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Helical Twisting Power Dependence of Blue Phase Stability for Chiral Nematic Liquid Crystal

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In this study, we investigated blue phase (BP) temperature range and helical twisting power (HTP) using various types of chiral nematic liquid crystal (LC) mixtures composed of two kinds of chiral dopants and four kinds of host nematic LCs with different core structures. We found that chiral nematic LC mixtures containing three-ring core structure host nematic LCs such as 5CCB and 5CT presented small HTP values compared to those containing two-ring core structure host nematic LCs such as 5CB and 5CH regardless of chiral dopant species. We also found that the BP was not present when the HTP was of a magnitude less than $35.64 \mu\text{m}^{-1}$, that the BP temperature range increased when the HTP was of a magnitude between 35.64 – $49.03 \mu\text{m}^{-1}$, and that it decreased when the HTP was of a magnitude between 51.60 – $63.03 \mu\text{m}^{-1}$ in cyano homologue chiral LC nematic LC mixtures.

Keywords Blue Phase; Chiral Nematic Liquid Crystal; Temperature Range; Chiral Dopant; Helical Twisting Power

1. Introduction

Blue phases (BPs) are liquid crystal (LC) phases that appear in the temperature range between the chiral nematic phase and isotropic liquid phase for a chiral nematic LC under high chirality condition. Also, smectic BPs which the smectic planes are strongly folded and stabilized by a high negative value of the saddle-splay elastic constant K_{24} are reported by DiDonna and Kamien[1-2]. In general, BPs consist of a double-twist cylinder and show three phases—blue phase I (BP I), blue phase II (BP II), and blue phase III (BP III)—as functions of temperature and chirality. BP I and BP II possess a three-dimensional cubic structure with lattice periods of several hundred nanometers in length [3–6] and therefore exhibit selective Bragg reflections in visible and ultraviolet (UV) light. Furthermore, BPs present very fast electro-optic response times of less than 1 ms due to the Kerr effect upon an applied electric field [7]. Therefore, BPs can be applied to high-performance optical devices [8–11], and it is possible to fabricate a

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low-cost, high-performance LC display without optical compensation film and surface alignment of the LC, since BPs are optically isotropic in the absence of an external electric field.

However, due to their narrow temperature range (typically less than a few degrees), the practical application of BPs has always been difficult. Recently, the polymer-stabilized blue phase (PS-BP) with a wide temperature range (greater than 60 K), including room temperature, was reported as a high-performance optical switch with a high-speed electro-optic response time in the order of 10^{-4} s [12]. Moreover, Coles et al. and Yoshizawa et al. reported the wide temperature ranges of BPs on cooling processes using a symmetric dimer mixture doped with a highly twisting chiral dopant [13] and a T-shaped chiral LC [14], respectively. However, the relationship between BP temperature ranges and the chemical structures and physical properties of chiral nematic LCs has not yet been experimentally clarified. Furthermore, there have been few reports on the helical twisting power (HTP) dependence of BP stability in chiral LC mixtures. Thus far, it has been reported that BP temperature range is dependent upon the chemical structures and physical properties of host LCs and chiral dopants in chiral LCs composed of chiral dopants and host nematic LCs. For example, Takezoe et al. reported that a wide temperature range of BPs was obtained in mixtures containing chiral dopants with relatively small HTP values, whereas mixtures containing chiral dopants with high HTP values showed narrow BP temperature ranges in chiral molecules doped in a non-chiral bent-core LC [15]. Furthermore, Kim et al. reported that the BP temperature range decreased when the concentration of chiral dopant was increased with high HTP to keep the chiral pitch approximately the same [16]. However, the relationship between BP temperature range and HTP in chiral nematic LCs with rod-like host nematic LCs has not yet been clarified.

In this study, we investigated BP temperature range and HTP using various types of chiral nematic LC mixtures composed of two kinds of chiral dopants and four kinds of host nematic LCs with different core structures.

