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Physical properties of a novel chiral material possessing a binaphthyl group

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Physical properties of a novel chiral material possessing a binaphthyl group

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A novel chiral dimeric compound, (*R*)-2,2′-bis{6-[4-(5-octylpyrimidine-2-yl)phenyloxy]hexyloxy}-1,1′-binaphthyl (**1**), has been prepared and its physical properties investigated. Compound **1** was found to show a monotropic smectic A phase. A twist grain boundary phase was observed in binary mixtures of compound **1** and its corresponding monomeric liquid crystal, 5-octyl-2-(4-hexyloxyphenyl)pyrimidine (**8-PYP-6O**). Pitch measurements in a mixture with a host material revealed that the binaphthyl dimer induces a stronger helical structure in the N* phase than in the SmC* phase. We also measured helical pitch values in N* and SmC* phases induced by other twin materials with a chiral centre. We discuss characteristic effects of axial chirality in liquid crystalline phases in comparison with that of centres of chilarity.

1. Introduction

The investigation of chirality in liquid crystals is an exciting area of liquid crystal science. Ferroelectricity and antiferroelectricity in chiral smectic phases are of particular interest because of their applications in display devices. Frustrated phenomena induced by chirality have been reported. Twist grain boundary (TGB) phases, blue phases, and the smectic Q phase have been observed and structure–property correlations investigated [1]. Furthermore we have reported an endothermic transition from the chiral smectic C (SmC*) to cubic phase on cooling, organized by chiral molecular recognition [2, 3]. Chiral liquid crystals have the potential to show unusual molecular assemblies. Many kinds of liquid crystalline materials possessing a centre of chirality have been investigated. Recently compounds possessing an axis or a plane of chirality have been reported [4–7]; a few examples of binaphthyl derivatives have been reported [8, 9].

Supramolecular assemblies composed of supermolecules, i.e. dimeric and oligomeric liquid crystals, is a current topic in the design of liquid crystalline materials. The coupling between chirality and a supermolecular system produces novel chirality-dependent phenomena. We have investigated the microscopic organization of molecules in smectic phases. ^{13}C NMR measurements suggest that (1) cooperative motion of the core parts contributes to the orientational order of the molecules in each layer, and (2) inter-layer permeation of the tails causes correlation between cores in adjacent layers [10, 11]. The correlation of molecular motions between adjacent molecules has been found to have a significant effect on long range order in smectic phases (figure 1). In order to enhance inter-layer correlations, the chiral twin material **MAB-8-PYP** was designed and found to induce a stronger helical structure in the chiral smectic C phase [12]. In order to enhance the intra-layer correlation, the U-shaped molecule **BOPPHB** was prepared and found to induce a smectic-like layer ordering in the nematic phase [13]. Thus we have designed coupling between chirality and the U-shaped system. In the present study, we have prepared a dimeric liquid crystalline material possessing a binaphthyl group and investigated the effects of axial chirality on physical properties liquid crystalline phases.

2. Experimental

2.1. *Characterization*

Purification of the final product was carried out using column chromatography over silica gel (63–210 µm) (Kanto Chemical Co., INC) using dichloromethane or a dichloromethane ethyl acetate mixture as the eluent, followed by recrystallization from ethanol. The purity of the final compound was checked by thin layer chromatography (TLC, aluminum sheets, silica gel 60 F254 from Merck); dichloromethane was used as the

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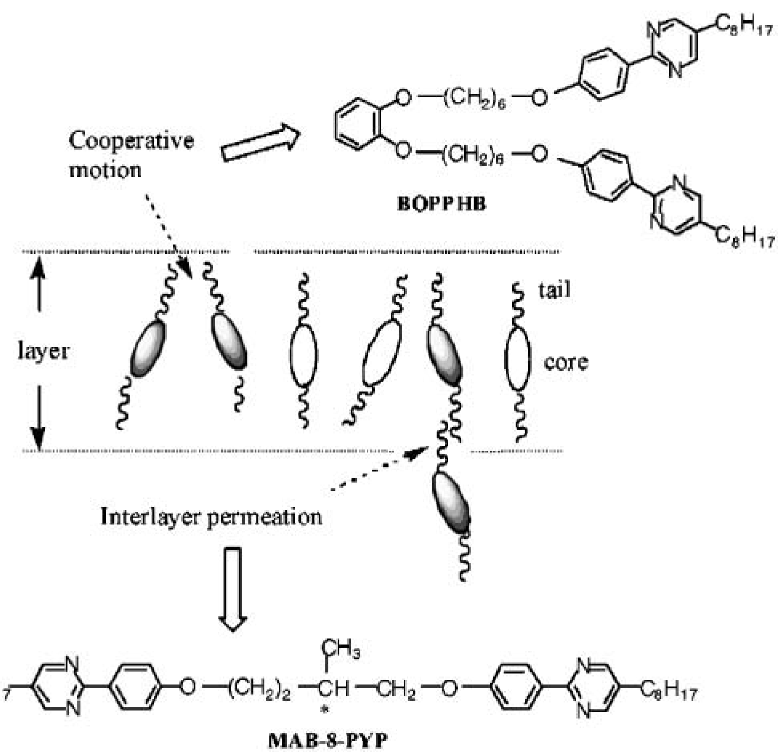


