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Two origins for twisting power of a binaphthyl derivative in a host nematic liquid crystal

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Two origins for twisting power of a binaphthyl derivative in a host nematic liquid crystal

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We prepare a series of homologues of novel binaphthyl derivatives, (*R*)-2, 2′-bis{ω-[4-(4-(octyloxycarbonyl)phenyl)phenyloxycabonyl]alkyloxy}-1, 1′-binaphthyl [**(*R*)-Bi-n**], and investigate their induced helical senses and pitches in different host nematic liquid-crystalline compounds. Pronounced odd–even effects were observed for the induced helical structure in each mixture with 5-heptyl-2-(4-hexyloxyphenyl)pyrimidine. Temperature-dependent helical twist inversion was observed for the mixture doped with the odd members, whereas a right-handed helix was observed for the mixture doped with the even members. On the other hand, a left-handed helix was induced in each mixture with 4-methyloxyphenyl 4-pentylcyclohexane. We discuss the change in sign of the induced pitch in terms of chirality transfer from the binaphthyl derivative to a host nematic liquid crystal.

1. Introduction

Chiral information transfer has attracted great interest in various fields of materials science [1–8]. The investigation of chirality in liquid crystals is an exciting area of liquid-crystal science [9]. Chirality-dependent frustrated phases have been investigated: twist grain boundary phases (TGB) and blue phases (BP) [10]. The appearance of these phases is created through competition between the chiral twisting force and the molecules' packing such that they fill the space uniformly. Ferroelectricity has been observed in chiral tilted smectic phases (see [11, 12] and references therein). The introduction of chirality into calamitic molecules engenders a reduction in the symmetry of the classical smectic C phase and creates the helical structure characteristic of the chiral smectic C phase, which can induce ferroelectricity. The question of how molecular chirality is translated into bulk chirality of the liquid-crystalline phase is a fundamental issue of liquid-crystal science. Chirality transfer processes in liquid-crystalline phases have therefore been investigated extensively [13–21].

Binaphthyl derivatives possessing axial chirality are known to induce chirality-dependent properties not only for organic synthesis, but also for liquid-crystal science. Akagi *et al*. reported an asymmetric synthesis of helical polyacetylene with a chiral nematic reaction field, which was prepared by adding a binaphthyl derivative to a host liquid crystal [22]. Kirste and Scherowsky investigated temperature-dependent helix inversion in induced chiral nematic phases of a binaphthyl ester and the nematic mixture [23]. They speculated that temperature-dependent conformational changes between the cisoid and transoid of the 1,1-binaphthyl derivative are responsible for that behaviour. We recently reported an unusual phase sequence of iso liq-blue phase-smectic A and a new type of helicity inversion for a homologous series of dimeric liquid-crystalline compounds possessing a binaphthyl group [24].

Some reports have described structure–property relationships of binaphthyl derivatives [25–27]. However, the origin of the twisting power in a liquid-crystalline phase remains unclear. To gain a better understanding of the chiral transfer from a binaphthyl derivative to a host nematic liquid crystal, we prepared a homologous series of novel chiral binaphthyl derivatives possessing two mesogenic moieties, (*R*)-2, 2′-bis{ω-[4-(4-(octyloxycarbonyl)phenyl)phenyloxycabonyl]alkyloxy}-1, 1′-binaphthyl [**(*R*)-Bi-n**], and then investigated their induced helical pitch and twist sense in different host nematic liquid crystals. Figure 1 shows the molecular structures of **(*R*)-Bi-n** and **(*R*)-Et-6**.

2. Experimental details

2.1 *Spectroscopic analysis*

The purities of all final compounds were checked using HPLC (JAIGEL-1H column, LC9101; Japan Analytical

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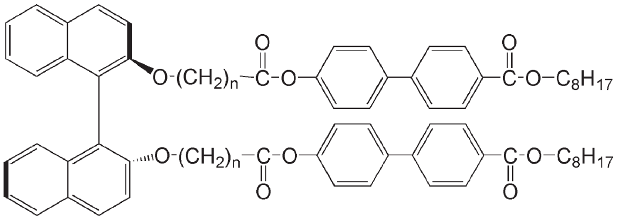
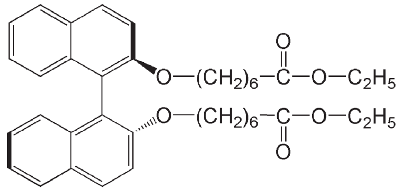


(*R*)-Bi-n



(*R*)-Et-6

Figure 1. Molecular structures of **(*R*)-Bi-n** and **(*R*)-Et-6**.

Industry Co., Ltd.). Chloroform was used as the eluent. The detection of products was achieved using UV irradiation (λ =254 nm).