2. Experiments

2.1 Preparation of Chiral Nematic LC Mixtures

Four kinds of cyano LC-1s having different core groups but the same terminal group (e.g., cyano and pentyl) and JC-1041XX (LC-2; JNC Co. Ltd., Tokyo) were used as chiral nematic LC mixtures composed of host nematic LCs. ISO-(6OBA)₂ and ZLI-4572 (Merck & Co. Inc., Whitehouse Station, NJ, USA) were used as chiral dopants, as shown in [Fig. 1. Here, JC-1041XX was used to obtain stable BPs. The four kinds of cyano homologue LC-1s used were 4'-pentyl-4-biphenylcarbonitrile (5CB, Sigma-Aldrich Corp., St. Louis, MO, USA), 4-(trans-4-pentylcyclohexyl)benzonitrile (5CH, Sigma-Aldrich), trans-4-[4-(4-n-pentylcyclohexyl)phenyl]benzonitrile (5CCB, Alfa Aesar, MA, USA), and 4-cyano-4'-n-pentyl-p-terphenyl (5CT, Alfa Aesar).

Eight kinds of chiral nematic LC mixtures were prepared as 7.5 wt% chiral dopant dissolved in the host nematic LC-1 and LC-2, as listed in Table 1. Specifically, for Samples 1–4, ISO-(6OBA)₂ was used as the chiral dopant, whereas for Samples 5–8, ZLI-4572 was used. To maintain the thermal stability, 5CB with the lower $\Delta T_{BP \rightarrow Iso}$ was added to 5CCB and 5CT LC with the high $\Delta T_{BP \rightarrow Iso}$ (more than 423 K) as the half-weight ratio. Furthermore, in the case of 5CH, 5CB was added as the half-weight ratio to ensure identical conditions with 5CCB and 5CT.

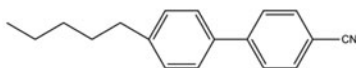
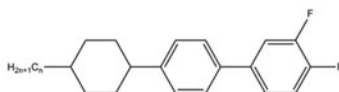
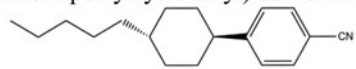
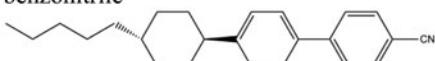
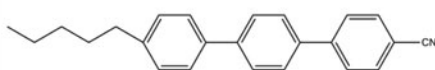
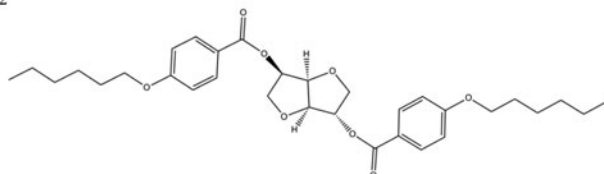
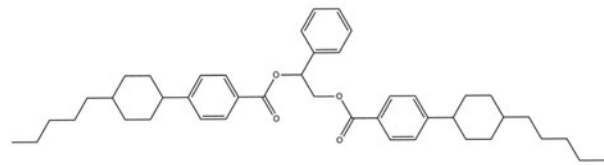
| Host nematic LC | |
|---|--|
| LC-1 | LC-2 |
| 1) 5CB 4'-pentyl-4-biphenylcarbonitrile  | 1) JC-1041XX K(Crystal)273~283 N(Nematic) 370 I(Isotropic) $\Delta n=0.142$  |
| 2) 5CH 4-(trans-4-pentylcyclohexyl) benzonitrile  | |
| 3) 5CCB trans-4-[4-(4-n-pentylcyclohexyl)phenyl] benzonitrile  | |
| 4) 5CT 4-cyano-4'-n-pentyl-p-terphenyl  | |
| Chiral dopant | |
| ISO-(6OBA) ₂  | |
| ZLI-4572  | |

Figure 1. Chemical structures of used host nematic LCs and chiral dopants.