Figure 1. Molecular design for a dimeric liquid crystal system.

solvent. Detection of products was achieved by UV irradiation (λ=254 and 365 nm). The purity of the final compound was also confirmed by normal phase HPLC (Intersil SIL 150A-5 column); a dichloromethane isopropylalcohol (85/15) mixture was used as the eluent. Detection of the product was achieved by UV irradiation (λ=254 nm).

The structure of the final product was determined by infrared (IR) spectroscopy (BIO RAD FTS-30) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JEOL JNM-GX270).

2.2. *Preparation of materials*

Optically active (*R*)-2,2′-dihydroxy-1, 1′-binaphthyl was obtained from Aldrich Chemical Company. 5-Octyl-2-(4-hydroxyphenyl)pyrimidine was obtained from Midori Chemical Corporation.

2.2.1. (R)-2, 2′-Bis{6-[4-(5-octylpyrimidine-2-yl)phenyloxy]hexyloxy}-1,1′-binaphtyl, 1. To a solution of 5-octyl-2-(4-hydroxyphenyl)pyrimidine (1.14 g, 4.0 mmol) and 1,6-dibromohexane (1.46 g, 6.0 mmol) in cyclohexanone (10 ml) was added potassium carbonate (0.55 g, 4.0 mmol). The reaction mixture was stirred at 80°C for 8 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with dichloromethane eluent. The intermediate product, 5-octyl-2-[4′-(6-bromohexyloxy)phenyl]pyrimidine, was obtained; yield 0.88 g (2.0 mmol, 50%).

To a solution of 5-octyl-2-[4′-(6-bromohexyloxy) phenyl]pyrimidine (290 mg, 0.65 mmol) and (*R*)-2, 2′-dihydroxy-1, 1′-binaphthyl (86 mg, 0.3 mmol) in cyclohexanone (5 ml) was added potassium carbonate (83 mg, 0.6 mmol). The reaction mixture was stirred at 100°C for 7 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a hexane/ethylacetate (7/3) mixture. The desired product, (*R*)-2,2′-bis{6-[4-(5-octylpyrimidine-2-yl)phenyloxy]hexyloxy}-1,1′-binaphthyl, was obtained; yield 85 mg (0.15 mmol, 50%). ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS): δ_H/ppm: 8.57(s,4H,Ar–**H**), 8.36(d,4H,Ar–**H**), 7.90(d,2H,Ar–**H**), 7.82(d,2H,Ar–**H**) 7.40(d,2H,Ar–**H**),7.31–7.13(m,6H,Ar–**H**),6.93(d,4H, Ar–**H**),3.79(t,8H,–$C\mathbf{H}_2$O–,*J*=6.6Hz)2.59(t,4H,Ar–$C\mathbf{H}_2$–, *J*=7.6 Hz),1.70–1.06(m, 46H, aliphatic-**H**). IR (KBr) ν_{max}/cm^{-1}: 2900, 1465, 1377, 722, Purity 100%.

