A blue phase observed for a novel chiral compound possessing molecular biaxiality $\ensuremath{^\dagger}$

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Received 3rd May 2005, Accepted 23rd June 2005 First published as an Advance Article on the web 11th July 2005 DOI: 10.1039/b506167a

Novel chiral compounds possessing molecular biaxiality, T-shaped and bend-shaped compounds, have been prepared and the physical properties investigated. The T-shaped chiral compound was found to show a blue phase with a wide temperature range on cooling. A double twist structure formed by the T-shaped compound can stabilize the blue phase. Furthermore, the compound induced a twist grain boundary phase in the binary mixture with its corresponding monomeric compound.

Introduction

Investigation of chirality in liquid crystals is one of the most exciting areas of liquid crystal science. Frustrated phenomena induced by chirality have been reported. Twist grain boundary (TGB) phases, blue phases, and smectic Q phases have been observed and structure-property correlations investigated.¹ Blue phases are of particular interest because they have a fluid lattice whose structure is stabilized by lattice defects. Appearance of blue phases results from the competition between the chiral twisting force and the desire for molecules to pack in ways such that they fill space uniformly. Theoretical and experimental works have demonstrated that chiral nematic liquid crystals with short pitch can form up to three distinct blue phases, i.e. blue phase I (BPI), blue phase II (BPII) and blue phase III (BPIII).²⁻⁴ Blue phases are normally found in a very narrow (~ 1 °C) temperature range between the isotropic liquid and a chiral nematic (N*) phase of sufficiently short pitch, except in a few cases where a SmA to BPI transition has been observed.^{5–7} Double twist cylinders are believed to exist in BPI and BPII. Meiboom et al. discovered that the local free energy of most chiral nematic liquid crystals could be reduced by a double twist structure.⁸ Such a structure requires energetically unfavourable disclinations between separate double twist regions. As the liquid crystal approaches the isotropic transition, the energy cost of disclinations lowers and a network of the double twist structures with disclinations might be more stable than the helical N* phase. Li et al. reported the observation of a different phase sequence I-BPs-TGBA-TGBC-SmC* in a fluoro-substituted chiral tolane derivative.9,10 Recently, there has also been experimental evidence for a smectic blue phase, which is observed between the isotropic and smectic phases.^{11,12} From the viewpoint of applications, blue phases are interesting for fast light modulators or tunable photonic crystals. However, the narrow temperature range is a critical problem. Kikuchi et al. reported

polymer-stabilized blue phases in which the temperature range is extended to more than 60 °C and they demonstrated fast electro-optical switching for the stabilized blue phase.¹³ Coles et al. reported that eutectic mixtures of two symmetric liquid crystal dimers doped with a small percentage of a highly twisting chiral additive shows the BPI of a very wide temperature range.¹⁴ On the other hand, many kinds of liquidcrystalline materials possessing a centre of chirality have been investigated. Recently compounds possessing an axis or a plane of chirality have been reported.^{15–18} A single chiral compound with a wide temperature range of a blue phase has never been obtained. Theoretical work suggests that biaxiality plays an important role in the blue phases.¹⁹ However, the biaxiality in most chiral nematic liquid crystals is slight, thus the double twist structure can not exist in a wide temperature range.

We reported a U-shaped molecule that induces a smecticlike layer ordering in the nematic phase and noted the possibility that the nematic (N) phase has biaxiality.²⁰ Thus we designed coupling between the axial chirality and the U-shaped system.^{21,22} We reported a homologous series of dimeric liquid-crystalline compounds possessing a binaphthyl group ((R)-n) and found an unusual phase sequence of I-BP-SmA.²¹ Furthermore, a new type of helical twist inversion was observed for the chiral system.²¹ The helical twist sense for compounds (R)-6, (R)-7, (R)-8 and (R)-9 was right-handed, however, that for compounds (R)-10, (R)-11 and (R)-12 was left-handed. In this paper, we have designed novel T-shaped and bent chiral compounds possessing molecular biaxiality, and investigated the chirality-dependent properties. The mesogens with lateral aromatic substituents were synthesized in Vorländer's group.²³ T-Shaped compounds in which the lateral substituents are attached via spacers have been reported.²³⁻²⁵ We report novel chiral effects in the chiral T-shaped molecule on appearance of frustrated phases.