2.2 Measurement of BP Temperature Range for Each Chiral Nematic Mixture

To measure the temperature range of BP, we used non-surface treatment sandwich-type glass cells with a gap of 10 μm . The vacant spaces of the cells were filled with Samples 1–8. The BP temperature range was evaluated based on the temperature dependence of the

Table 1. Chemical composition of eight kinds of chiral LC mixtures

| | LC-1 | | LC-2 | Chiral dopant |
|----------|--------------------|----------------|------------------------|------------------------------------|
| Sample 1 | 5CB 46.25 wt% | | | |
| Sample 2 | 5CB 23.125 wt% | 5CH 23.125 wt% | JC-1041XX 46.25 wt% | ISO-(6OBA) ₂ 7.5 wt% |
| Sample 3 | 5CCB 23.125 wt% | | | |
| Sample 4 | 5CT 23.125 wt% | | | |
| Sample 5 | 5CB 46.25 wt% | | | ZLI-4572 7.5 wt% |
| Sample 6 | 5CB 23.125 wt% | 5CH 23.125 wt% | | |
| Sample 7 | 5CCB 23.125 wt% | | | |
| Sample 8 | 5CT 23.125 wt% | | | |

optical texture changes observed by a polarizing optical microscope (POM, Nikon, Tokyo, Japan) under crossed Nicols. The temperature of each cell was precisely controlled with a hot stage that was calibrated to an accuracy of ± 0.1 K (Linkam LK-600PM). The cooling and heating ratio of the cell was set to 0.2 K/min.

2.3 Measurement of HTP for Each Chiral Nematic Mixture

The HTP corresponding to the molecular chirality was calculated based on the following equation: $HTP = 1 / (P \times C)$. Here, P is the chiral pitch and C is the weight concentration of the chiral dopant dissolved in the host nematic LCs. The chiral pitch of each chiral nematic LC was measured by observing the disclination line in the wedge cell with a $\tan\theta$ of 0.0078 by POM under crossed Nicols. In addition, C was 7.5 wt%, and the measurement temperature was $T_{BP \rightarrow Ch} - 0.5$ K.

3. Results and Discussion

3.1 HTP Values of Eight Kinds of Chiral Nematic LC Mixtures

Table 2 shows the HTP values of eight kinds of chiral nematic LC mixtures at $T_{BP \rightarrow Ch} - 0.5$ K. Table 2 reveals that Samples 1–4 containing ISO-(6OBA)₂ has large HTP values compared to Samples 5–8 containing ZLI-4572 in identical host nematic LC mixtures. Thus, ISO-(6OBA)₂ induced higher HTP values than ZLI-4572 in identical host nematic LCs. Furthermore, Samples 3, 4, 7, and 8 containing three-ring core structure host nematic LCs (e.g., 5CCB and 5CT) presented small HTP values compared to Samples 1, 2, 5, and 6 containing two-ring core structure host nematic LCs (e.g., 5CB and 5CH) regardless of chiral dopant species. Therefore, these results imply that the HTP values of chiral nematic LCs are decreased with an increase in the number of rings of the core structures in host nematic LCs. However, a clear relationship between HTP values and core structures in two-ring host nematic LCs (e.g., 5CB and 5CH) could not be found.

Table 2. HTP values for eight kinds of chiral nematic LC mixtures

| | LC mixture | HTP(μm^{-1}) |
|----------|--|---------------------------|
| Sample 1 | 5CB / JC-1041XX / ISO-(6OBA) ₂ | 59.25 \pm 0.17 |
| Sample 2 | (5CH/5CB) / JC-1041XX / ISO-(6OBA) ₂ | 63.03 \pm 0.18 |
| Sample 3 | (5CCB/5CB) / JC-1041XX / ISO-(6OBA) ₂ | 55.87 \pm 0.23 |
| Sample 4 | (5CT/5CB) / JC-1041XX / ISO-(6OBA) ₂ | 51.60 \pm 0.10 |
| Sample 5 | 5CB / JC-1041XX / ZLI-4572 | 49.03 \pm 0.10 |
| Sample 6 | (5CH/5CB) / JC-1041XX / ZLI-4572 | 44.88 \pm 0.11 |
| Sample 7 | (5CCB/5CB) / JC-1041XX / ZLI-4572 | 35.64 \pm 0.26 |
| Sample 8 | (5CT/5CB) / JC-1041XX / ZLI4-4572 | 33.99 \pm 0.09 |