2.3. *Liquid crystalline and physical properties*

The initial assignments and corresponding transition temperatures for the final product were determined by thermal optical microscopy using a Nikkon Optiphoto POL polarizing microscope equipped with a Mettler

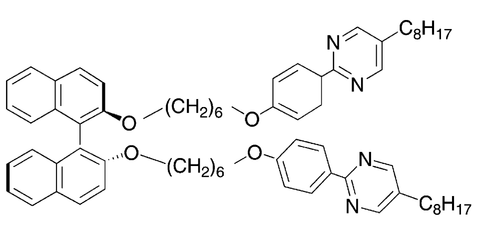
FP82 microfurnace and FP80 control unit. The heating and cooling rates were 5°C min^{-1}, unless otherwise indicated. Temperatures and enthalpies of transition were investigated by differential scanning calorimetry (DSC) using a Seiko DSC 6200 calorimeter. The material was studied at a scanning rate of 5°C min^{-1}, for both heating and cooling cycles, after being encapsulated in aluminum pans. The helical pitch in the N* phase was measured by the Cano wedge method for a chiral nematic mixture consisting of a nematic liquid crystalline material, 4-hexyloxy-4′-cyanobiphenyl (**6OCB**, purchased from BDH) and the chiral additive. The mixture was studied using the contact method, and its helical twist sense was established. The definition of the helical twist senses used in this article is the same as that of Goodby [14]. The helical pitch in a SmC* phase was measured for mixtures composed of 5-octyl-2-(4-hexyloxyphenyl)pyrimidine (**8-PYP-6O**) and each chiral additive. The SmC* helical pitch was obtained directly by measuring the distance between the lines corresponding to the full pitch under the polarized light microscope for a homogeneously aligned sample in a cell with 300 μm spacing.

3. Results and discussion

3.1. *Liquid crystalline properties*

The molecular structure, and the temperatures and enthalpies of transition for compound **1** determined by optical microscopy and DSC are shown in figure 2. Compound **1** showed only a smectic A phase; no recrystallization was detected. There is a marked hysteresis in the transition behaviour between cooling and heating cycles for this compound.

We investigated the transition behaviour of binary mixtures of **8-PYP-6O** and compound **1**. The phase diagram on cooling is shown in figure 3; transition temperatures were determined by optical microscopy. A twist grain boundary phase was observed for mixtures containing 10–50 wt% of compound **1**. Optical photomicrographs of the TGBA phase of a mixture containing 10 wt% of compound **1** are shown in figure 4.



1

Iso Liq 29 °C (6.0 kJmol^{-1}) SmA mp 32 °C

Figure 2. Molecular structure, and temperatures and enthalpies of transition for compound **1**.

3.2. *Pitch measurements*

The helical twist sense induced by compound **1** in both N* and SmC* phases was found to be left–handed. The helical pitch values in the N* and SmC* phases for the mixture with a host compound are shown in figure 5. Squares show helical pitch values in the N* phase for the chiral mixture consisting of **6OCB** and 2 wt% of compound **1**. Circles show those in the N* and SmC* phases for the mixture consisting of **8-PYP-6O** and 2 wt% of compound **1**. The helical pitches in the N* phase were shorter than those in the SmC* phase, indicating that compound **1** induces stronger twisting power in the N* phase than in the SmC* phase. The temperature dependence of the helical pitches in the SmC* phase was found to be larger than that in the N* phase.

We then compared the twisting power of the axial chirality with that of a chiral centre in liquid crystalline phases. Helical pitches in the N* and SmC* phases for a mixture consisting of a host material and 2 wt% of each chiral compound are shown in table 1. Compound **1** was found to induce shorter helical pitches in the N* and SmC* phases than those induced by the monomeric compound **4**. Compound **2** (**MAB-8-PYP**) induced a strong helical structure in the SmC* phase [12]. On the other hand, compound **1** induced stronger helical structure in the N* phase than in the SmC* phase. However, compound **3**, having a chiral centre coupled with a U-shaped system, was found to induce a long helical pitch in both N* and SmC* phases. The

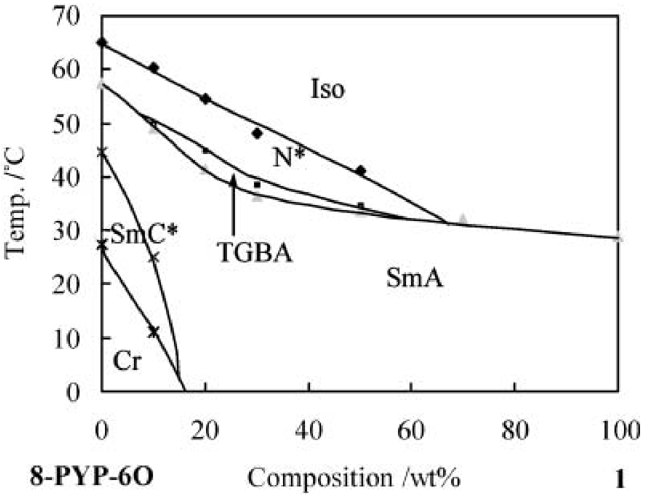


Figure 3. Binary phase diagram for mixtures of **8-PYP-6O** and compound **1**.