Infrared (IR) spectroscopy (FTS-30; Bio-Rad Laboratories, Inc.) and proton nuclear magnetic resonance (^{1}H NMR) spectroscopy (JNM-GX270, JNM-A400 or JNM-ECA500; JEOL) elucidated the structures of the final products.

2.2 *Preparation of materials*

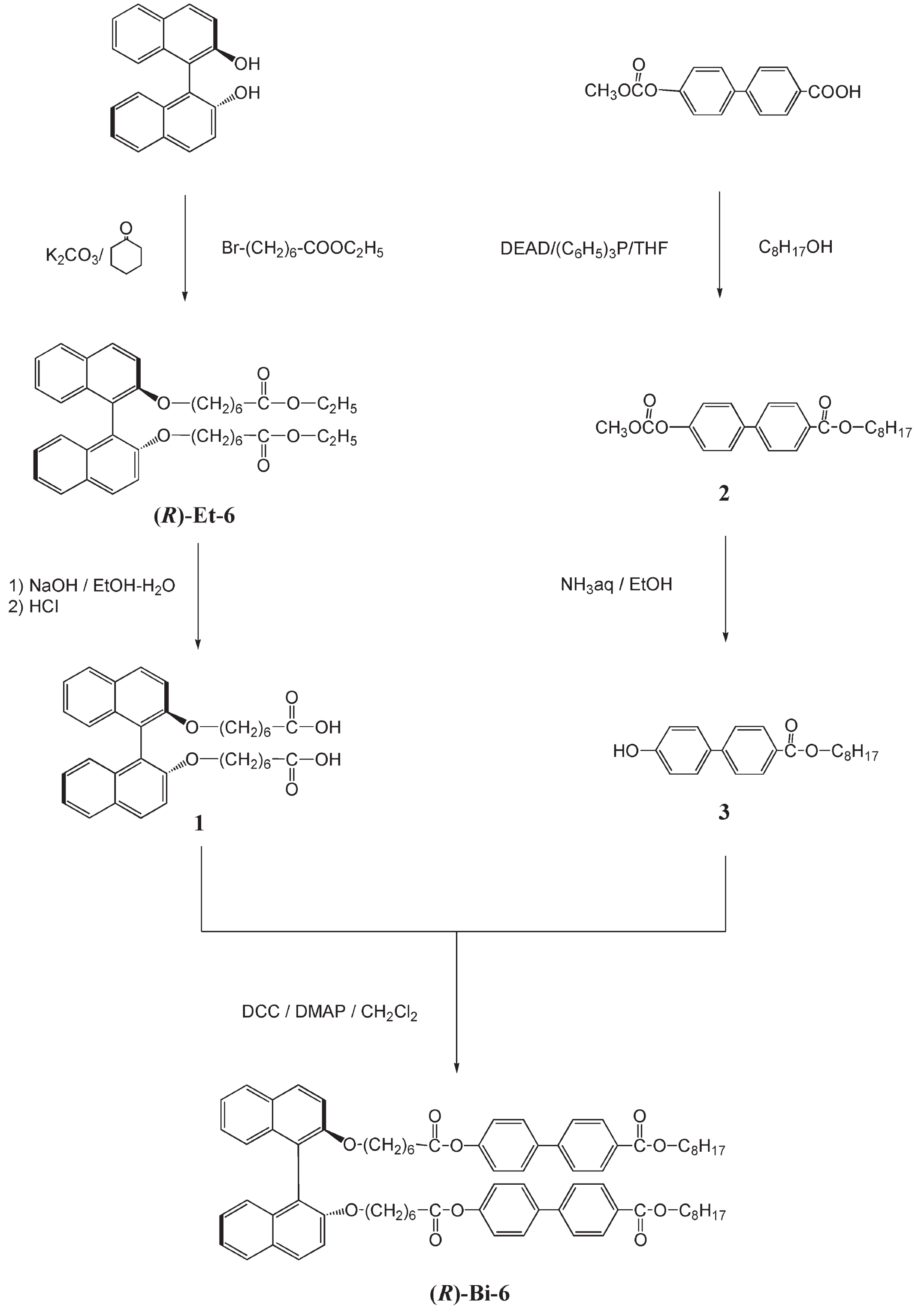
The chiral compounds **(*R*)-Et-6** and **(*R*)-Bi-6** were prepared by the synthesis outlined in scheme 1. (*R*)-1, 1′-Bi(2-naphthol) was purchased from Tokyo Kasei Kogyo Co., Ltd.