3.2 BP Temperature Range of Chiral Nematic Mixtures with Various Types of Chiral Dopants and Host Nematic LCs

Table 3 shows the phase transition temperature and BP temperature range (ΔT_{BP}) of four chiral nematic LC mixtures containing ISO-(6OBA)₂ on heating and cooling. Samples 3 and 4 containing three-ring core structure compounds (e.g., 5CCB and 5CT) presented a wide ΔT_{BP} compared to Samples 1 and 2 containing two-ring core structure compounds (e.g., 5CB and 5CH) on heating and cooling.

Table 4 shows the phase transition temperature and ΔT_{BP} of four chiral nematic LC mixtures containing ZLI-4572 on heating and cooling. For Samples 5 and 6 containing 5CB and 5CH, ΔT_{BP} was 0.5–0.7 K on heating and 0.8–1.3 K on cooling, but for Samples 7 and 8 containing 5CCB and 5CT, BP was not observed on either heating or cooling. The results of Tables 3 and 4 suggest that Samples 1–4 with high HTP values containing ISO-(6OBA)₂ presented a wider BP temperature range than Samples 5–8 with low HTP values containing ZLI 4572 on heating and cooling.

Table 3. Phase transition temperature and ΔT_{BP} of four chiral nematic LC mixtures containing ISO-(6OBA)₂ on heating and cooling

| 7.5 wt% ISO-(6OBA) ₂ in host nematic LCs | | Phase transition temperature (K) on heating | | | Phase transition temperature (K) on cooling | | |
|--|----------------------|--|---------------------|------------------------|--|--------------------|------------------------|
| | | $T_{\text{ch-BP}}$ | $T_{\text{BP-Iso}}$ | ΔT_{BP} | $T_{\text{Iso-BP}}$ | $T_{\text{BP-ch}}$ | ΔT_{BP} |
| Host LC | (5CB/JC-1041XX) | 318.05 | 318.95 | 0.9 | 318.95 | 316.25 | 2.7 |
| | (5CH/5CB/JC-1041XX) | 320.85 | 322.05 | 1.2 | 322.75 | 320.55 | 2.2 |
| | (5CCB/5CB/JC-1041XX) | 362.45 | 367.15 | 4.7 | 367.65 | 361.85 | 5.8 |
| | (5CT/5CB/JC-1041XX) | 367.65 | 372.75 | 5.1 | 372.75 | 366.75 | 6.0 |

Table 4. Phase transition temperature and ΔT_{BP} of four chiral nematic LC mixtures containing ZLI-4572 on heating and cooling

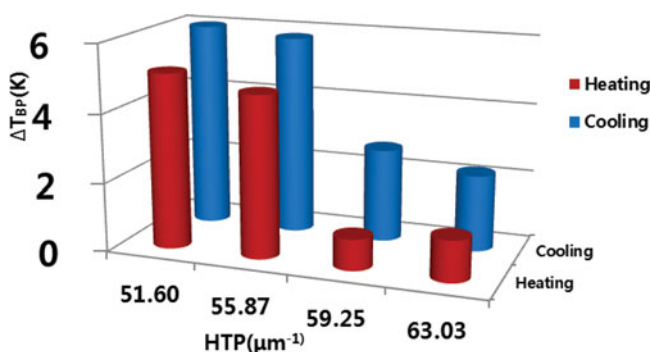
| 7.5 wt% ZLI-4572 in host nematic LCs | | Phase transition temperature (K) on heating | | | Phase transition temperature (K) on cooling | | |
|--------------------------------------|----------------------|---|--------------|-----------------|---|-------------|-----------------|
| | | T_{ch-BP} | T_{BP-Iso} | ΔT_{BP} | T_{Iso-BP} | T_{BP-ch} | ΔT_{BP} |
| Host LC | (5CB/JC-1041XX) | 325.35 | 326.05 | 0.7 | 326.05 | 324.75 | 1.3 |
| | (5CH/5CB/JC-1041XX) | 328.95 | 329.45 | 0.5 | 329.35 | 328.55 | 0.8 |
| | (5CCB/5CB/JC-1041XX) | . | . | 0 | . | . | 0 |
| | (5CT/5CB/JC-1041XX) | . | . | 0 | . | . | 0 |

