature control unit (Japan High Tech LK-600PM). The heating and cooling rates were 0.1°C min⁻¹. Temperatures and enthalpies of transition for the final product and the intermediate compounds were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200 calorimeter. Heating and cooling rates were 5°C min⁻¹, after encapsulation in aluminium pans. The helical pitch in the N* phase was

measured by the Cano wedge technique for a chiral nematic mixture consisting of each host nematic liquid-crystalline material and 2 wt % of a chiral additive.

3. Results and discussion

3.1. Synthesis

We designed a new liquid crystal oligomer, 4-(4-cyanophenyl)phenyl 4-octyloxy-2- $\{7-\{4-[4-(4\text{-hexylphenyl})-2,3\text{-difluorophenyl}]phenoxy\}$ heptanoyloxy} benzoate (**1**), the molecular structure of which is shown in figure 1. Compound **1** was prepared by the synthesis outlined in scheme 1. Purification of the final product was carried out using column chromatography over silica gel with a dichloromethane/hexane (9/1) mixture as the eluent, followed by the recrystallization from ethanol. The structure was elucidated using IR and ^1H NMR measurements.

3.2. Phase transition properties

Temperatures and enthalpies of transition for compound **1** were I 150°C (2.1 kJ mol $^{-1}$) N -12.6°C glass on cooling and the melting temperature was 71°C. Compound **1** exhibited a wide temperature range of the nematic phase in spite of being far from a rod-like structure. Although we have not determined the real molecular structure in the N phase, a λ -shaped structure is probably favoured on the basis of the more elongated shape, which is more compatible with a nematic phase than a T-shaped structure.

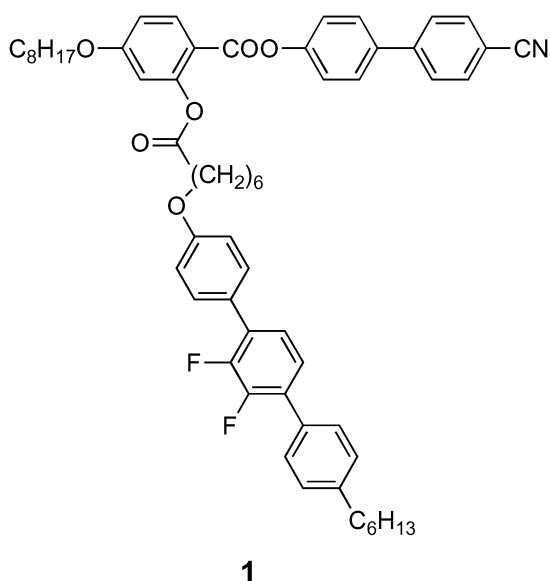


Figure 1. Molecular structure of compound **1**.