2.2.1 (*R*)-2, 2′-Bis[6-(ethyloxycarbonyl)hexyloxy]-1, 1′-binaphthyl [(*R*)-Et-6]. Potassium carbonate (0.41 g, 3.0 mmol) was added to a solution of (*R*)-1, 1′-bi(2-naphthol) (0.71 g, 3.0 mmol) and ethyl 7-bromoheptanoate (0.43 g, 1.5 mmol) in cyclohexanone (20 ml). The reaction mixture was stirred at 140°C for 7 h. After filtration of the precipitate, the solvent was removed by evaporation. The residue was purified using column chromatography on silica gel with a toluene and ethyl acetate (15:1) mixture as the eluent, giving the desired product as a colourless liquid; yield: 0.66 g (73 %). ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.91 (d, 2H, Ar–**H,** J=8.9 Hz), 7.83 (d, 2H, Ar–**H,** J=8.4 Hz), 7.39 (d, 2H, Ar–**H**, J=8.9 Hz), 7.32–7.13 (m, 6H, Ar–**H**), 4.15–4.07 (q, 4H, –COO–$\mathbf{CH_2}$, J=7.1 Hz), 4.00–3.82 (m, 4H, –O$\mathbf{CH_2}$), 2.07 (t, 2H, –OCO$\mathbf{CH_2}$–, J=7.7 Hz), 1.43–1.22 (m, 14H, aliphatic–**H**), 1.04–0.86 (m, 8H, aliphatic–**H**); IR (neat) ν_{max}/cm^{-1}: 2938, 1734, 1270, 1243; purity: 100%.

2.2.2 (*R*)-7, 7′-[(1, 1′-Binaphthalene)-2, 2′-diylbisoxy] bisheptanoic acid [1]. (*R*)-2, 2′-Bis[6-(ethyloxycarbonyl) hexyloxy]-1, 1′-binaphthyl (0.60 g, 1.0 mmol) was added to a solution of NaOH (0.92 g, 2.3 mmol) in an ethanol (40 ml) and water (10 ml) mixture. The resulting solution was stirred at 100°C for 9 h. After removal of the ethanol by evaporation, the residue was acidified using aqueous HCl. The solution was extracted with dichloromethane. The organic layers were combined, dried over magnesium sulphate, filtered and evaporated. The residue was washed with hexane to give the desired compound; yield 0.47 g (86%). ^{1}H NMR (270 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 7.91 (d, 2H, Ar–**H**, J=8.9 Hz), 7.83 (d, 2H, Ar–**H**, J=7.8 Hz), 7.39 (d, 2H, Ar–**H**, J=9.2 Hz), 7.32–7.11 (m, 6H, Ar–**H**), 4.00–3.82 (m, 4H, –O$\mathbf{CH_2}$–), 2.16 (t, 4H, HOCOC$\mathbf{H_2}$–, J=7.4 Hz), 1.45–1.26 (m, 8H, aliphatic–**H**), 1.10–0.86 (m, 8H, aliphatic–**H**).

2.2.3 Octyl 4-methoxycarbonyloxybiphenyl-4′-carboxylate [2]. Triphenylphosphine (1.2 g, 2.7 mmol) in THF (18 ml) was added to a solution of 4-methoxycarbonyloxybiphenyl-4′-carboxylic acid (1.0 g, 3.7 mmol), octanol (0.48 g, 3.7 mmol) and diethylazodicarboxylate (1.6 g, 3.7 mmol) in tetrahydrofuran (THF, 50 ml). The reaction mixture was stirred at room temperature for 24 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 and ethyl acetate (13:1) mixture as the eluent. The desired product was obtained; yield 0.51 g (49%). ^{1}H NMR (400 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.11 (d, 2H, Ar–**H,** J=8.8 Hz), 7.63 (d, 4H, Ar–**H**, J=8.3 Hz), 7.28 (m, 2H, Ar–**H**), 4.34 (t, 2H, –COO–$\mathbf{CH_2}$, J=6.6 Hz), 3.94 (s, 3H, –O$\mathbf{CH_3}$), 1.82–1.29 (m, 12H, aliphatic–**H**), 0.89 (t, 3H, –$\mathbf{CH_3}$, J=6.8 Hz).

2.2.4 Octyl 4-hydroxybiphenyl-4′-carboxylate [3]. An aqueous ammonia solution (28–30%, 3 ml) was added to a solution of compound **2** (0.49 g, 5.0 mmol) in ethanol (21 ml). The reaction mixture was stirred at room temperature for 26 h. The solvent was removed by evaporation. Water was added to the residue; the solution was extracted using diethyl ether (50 ml). The combined organic layers were dried over magnesium sulphate. After the drying agent and the solvent were removed, the desired product was obtained without further purification; yield 0.37 g (86%). ^{1}H NMR



Scheme 1. Synthesis of **(*R*)-Et-6** and **(*R*)-Bi-6**.