3.3 Relationship Between BP Temperature Range and HTP in Chiral Nematic LC Mixtures

Figure 2 shows the relationship between ΔT_{BP} and HTP values for four kinds of chiral nematic LCs composed of 7.5 wt% ISO-(6OBA)₂ in host nematic LCs. This shows that ΔT_{BP} decreased with increases in HTP values on both heating and cooling.

Figure 3 shows the relationship between ΔT_{BP} and HTP values for four kinds of chiral nematic LCs composed of 7.5 wt% ZLI-4572 in host nematic LCs. In this case, ΔT_{BP} increased with increases in HTP values on both heating and cooling. Thus, Figures 2 and 3 reveal that ΔT_{BP} tends to increase according to HTP when HTP range between $35.64 \mu\text{m}^{-1}$ and $49.03 \mu\text{m}^{-1}$, whereas ΔT_{BP} tends to decrease according to HTP when HTP range between $51.6 \mu\text{m}^{-1}$ and $63.03 \mu\text{m}^{-1}$, even though different chiral dopants were used.

Therefore, the BP was not present when the HTP value was of a magnitude less than $35.64 \mu\text{m}^{-1}$, the BP temperature range increased when the HTP value was of a magnitude

**Figure 2.** Relationship between ΔT_{BP} and HTP in four kinds of chiral nematic LCs of 7.5 wt% ISO-(6OBA)₂ in host nematic LCs.

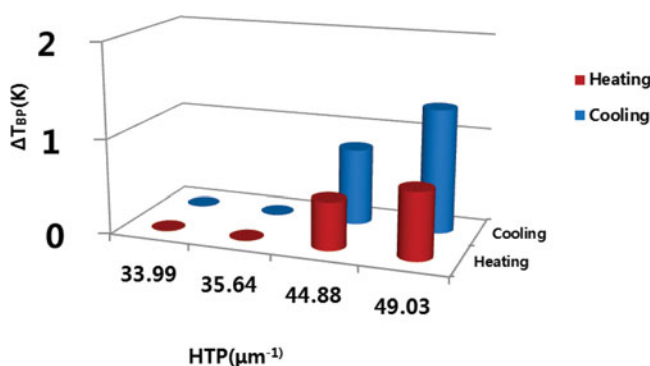


Figure 3. Relationship between ΔT_{BP} and HTP in four kinds of chiral nematic LCs of 7.5 wt% ZLI-4572 in host nematic LCs.

between 35.64–49.03 μm^{-1} and it decreased when the HTP value was of a magnitude between 51.60–63.03 μm^{-1} .

4. Conclusions

We found that chiral nematic LC mixtures containing three-ring core structure host nematic LCs (e.g., 5CCB and 5CT) presented small HTP values compared to those containing two-ring core structure host nematic LCs (e.g., 5CB and 5CH) regardless of chiral dopant species.

We also found that the BP was not present when the HTP value was of a magnitude less than 35.64 μm^{-1} , the BP temperature range increased when the HTP value was of a magnitude between 35.64–49.03 μm^{-1} , and it decreased when the HTP value was of a magnitude between 51.60–63.03 μm^{-1} in cyano homologue chiral nematic LC mixtures.

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