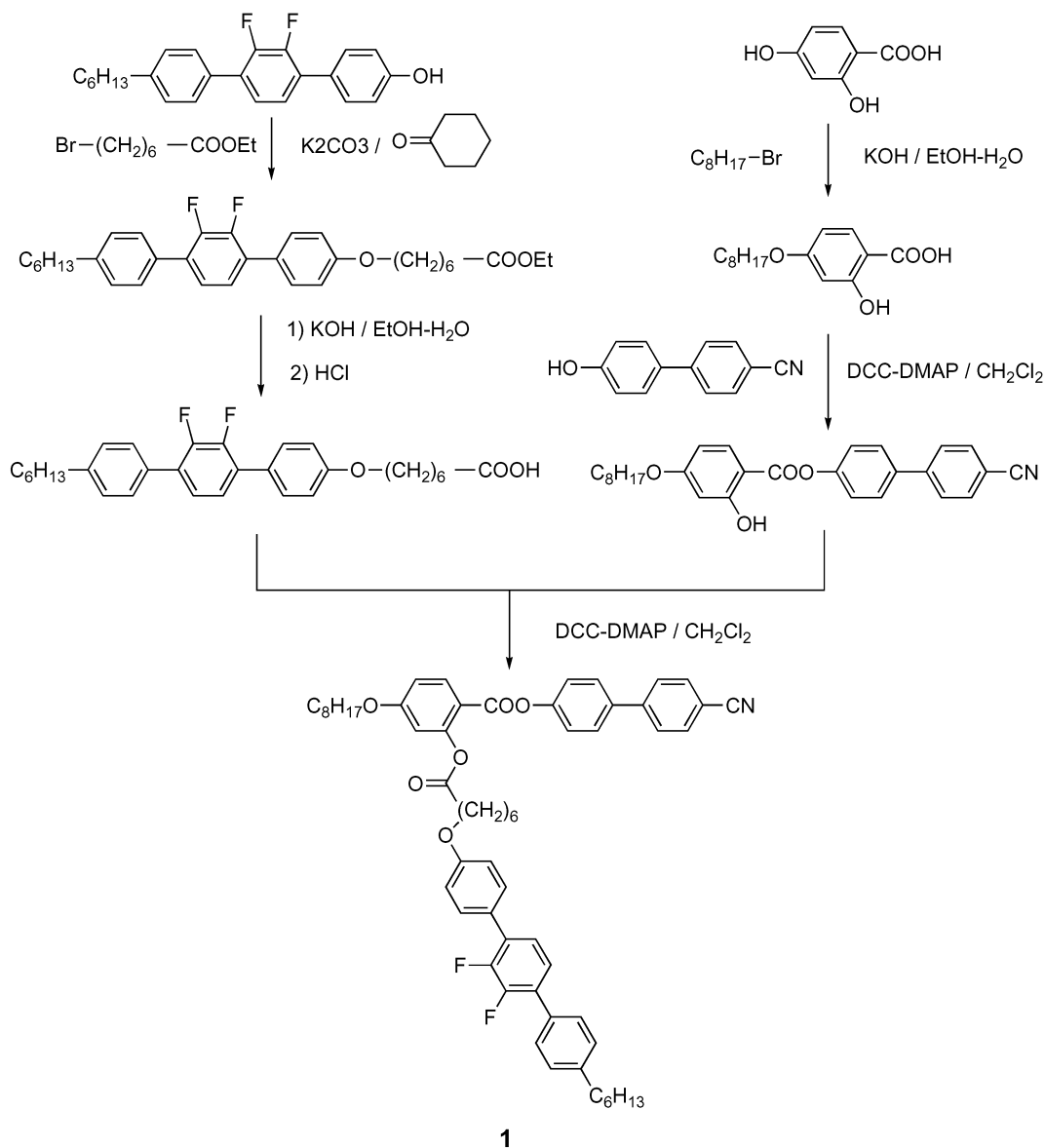
3.3. Miscibility studies

We investigated transition behaviour of binary mixtures of compound **1** and a chiral smectic liquid crystal (**S811**). The molecular structure and transition temperatures of **S811** are shown in figure 2. **S811** is a conventional rod-like chiral liquid crystal with moderate twisting power.

Figure 3 shows the binary phase diagram between **S811** and compound **1**. For mixtures containing 30–60 wt % of **S811**, blue phases were found to be induced. In a mixture of **S811** (40 wt %) and compound **1** (60 wt %), a platelet texture with various colours appeared at 70.2°C, and then it changed to a typical N* texture at 65.1°C. The platelet texture without fine strips (figure 4a) is characteristic of BPII, therefore we assigned the blue phase as BPII. On heating, the N* phase changed to BPII reversibly. In a mixture of **S811** (45 wt %) and compound **1** (55 wt %), a blue colour of low birefringence appeared at 65.7°C. The blue colour phase was clearly observed in uncovered regions of the mixture. The blue phase showed fluidity and did not appear as platelets. These observations indicate that the phase is amorphous BPIII. The blue colour changed to a platelet texture at 65.0°C, which is attributed to a phase transition from amorphous BPIII to cubic BPII. On further cooling, the BPII changed to an N* phase at 56.6°C. The temperature range of the blue phases was over 9 K in the mixture. On heating, the N* phase changed to BPIII at 63.5°C, and then it changed to liquid at 65.7°C. The BPII was not observed on heating. In a mixture of **S811** (50 wt %) and compound **1** (50 wt %), isotropic liquid changed to BPIII at 49.3°C. The blue colour texture at 42.0°C is shown in figure 4b. The BPIII changed to an N* phase at 41.2°C. The BPIII–N* phase transition is reversible; however, the BPIII and N* phase are both monotropic.