(400 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.08 (d, 2H, Ar–**H,** J=8.3 Hz), 7.61 (d, 2H, Ar–**H**, J=8.8 Hz), 7.52 (d, 2H, Ar–**H**, J=8.8 Hz), 6.94 (d, 2H, Ar–**H**, J=8.8 Hz), 5.10 (s, 1H, Ar–O**H**), 4.33(t, 2H, –COO–C**H**$_2$, J=6.6 Hz), 3.94 (s, 3H, –OC**H**$_3$), 1.82–1.29 (m, 12H, aliphatic–**H**), 0.89 (t, 3H, –C**H**$_3$, J=6.8 Hz).

2.2.5 (*R*)-2, 2′-Bis{6-[4-(4-(octyloxycarbonyl)phenyl) phenyloxycarbonyl]hexyloxy}-1, 1′-binaphthyl [(*R*)-Bi-6]. Compound **3** (0.14 g, 0.50 mmol), *N, N*′-dicyclohexylcarbodiimide (0.12 g, 0.60 mmol) and 4-(*N, N*-dimethylamino)pyridine (0.06 g, 0.05 mmol) were added to a solution of compound **1** (0.16 g, 0.25mmol) in dichloromethane (12 ml). The resulting solution was stirred at room temperature for 27 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 and ethyl acetate (39:1) mixture as the eluent and then washed with ethanol, giving the desired product as a colourless liquid; yield 0.26 g (55%). ^{1}H NMR (400 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.10 (d, 2H, Ar–**H**, J=8.3 Hz), 7.94 (d, 2H, Ar–**H**, J=9.3 Hz), 7.86 (d, 2H, Ar–**H**, J=7.8 Hz), 7.64–7.61 (m, 8H, Ar–**H**), 7.42 (d, 2H, Ar–**H**, J=8.8 Hz), 7.34–7.15 (m, 10H, Ar–**H**), 4.34 (t, 4H, –COO–$\mathbf{CH_2}$, J=6.6 Hz), 4.04–3.88 (m, 4H, –O$\mathbf{CH_2}$–), 2.35 (t, 4H, –OCO$\mathbf{CH_2}$–, J=7.6 Hz), 1.82–0.87 (m, 46H, aliphatic–**H**); IR (neat) ν_{max}/cm^{-1}: 2930, 1759, 1717, 1274; HPLC: 100%.

The other compounds presented in this paper were obtained using a similar method to that for **(*R*)-Bi-6**. Analytical data for the other compounds are listed below.

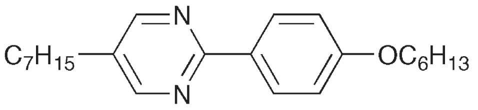
2.2.6 (*R*)-2, 2′-Bis{5-[4-(4-(octyloxycarbonyl)phenyl) phenyloxycarbonyl]pentyloxy}-1, 1′-binaphthyl [(*R*)-Bi-5]. ^{1}H NMR (400 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.10 (d, 4H, Ar–**H**, J=8.3 Hz), 7.95 (d, 2H, Ar–**H**, J=9.3 Hz), 7.88 (d, 2H, Ar–**H**, J=8.3 Hz), 7.63–7.59 (m, 8H, Ar–**H**), 7.43 (d, 2H, Ar–**H**, J=9.3 Hz), 7.35–7.12 (m, 10H, Ar–**H**), 4.33 (t, 4H, –COO–$\mathbf{CH_2}$, J=6.6 Hz), 4.07–3.90 (m, 4H, –O$\mathbf{CH_2}$–), 2.35 (t, 4H, –OCO$\mathbf{CH_2}$–, J=7.6 Hz), 1.82–0.87 (m, 42H, aliphatic–**H**); IR (neat) ν_{max}/cm^{-1}: 2927, 1757, 1714, 1275; HPLC: 100%.

2.2.7 (*R*)-2, 2′-Bis{7-[4-(4-(octyloxycarbonyl)phenyl) phenyloxycarbonyl]heptyloxy}-1, 1′-binaphthyl [(*R*)-Bi-7]. ^{1}H NMR (500 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.10 (d, 4H, Ar–**H**, J=8.0 Hz), 7.93 (d, 2H, Ar–**H**, J=9.2 Hz), 7.85 (d, 2H, Ar–**H**, J=8.0 Hz), 7.64–7.60 (m, 8H, Ar–**H**), 7.41 (d, 2H, Ar–**H**, J=8.6 Hz), 7.32–7.15 (m, 10H, Ar–**H**), 4.33 (t, 4H, –COO–$\mathbf{CH_2}$, J=6.6 Hz), 4.01–3.88 (m, 4H, –O$\mathbf{CH_2}$–), 2.48 (t, 4H, –OCO$\mathbf{CH_2}$–, J=7.8 Hz), 1.81–0.87 (m, 50H, aliphatic–**H**); IR (KBr) ν_{max}/cm^{-1}: 2929, 1758, 1716, 1275; HPLC: 100%.