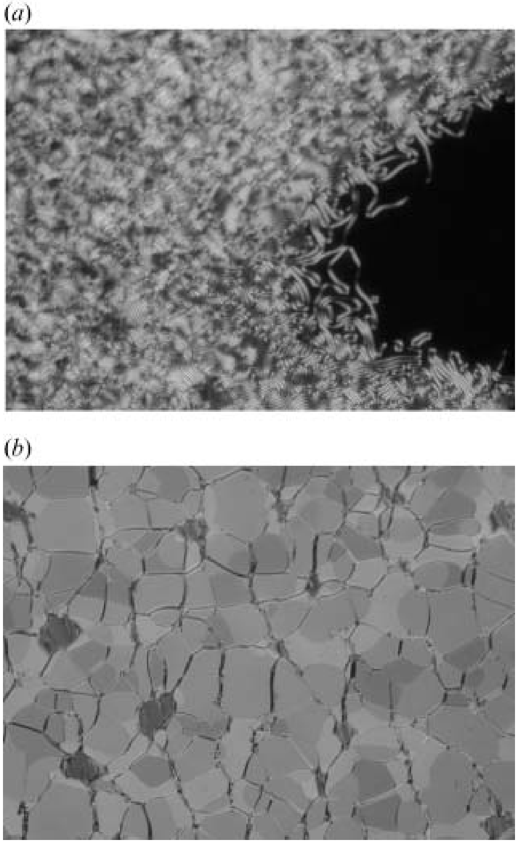


Figure 4. (*a*) Filament texture of the TGBA phase of a mixture containing 10 wt% of compound **1** between untreated glass plates at the transition to the SmA phase. (*b*) Texture of the TGBA phase in a cell of gap d=8 µm with planar boundary conditions.

preparation and transition behaviour of compound **3** were reported elsewhere [15].

3.3. *Models for twisting power of the dimeric systems*

Figure 6 shows possible models for the twisting power induced by each chiral twin molecule. The short pitches induced by **MAB-8-PYP** in the SmC* phase are explained by an intercalated chirality model, figure 6 (*c*) [12]. With respect to compound **1**, effective coupling between the stereo structure of the binaphthyl group and conformation of the two mesogenic parts is thought to occur, and the twisting power of the axial chirality can transfer to host molecules via core–core interactions in the N phase, figure 6 (*a*). The difference in twisting power between compound **1** and **MAB-8-PYP** can result from the mechanism of the induced twist in the nematic versus the smectic phases [16, 17]. Axial chirality can exist in the inter-phase region between adjacent layers in the SmA and SmC* phases, figure 6 (*b*). Appearance of the TGBA phase in mixtures

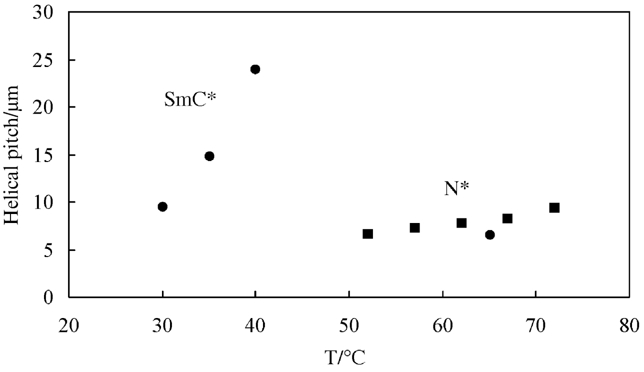


Figure 5. Temperature dependence of helical pitch values induced by compound **1** in the N* and SmC* phases. Squares show helical pitch values in the N* phase for a chiral mixture consisting of **6OCB** and 2 wt% of compound **1**. Transition temperatures (°C) of the mixture were I 77 N* 37 Cr (cooling). Circles show helical pitch values in the N* and SmC* phases for the mixture consisting of **8-PYP-6O** and 2 wt% of compound **1**. Transition temperatures (°C) of the mixture were I 73 N* 61 SmA 43 SmC* (cooling). The helical pitch in the N* phase for the mixture was obtained by measuring the distance between the lines corresponding to the half pitch in the finger print texture.