For comparison, we then investigated the effects of monomeric molecules, i.e. compounds **2** and **3**, on stabilizing the blue phases. The molecular structures and transition temperatures of the compounds are shown in figure 5.

Figure 6a shows the binary phase diagram between **S811** and compound **2**. For mixtures containing 30–40 wt % of **S811**, the cubic BPII was found to be induced. In a mixture of **S811** (30 wt %) and compound **2** (70 wt %), a platelet texture appeared from the liquid at 102.2°C. The BPII changed to an N* phase at 97.6°C. On further cooling, a filament texture characteristic to a twist grain boundary (TGBA) phase appeared at 64.0°C and then it changed to a SmA phase at 62.7°C. BPII and TGBA phases were found to be induced in the binary system; however, BPIII was not observed.



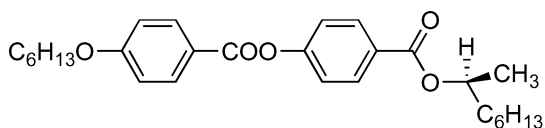
Scheme 1. Synthesis of compound 1.

Figure 6b shows the binary phase diagram between **S811** and compound **3**. A blue phase was not observed in the binary system. With respect to stability of an N^* phase in a binary system between **S811** and each host material, there is marked difference between compound **1** and the corresponding monomeric compounds. In the binary system of **S811** and compound **1**, the N^* phase appeared in the mixtures containing at least above 30 wt % of compound **1**. On the other hand, in the binary system of **S811** and compound **2**, and in that of **S811** and compound **3**, the N^* phase appeared in the mixtures containing above 60 wt % of each monomeric compound. These results indicate that the λ -shaped

structure of compound **1** destabilizes formation of the smectic layer structures.

3.4. Pitch measurements

We investigated twisting power induced by **S811** in each host nematic materials. We observed helical pitch at $T_{I-N^*} - 5^\circ\text{C}$ in the N^* phase for a mixture consisting of each host compounds and 2 wt % of **S811**. The helical pitch value for compound **1** was $2\ \mu\text{m}$. The pitch values for compounds **2** and **3** were $5\ \mu\text{m}$ and $7\ \mu\text{m}$, respectively. Significant host-dependency can be seen for the helical pitches. The oligomer **1** that stabilizes both cubic BP and amorphous BPIII has the shortest pitch among them. The



S811: Cr 41 [SmA 22] I

Figure 2. Molecular structure and transition temperatures ($^{\circ}\text{C}$) of **S811**.

nonlinear shape of compound **1** is thought to induce the short pitch as compared to compounds **2** and **3**.