2.2.8 (*R*)-2, 2′-Bis{8-[4-(4-(octyloxycarbonyl)phenyl) phenyloxycarbonyl]octyloxy}-1, 1′-binaphthyl [(*R*)-Bi-8]. ^{1}H NMR (500 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.10 (d, 4H, Ar–**H**, J=8.1 Hz), 7.93 (d, 2H, Ar–**H**, J=9.2 Hz), 7.85 (d, 2H, Ar–**H**, J=8.6 Hz), 7.63–7.60 (m, 8H, Ar–**H**), 7.41 (d, 2H, Ar–**H**, J=9.2 Hz), 7.32–7.14 (m, 10H, Ar–**H**), 4.33 (t, 4H, –COO–$\mathbf{CH_2}$, J=6.6 Hz), 3.99–3.87 (m, 4H, –O$\mathbf{CH_2}$–), 2.54 (t, 4H, –OCO$\mathbf{CH_2}$–, J=7.5 Hz), 1.81–0.87 (m, 54H, aliphatic–**H**); IR (KBr) ν_{max}/cm^{-1}: 2928, 1755, 1719, 1275; HPLC: 100%.

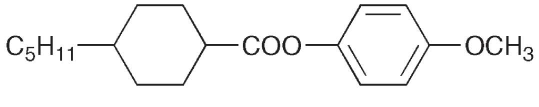
2.3 *Physical properties*

The initial phase assignments and corresponding transition temperatures for the products were determined by thermal optical microscopy using a polarizing microscope (POL, Optiphoto; Nikon Corp.) equipped with a microfinance (FP82; Mettler Inst. Corp.) and control unit (FP80). The heating and cooling rates were 5°C min^{-1}. Temperatures and enthalpies of transition were investigated using differential scanning calorimetry (DSC; DSC 6200 calorimeter, Seiko Corp.). The materials were studied at a scanning rate of 5°C min^{-1} for both heating and cooling cycles after being encapsulated in aluminium pans. The helical pitch in the N* phase was measured using the Cano wedge technique for a chiral nematic mixture consisting of a host nematic liquid-crystalline material and 2 wt% of each chiral additive. The mixtures were studied using the contact method; their chiral nematic helical twist senses were established. The standard materials used in the contact study were (*R*)-3-methyladipic acid bis [4-(5-octyl-2-pyrimidinyl)phenyl]ester [28] and (*S*)-2-methylbutyl 4-(4-decyloxybenzylideneamino)cinnamate



7-PYP-6O

Iso 68.0 N 36.5 recryst mp 47



MP-5-CA

Iso 70.1 N 16.1 recryst mp 40

Figure 2. Molecular structures and transition temperatures (°C) of the host nematic liquid crystals.