Experimental

The T-shaped chiral compound (T-1) was prepared by the synthesis outlined in Scheme 1. Synthetic procedures for T-1 and the bend-shaped compound (B-1) are listed in electronic supplementary information (ESI). \dagger

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 $[\]dagger$ Electronic supplementary information (ESI) available: Synthetic procedures for T-1 and the bent compound (B-1). See http://dx.doi.org/ 10.1039/b506167a



Liquid-crystalline and physical properties

The initial assignments and corresponding transition temperatures for the final products were determined by thermal optical microscopy using a Nikkon Optiphoto POL polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit. The heating and cooling rates were 5 °C min⁻¹. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200 calorimeter. The material was studied at a scanning rate of 5 °C min⁻¹, for both heating and cooling cycles, after being encapsulated in aluminium pans. The helical



Scheme 1 Synthesis of compound T-1.

pitch in the N* phase was measured by the Cano wedge method for a chiral nematic mixture consisting of nematic liquid-crystalline material, 4-hexyl-4'-cyanobiphenyl (6CB) (purchased from BDH) and each chiral additive. The helical pitch in the SmC* phase was measured by observing the length between the dechiralization lines corresponding to the full pitch band for a mixture consisting of 5-octyloxy-2-(4hexyloxyphenyl)pyrimidine (8-PYP-6O) and each chiral additive. The helical pitches were measured at room temperature. The mixtures were studied using the contact method and their chiral helical twist senses were established. The definition of the helical twist senses used in this article is the same as that of Goodby.²⁶

Results and discussion

Liquid-crystalline properties

Transition temperatures and enthalpies of transition for T-1 and B-1 are shown in Table 1. Phase transition behaviour of T-1 was investigated by optical microscopy and DSC. On cooling (5 °C min⁻¹) the isotropic liquid exhibited a blue colour of low birefringence (Fig. 1(a)). The blue colour was clearly observed in uncovered regions of T-1. The blue coloured phase showed fluidity and did not appear as platelets which is usually observed in BPI. These observations indicate that the phase is BPIII. On further cooling the BP changed to a chiral nematic phase (Fig. 1(b)). The temperature range of the

Table 1 Transition temperatures (°C) on cooling and enthalpies (kJ mol⁻¹) of transition (in brackets) for compounds T-1 and B-1

	Recryst. ^a	N*	BP	Ι	Mp^b
T-1 B-1	• 80 (31)	• 15 ^c	• 28 (1.4)	•	63 (66) 81 (30)

^{*a*} T-1 was not crystallized on cooling at a rate of 5 °C min⁻¹. ^{*b*} The melting points were measured by DSC. ^{*c*} The enthalpy of the BP to N* transition for T-1 was too small to be detected.

BP was about 13 °C. On the other hand, **B-1** did not show any liquid-crystalline phase.

T-1 exhibited BP and N* phases. Some achiral T-shaped compounds were reported to show a N phase.²³ Blue phases



are normally found in a very narrow (~1 °C) temperature range. **T-1** showed the BP with a wide temperature range. Nakata *et al.* reported that a mixture consisting of chiral nematic material and achiral bend compound induces a blue phase.²⁷ Furthermore, Blatch *et al.* reported that blue phase I behaviour was observed in a very narrow temperature range (0.6 °C) between isotropic liquid and N* phases for the odd non-symmetric dimers, whereas a direct I–N* transition was observed for the even non-symmetric dimers.²⁸ The conformation of **T-1** in the liquid-crystalline phases is not clear. MM2 calculations suggest that **T-1** exists as a λ -shaped structure rather than a T-shaped structure. **T-1** has two possible molecular long axes, *i.e.* an axis through the biphenylbenzoate unit and the other through the phenylpyrimidine unit. We can





Fig. 1 Photomicrographs of (a) the blue phase at 25 $^{\circ}$ C and (b) the N* phase at 10 $^{\circ}$ C of T-1 in an uncovered region on a glass slide. Magnification \times 100.



Fig. 2 A schematic representation for the double twist arrangement by T-1.

say that **T-1** has molecular biaxiality. Thus coupling between the molecular biaxiality and chirality is thought to induce the blue phase. Fig. 2 shows a schematic model for the double twist arrangement by **T-1**.