3.5. Stabilizing the blue phases

The cubic BPII was observed in binary mixtures of **S811** and compound **1**, and in those of **S811** and compound

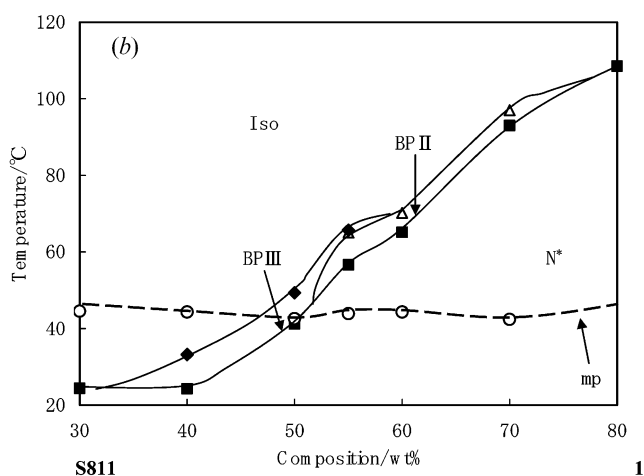
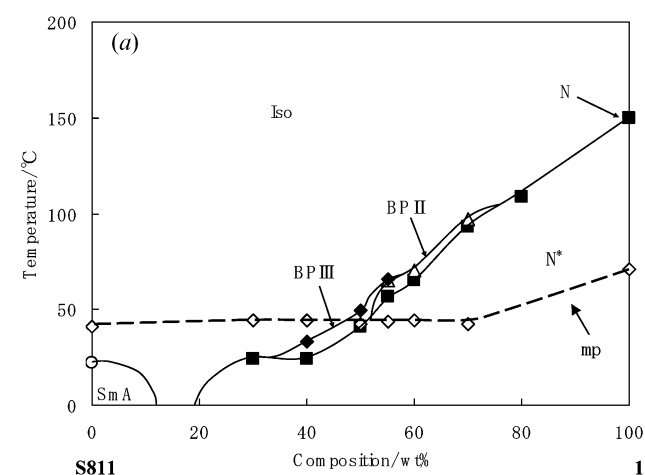


Figure 3. (a) Phase diagram between **S811** and compound **1** on cooling. The dotted line indicates melting temperatures. (b) The expansion of the region where the blue phases are present. (I= isotropic liquid; N= nematic phase; N*= chiral nematic phase; BPII= cubic blue phase II; BPIII= amorphous blue phase III, SmA= smectic A phase; m.p.= melting point).

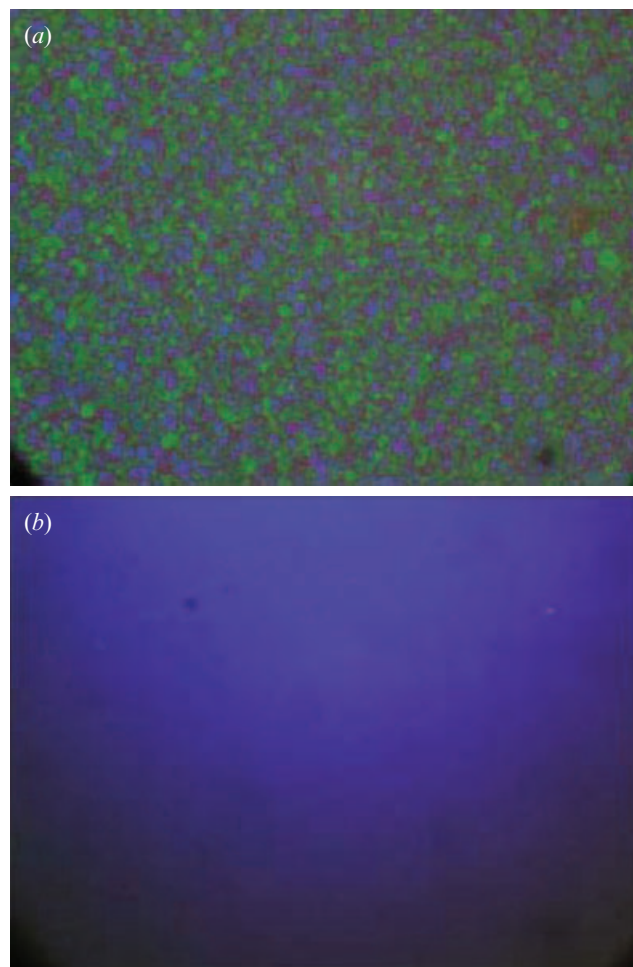


Figure 4. (a) Photomicrograph of the cubic BPII at 67°C in a mixture consisting of 40wt % of **S811** and 60wt % of compound **1**, and (b) photomicrograph of the BPIII at 42°C in a mixture consisting of 50wt % of **S811** and 50wt % of compound **1**.