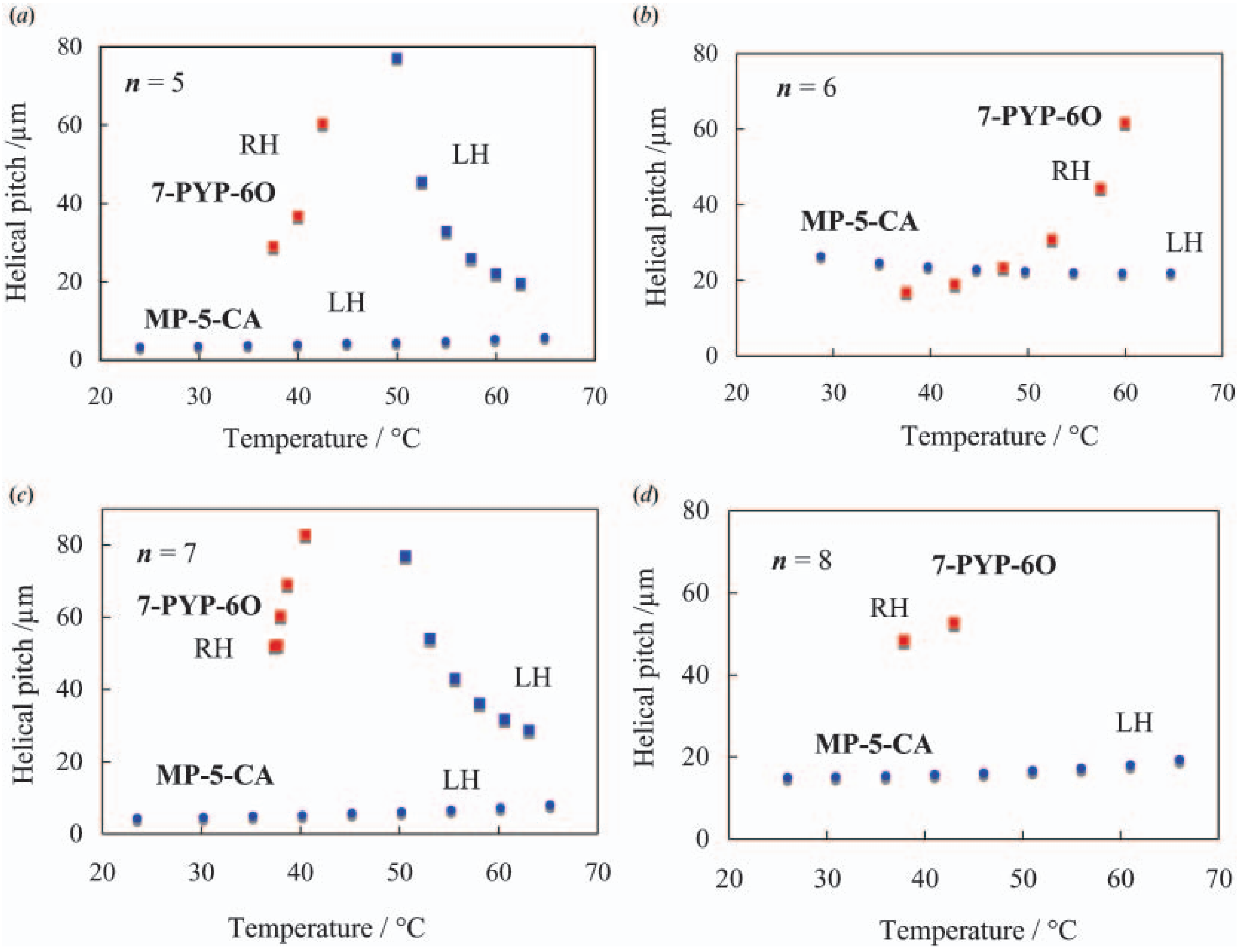


Figure 3. Temperature dependencies of N* helical pitch values induced by each **(*R*)-Bi-n** in the mixture with **7-PYP-6O** and that with **MP-5-CA**. A chiral mixture consists of 2 wt% of each chiral additive and a host material. Blue indicates a LH helical sense; red indicates a RH helical sense. See online version for colour.

(DOBAMBC [29]). The helical twist definition used in this article is identical to that used by Goodby [30].

3. Results and discussion

The chiral compounds possessing mesogenic moieties, (*R*)-2, 2′-bis{ω-[4-(4-(octyloxycarbonyl)phenyl)phenyloxycarbonyl]alkyloxy}-1, 1′-binaphthyl [**(*R*)-Bi-n**], and the corresponding binaphthyl derivative without the mesogenic moieties, (*R*)-2, 2′-bis[6-(ethyloxycarbonyl)-hexyloxy]-1, 1′-binaphthyl [**(*R*)-Et-6**], were prepared according to the synthesis outlined in scheme 1. The purity of each final compound was verified as 100% using high-performance liquid chromatography (HPLC) analysis. Their structures were elucidated using IR and ^{1}H NMR. The transition properties of **(*R*)-Bi-n** and **(*R*)-Et-6** are listed in table 1.

We investigated the chirality transfer from each binaphthyl derivative to a host nematic liquid crystal. A macroscopic measure of this chirality transfer is the helical pitch or helical twisting power (HTP). We observed the helical sign and pitch induced by each chiral dopant in different host nematic compounds. Molecular structures and transition temperatures of the host liquid-crystalline compounds are shown in figure 2. Both host compounds show N phases, but have different mesogenic cores.