Pitch measurements

We investigated the twisting power of each chiral compound. The helical pitch values and their helical twist senses in the N* and SmC* phases are listed in Table 2.

Both compounds were found to have the same magnitude of twisting power in the N* and SmC* phases.

Miscibility studies

We investigated the transition behaviour of binary mixtures between **8-PYP-6O** and **T-1**. The phase diagram on cooling is shown in Fig. 3(a). The transition temperatures were determined by optical microscopy. The N phase of both materials proved to be miscible across the full composition range. The BP was observed for the mixtures containing more than 50 wt% of **T-1**. Furthermore, a twist grain boundary phase was found to appear for a mixture containing 10 wt% of **T-1**. An optical photomicrograph of the TGBA phase of the mixture is shown in Fig. 4. Fig. 3(b) shows the phase diagram between **8-PYP-6O** and **B-1**. A SmA phase was found to be induced for mixtures containing more than 60 wt% of **B-1**. A SmC* phase was also induced for mixtures containing more than 75 wt% of **B-1**. However, no frustrated phase was observed in the binary phase diagram.

Pitch measurements reveal that **T-1** and **B-1** have the same magnitude of twisting power in the N* and SmC* phases. **T-1** induced frustrated phases, *i.e.* TGBA and blue phases, in the binary mixture with **8-PYP-6O**, however, **B-1** did not induce any. The appearance of the TGBA phase is attributed to the difference in molecular structure between **T-1** and **B-1**. Possible molecular organization models in the SmA phase of the mixture with each chiral compound are shown in Fig. 5 and Fig. 6.

The phenylpyrimidine group of **T-1** can happily exist in layer structures composed of the host molecules, and the chiral part of **T-1** is thought to localize in the inter-phase region (Fig. 5(a)). Thus, the appearance of the TGBA phase in the mixture between **8-PYP-6O** and **T-1** may be a result of the competition between twist deformation owing to the molecular chirality localized in the inter-phase region and the desire for the molecules to form a layered structure. However, it is not realistic that the long rods should lie between the alkyl chains at the interlayer interfaces parallel to these interfaces. We

Table 2 Helical pitch (μ m) in the N* and SmC* phases for a mixture consisting of 2 wt% of each chiral compound and the helical twist senses (in brackets), *i.e.* right-hand (RH) or left-hand (LH)^a

Compound	SmC*	N*
T-1	20 (RH)	7 (RH)
B-1	20 (RH)	8 (RH)

^{*a*} Helical pitch (μ m) in the N* phase for a chiral nematic mixture of **6CB** and 2 wt% of each chiral compound and that in the SmC* phase for a chiral mixture of **8-PYP-6O** and 2 wt% of each chiral compound were observed at room temperature.



Fig. 3 (a) Binary phase diagram on cooling for mixtures of **8-PYP-6O** and **T-1**, and (b) binary phase diagram on cooling for mixtures of **8-PYP-6O** and **B-1**.

recently reported that a λ -shaped molecule induces layer deformation.²⁹ Fig. 5(b) shows another possibility. **T-1** adopts a λ -shaped structure, with the two rods arranged nearly parallel, in each layer. The strong frustration could be induced by splaying of the two rods. Coupling between the twist owing to the molecular chirality and the splay of the two core units may induce the TGBA phase. Further investigation is necessary to understand the appearance of the TGBA phase in



Fig. 4 Filament texture of the TGBA phase of a mixture containing 10 wt% of **T-1** between untreated glass plates at the transition to the SmA phase.





Fig. 5 Possible molecular organization models for a mixture of 8-PYP-6O and T-1.



Fig. 6 Possible molecular organization model for a mixture 8-PYP-6O and B-1.

this system. On the other hand, the phenylpyrimidine group and the chiral part of **B-1** can exist in adjacent layers (Fig. 6).

Conclusion

We have designed novel chiral compounds possessing molecular biaxiality. The T-shaped compound was found to show a blue phase with a wide temperature range. Coupling between the molecular biaxiality and chirality is thought to produce a stable double twist structure of the blue phase. Furthermore, the T-shaped compound induced a TGBA phase in the mixture with its corresponding monomeric compound.

Acknowledgements

We thank Dr Isa Nishiyama for helpful discussions. This work was partly supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, Culture, and Technology in Japan (No. 15550156). We also acknowledge the input of a referee.

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