2, indicating that the 1,4-bisphenyl-2,3-difluorobenzene group contributes to the appearance of the cubic BP. Amorphous BPIII was induced only in binary mixtures of **S811** and compound **1**. The λ -shaped structure of compound **1** is thought to play an important role in stabilizing BPIII, which is consistent with T-shaped chiral compound stabilizing the BPIII [13].

Theoretical studies have demonstrated that the blue phases can be stabilized by the increase of chirality [16–

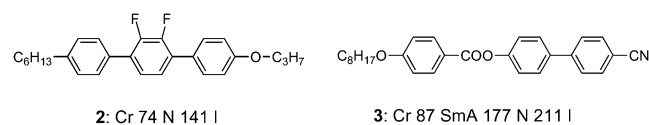


Figure 5. Molecular structures and transition temperatures ($^{\circ}\text{C}$) for the corresponding monomeric compounds.

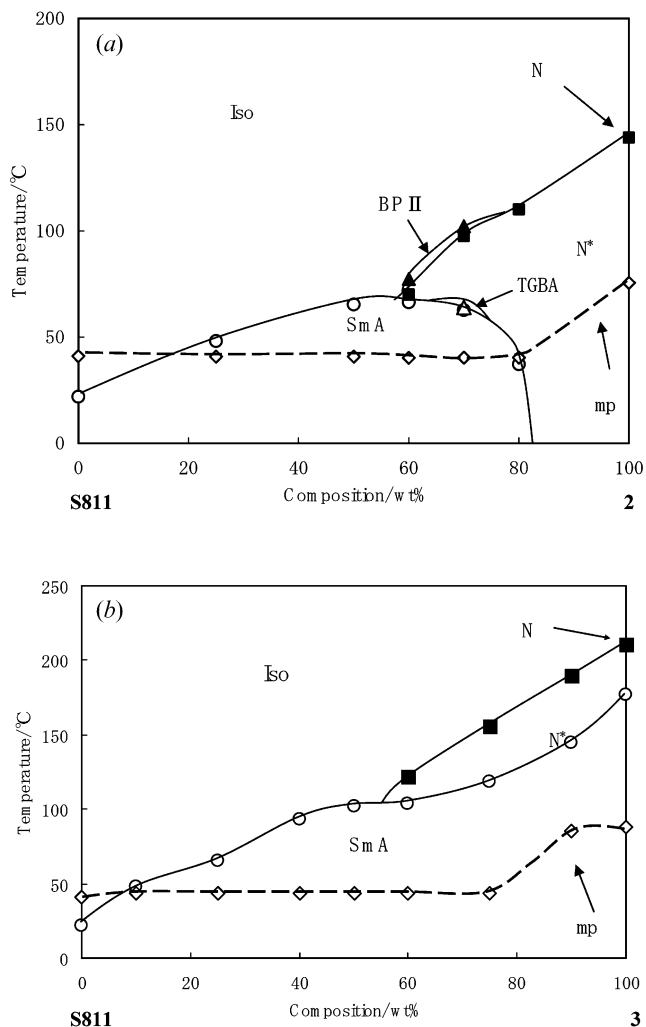


Figure 6. (a) Phase diagram between **S811** and compound **2**, and (b) that between **S811** and compound **3**, on cooling. The dotted lines indicate melting temperatures. (I= isotropic liquid; N= nematic phase; N*= chiral nematic phase; BPII= cubic blue phase II; SmA= smectic A phase; m.p.= melting point).