Figure 3 shows the temperature dependence of chiral nematic (N*) helical pitch values induced by each **(*R*)-Bi-n** in the different host compounds. With respect to each mixture with **MP-5-CA**, all chiral additives were found to induce left-handed (LH) helical structures, and the respective temperature dependences of the induced pitches were small. The pitch shortens at lower

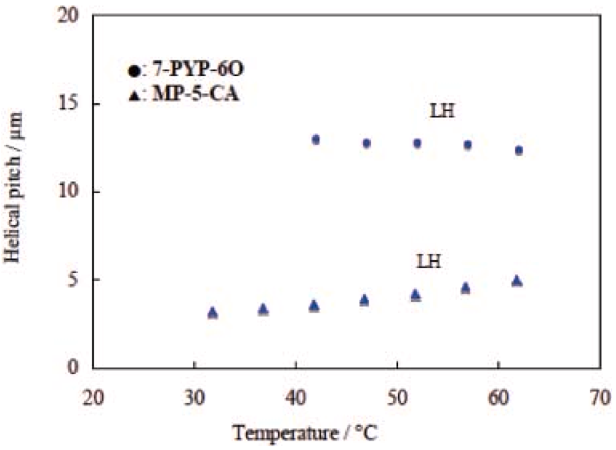


Figure 4. Temperature dependencies of N* helical pitch values induced by **(*R*)-Et-6** in the mixture with **7-PYP-6O** and that with **MP-5-CA**. A chiral mixture consists of 2 wt% of each chiral additive and a host material.

temperatures for **(*R*)-Bi-5**, **(*R*)-Bi-7** and **(*R*)-Bi-**8 in the mixtures, but increases for **(*R*)-Bi-6**. We do not have a clear explanation for this difference. With respect to the mixtures with **7-PYP-6O**, however, the induced helical structures were found to depend on the parity of the spacers of **(*R*)-Bi-n**. Temperature-dependent helical twist inversion was observed in the mixture doped with **(*R*)-Bi-5** and that doped with **(*R*)-Bi-7**. On the other hand, **(*R*)-Bi-6** was found to induce a right-handed (RH) helical structure in the mixture. The pitch values became markedly shorter with decreasing temperature. Furthermore, **(*R*)-Bi-8** induced a RH helical structure in the mixture. The induced pitches were longer than those induced by **(*R*)-Bi-6**. With respect to the mixture with **7-PYP-6O**, the pitches above 48°C in the N* phase were too long to be observed.

To clarify the effects of the binaphthyl group on twisting power, we investigated a helical structure induced by **(*R*)-Et-6**. Figure 4 shows the temperature dependence of N* helical pitch values induced by **(*R*)-Et-6** in each host material. Actually, **(*R*)-Et-6** was found to induce a LH helical structure in each host. The respective temperature dependences of the induced pitches were small.

Table 1. Phase transition temperatures on cooling of **(*R*)-Bi-n** and **(*R*)-Et-6**.

Compound	Phase transition temperature (°C) on cooling	
(*R*)-Bi-5	Iso Liq 2.1 glass	mp 64
(*R*)-Bi-6	Iso Liq 0.5 glass	mp 36
(*R*)-Bi-7	Iso Liq −0.1 glass	mp 49
(*R*)-Bi-8	Iso Liq −3.2 glass	mp 54
(*R*)-Et-6	Iso Liq< −50	

The helical sense and temperature dependence of the induced pitch are different for **(*R*)-Bi-6** possessing the two biphenyl moieties in different host liquid crystals. However, they are identical to those of **(*R*)-Et-6** without the mesogenic moieties. The chiral induction behaviour of molecules with atropisomeric biphenyl cores in ferroelectric liquid crystals was explained by chiral molecular recognition that a favourable structural match exists between chiral dopant and host molecules to undergo chirality transfer via core–core interactions [17]. Intramolecular and intermolecular chirality transfer processes have been investigated in systems of atropisomers as chiral dopants (see [18–20] and references therein). As **(*R*)-Et-6** has no biphenyl moiety that undergoes intermolecular core–core interactions with the neighbouring host molecules, the induced LH helical structure in each host is attributable to the axial chirality of **(*R*)-Et-6**. An optically pure 2, 2′-substituted 1, 1′-binaphthyl molecule can exist in either of two conformations: cisoid or transoid. Molecular–mechanical calculations were carried out using Chem3D MM2 programs (CambridgeSoft.Com) [31]. The MM2 calculations of **(*R*)-Bi-6** suggest that the cisoid conformation is more stable than the transoid. For the initial molecular configuration used for calculations, we assumed the cisoid conformer. The energy difference between the cisoid and transoid conformers of **(*R*)-Bi-6** was estimated to be 26 kJ mol^{-1}. For that reason, we assumed the cisoid conformer for **(*R*)-Bi-6**. Figure 5 shows a model for chirality transfer from **(*R*)-Bi-6** to a host nematic liquid crystal. The (*R*)-binaphthyl unit of **(*R*)-Bi-6** itself can induce a LH helical structure in a host nematic liquid crystal in much the same way as **(*R*)-Et-6**, and can organize the twist configuration of the two biphenyl groups, which is thought to be responsible for inducing another helicity. The host-dependent helical twist inversion for **(*R*)-Bi-6** can be explained as follows. In the mixture with **7-PYP-6O**, core–core interactions between a phenylpyrimidine moiety of **7-PYP-6O** and each biphenyl moiety of **(*R*)-Bi-6** can occur. RH helicity produced by the twist configuration of the biphenyl moieties of **(*R*)-Bi-6** is thought to be transferred to the host molecules via the core–core interactions. On the other hand, in the mixture with **MP-5-CA**, such a structural match cannot exist between 4-methoxy cyclohexanecarboxylate of **MP-5-CA** and a biphenyl moiety of **(*R*)-Bi-6**. The **(*R*)-Bi-5**, **(*R*)-Bi-7** and **(*R*)-Bi-8** were also found to induce a LH helical structure in the mixture with **MP-5-CA**. Therefore, the axial chirality of **(*R*)-Bi-n** is thought to be transferred to the host nematic liquid crystal.