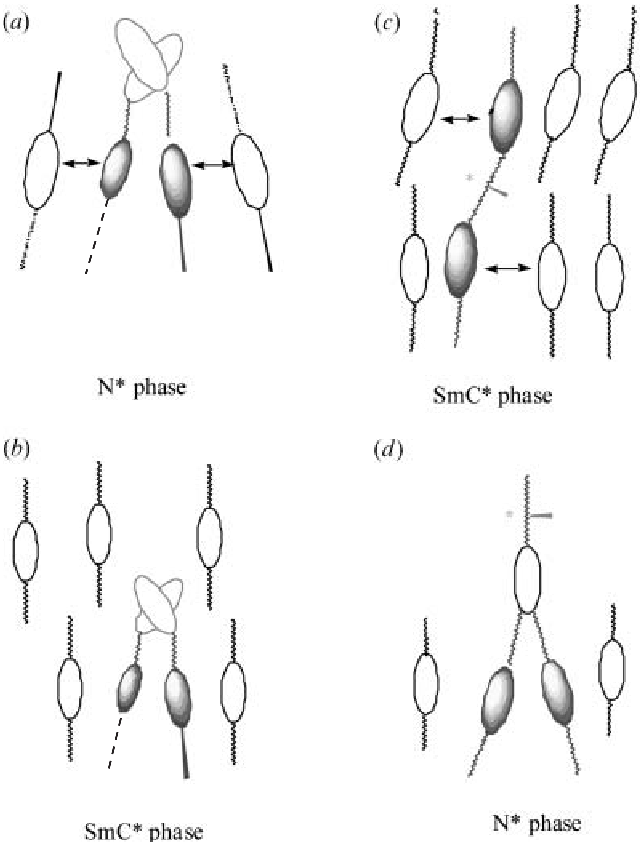
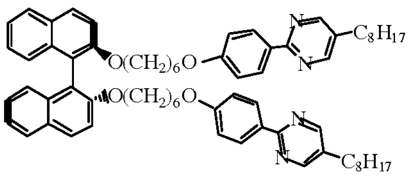
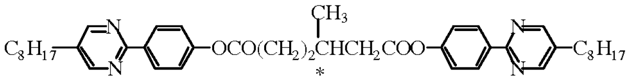
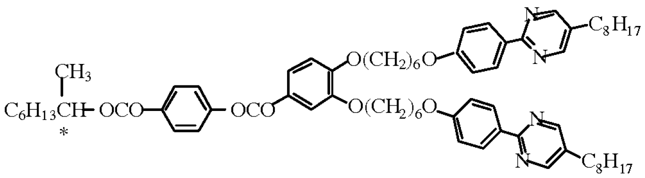
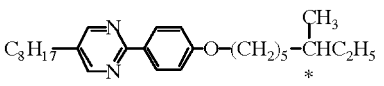


Figure 6. Possible models to explain the helical twisting power of the dimeric molecules.

Table 1. Helical pitch values (μm) in the N* and SmC* phases induced by each chiral material. The helical pitch for the N* phase was measured at $T_{\mathrm{IN*}}-5^{\circ}\mathrm{C}$ by the Cano wedge method for a mixture consisting of **6OCB** and 2 wt% of each chiral additive. The helical pitch for the SmC* phase was observed at $T_{\mathrm{AC*}}-5^{\circ}\mathrm{C}$ by measuring the distance between the lines corresponding to the full pitch.

	Chiral compound	N*	SmC*
1		8	15
2		11	5
3		33	–[a]
4		49	–[a]

[a] Too long to be observed.

of **8-PYP-6O** and compound **1** may be a result of the competition between twist deformation owing to the axial chirality localized in the inter-phase region and the desire for the molecules to form a layered structure. However, coupling between the stereo structure of the chiral centre and the core parts seems to be weak for compound **3**, figure 6 (*d*). Thus the twisting power of the chiral centre cannot transfer to the surrounding host molecules.

4. Conclusions

We have prepared a novel chiral binaphthyl derivative possessing two mesogenic phenylpyrimidine groups and found that it shows a monotropic SmA phase. Pitch measurements revealed that the chiral dimer induces a strong helical structure in the N* phase. Furthermore, a TGBA phase appeared in mixtures of the chiral dimer and its corresponding monomeric liquid crystal. The axial chirality localized in the inter-phase region between adjacent layers in the smectic phases can produce the TGBA phase.

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