18] and/or the decrease of the surface elastic constant [19]. Recently, Alexander and Yeomans reported that the region of stability of the cubic blue phases is reduced when the bend elastic constant is larger than splay and when twist is smaller than the other two [20]. Therefore, induction of cubic BP and amorphous BPIII in binary mixtures of **S811** and compound **1** can result from: (i) the stronger chiral interaction between the chiral additive and the fluorine-containing host molecule; and (ii) the smaller bend elastic constant due to the λ -shaped structure of the host molecule, which decreases the free energy around the defects.

4. Conclusions

We prepared a novel liquid crystal oligomer in which two nematic liquid crystals are organized in a single molecule and found that the liquid crystal oligomer shows a wide temperature range of a nematic phase. The cubic BPII and amorphous BPIII were found to be induced in binary mixtures of the liquid crystal oligomer and a chiral smectic liquid crystal, and the temperature range of the blue phases was more than 9 K. The present finding could result in a new approach for the stabilization of blue phases.

Acknowledgements

This work was partly supported by a Grant for Priority Research Designated by the President of Hirosaki University and a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (No. 19550175).

References

- [1] P.G. de Gennes, J. Prost. *The Physics of Liquid Crystals*, second edn, Oxford University Press, London (1993).
- [2] D.C. Wright, N.D. Mermin. *Rev. Mod. Phys.*, **61**, 385 (1989).
- [3] P.P. Crooker. *Liq. Cryst.*, **5**, 751 (1989).
- [4] P.P. Crooker. In *Chirality in Liquid Crystals*, H.S. Kitzerow, C. Bahr (Eds), Chap. 7, p. 186, Springer, New York (2001).
- [5] H. Stegemeyer, T. Blumel, K. Hiltrop, H. Onusseit, F. Porsch. *Liq. Cryst.*, **1**, 3 (1986).
- [6] E. Dubois-Violette, B. Pansu. *Mol. Cryst. liq. Cryst.*, **165**, 151 (1988).
- [7] E.P. Koistinen, P.H. Keyes. *Phys. Rev. Lett.*, **74**, 4460 (1995).
- [8] H.-S. Kitzerow, P.P. Crooker. *Phys. Rev. Lett.*, **67**, 2151 (1991).
- [9] R.M. Hornreich. *Phys. Rev. Lett.*, **67**, 2155 (1991).
- [10] M. Nakata, Y. Takanishi, J. Watanabe, H. Takezoe. *Phys. Rev. E*, **68**, 041710 (2003).
- [11] A. Chanishvili, G. Chilaya, G. Petriashvili, P.J. Collings. *Phys. Rev. E*, **71**, 051705 (2005).
- [12] H. Kikuchi, M. Yokota, Y. Hisakado, H. Yang, T. Kajiyama. *Nature Mater.*, **1**, 111 (2002).
- [13] A. Yoshizawa, M. Sato, J. Rokunohe. *J. Mater. Chem.*, **15**, 3285 (2005).
- [14] H.-S. Kitzerow. *ChemPhysChem*, **7**, 63 (2006).
- [15] H.J. Coles, M.N. Pivnenko. *Nature*, **436**, 997 (2005).
- [16] V.A. Belyakow, V.E. Dmitrienko. *Usp. Fiz. Nauk*, **146**, 369 (1985).
- [17] T. Seideman. *Rep. Prog. Phys.*, **53**, 659 (1990).
- [18] R.M. Hornreich, S. Shtrikman. *Mol. Cryst. liq. Cryst.*, **165**, 183 (1988).
- [19] J.P. Sethna. In *Theory and Applications of Liquid Crystals*, J.L. Ericksen, D. Kinderlehrer (Eds), p. 305, Springer-Verlag, New York (1987).
- [20] G.P. Alexander, J.M. Yeomans. *Phys. Rev. E*, **74**, 061706 (2006).