Next we address the odd–even effects for the twisting power of **(*R*)-Bi-n** in the mixture with **7-PYP-6O**. With

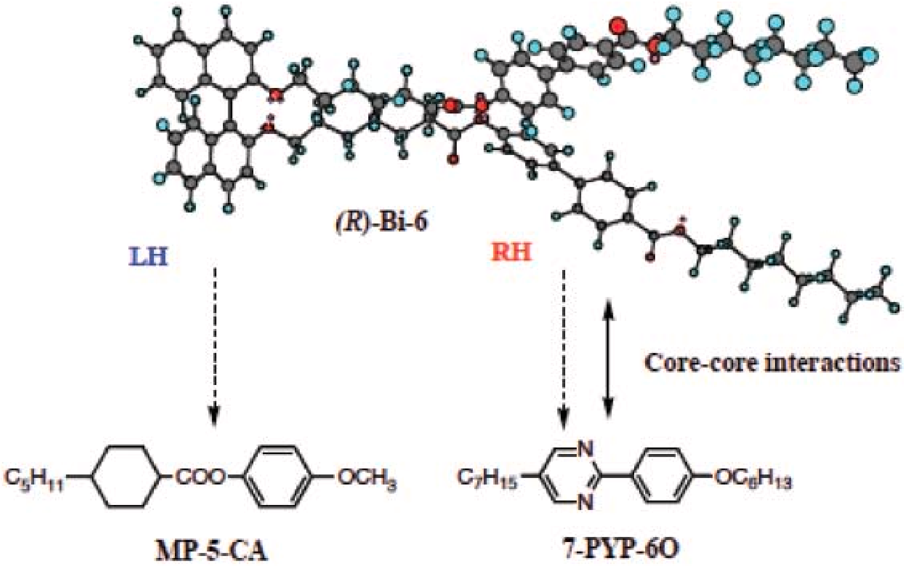


Figure 5. A model for chirality transfer from **(*R*)-Bi-6** to a host nematic liquid crystal.

respect to **(*R*)-Bi-8**, a RH helical structure was induced in the mixture and the helical pitch became shorter with decreasing temperature. Although the pitches induced by **(*R*)-Bi-8** were longer than that of **(*R*)-Bi-6**, the twist configuration of the two mesogenic groups is thought to induce a RH helical structure in **7-PYP-6O** via favourable core–core interactions. With respect to **(*R*)-Bi-n** with odd-numbered spacers, we do not have sufficient explanation for the temperature-dependent helical twist inversion. A possible mechanism is described below. More than by even members, helical pitches induced by odd members induced shorter pitches in the mixture with **MP-5-CA**. The twisting power of the axial chirality of the odd members is therefore stronger than that of the even members. The twist inversion can be interpreted in terms of competition between axial chirality of the binaphthyl group and twist configuration of the biphenyl moieties. The axial chirality can induce a LH helical structure in the higher-temperature region, whereas the twist configuration can induce a RH structure in the lower-temperature region.

4. Conclusions

We have investigated the structure–property relationship in chirality transfer from a binaphthyl derivative to a host nematic liquid crystal. **(*R*)-Bi-n** possessing two biphenyl moieties was found to induce different helical structures, i.e. opposite twist senses and distinct temperature dependence of helical pitch, in two host nematic liquid crystals, **7-PYP-6O** and **MP-5-CA**. Furthermore, odd–even effects were observed for the induced helical structure in mixtures with **7-PYP-6O**. Temperature-dependent helical twist inversion was observed for mixtures with **(*R*)-Bi-n** with odd-numbered spacers, whereas a RH helix was observed for mixtures with **(*R*)-Bi-n** with even-numbered spacers. The specific twist interaction of **(*R*)-Bi-n** is explainable in that it has two origins for the twisting power: an asymmetric axis of the binaphthyl unit and a twist configuration of the two biphenyl moieties.

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