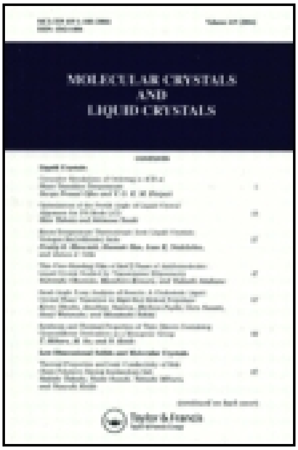

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Twisting Power of a Novel Binaphthyl Derivative Possessing Laterally Attached Mesogenic Units

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Twisting Power of a Novel Binaphthyl Derivative Possessing Laterally Attached Mesogenic Units

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*We prepared a novel binaphthyl derivative possessing laterally attached mesogenic units, (R)-2, 2′-bis{6-[2-(4-octyloxyphenyloxycarbonyloxy)-5-octyloxyphenyloxycarbonyl]hexyloxy}-1,1′-binaphthyl [(**R**)-**1**], and that possessing terminally attached mesogenic units, (R)-2, 2′-bis{6-[4-(4-octyloxyphenyloxycarbonyl)phenyloxycarbonyl]hexyloxy}-1, 1′-binaphthyl [(**R**)-**2**]. We investigated their induced helical senses and pitches in the chiral nematic (N^*) and chiral smectic C (SmC^*) phases in the mixture with a host liquid crystal. (**R**)-**1** induced a left-handed (LH) helix in the N^* phase, whereas (**R**)-**2** induced a right-handed (RH) helix. We discuss chirality transfer from each binaphthyl derivative to a host liquid crystal.*

Keywords: binaphthyl; chirality; liquid crystal

1. INTRODUCTION

Investigation of chirality in liquid crystals is an exciting area of liquid crystal science [1]. Chirality-dependent frustrated phases have been investigated: twist grain boundary phases (TGB) and blue phases (BP) [2]. The appearance of these phases is created through competition between chiral twisting force and the molecules' packing such that they fill the space uniformly. 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

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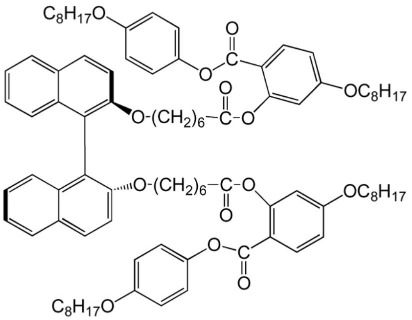
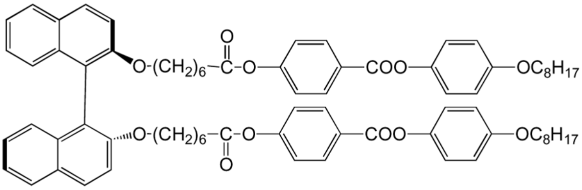
extensively [3–9]. Binaphthyl derivatives possessing axial chirality are known to induce chirality-dependent properties not only for organic synthesis, but also for liquid crystal science. Akagi *et al*. reported an asymmetric synthesis of helical polyacetylene with a chiral nematic reaction field, which was prepared by adding a binaphthyl derivative to a host liquid crystal [10]. Kirste and Scherowsky investigated temperature-dependent helix inversion in induced chiral nematic phases of a binaphthyl ester and a nematic mixture [11]. They speculated that temperature-dependent conformational changes between cisoid and transoid of the 1,1-binapthyl derivative are responsible for that behaviour. We have investigated chirality transfer from a binaphthyl derivative to a host nematic liquid crystal. We found that: 1) host-guest molecular recognition affects on the chirality transfer [12] and 2) two mesogenic parts connected via a binaphthyl group can induce a helical structure [13].

For the present study, we prepared a novel binaphthyl derivative possessing laterally attached mesogenic units [(***R***)-**1**] and that possessing terminally attached mesogenic units [(***R***)-**2**], and investigated



(*R*)-1



(*R*)-2

FIGURE 1 Molecular structures of (***R***)-**1** possessing laterally attached mesogenic units and (***R***)-**2** possessing terminally attached mesogenic units.

there induced helical senses and pitches in the chiral nematic (N^*) and chiral smectic C (SmC^*) phases in the mixture with a host liquid crystal. Figure 1 shows the molecular structures.

2. EXPERIMENTAL

2.1. Spectroscopic Analysis

The purities of all final compounds were checked using HPLC (JAIGEL-1H column, LC9101; Japan Analytical Industry Co., Ltd.). Chloroform was used as eluent. Detection of products was achieved using UV irradiation ($\lambda = 254\,\text{nm}$).

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

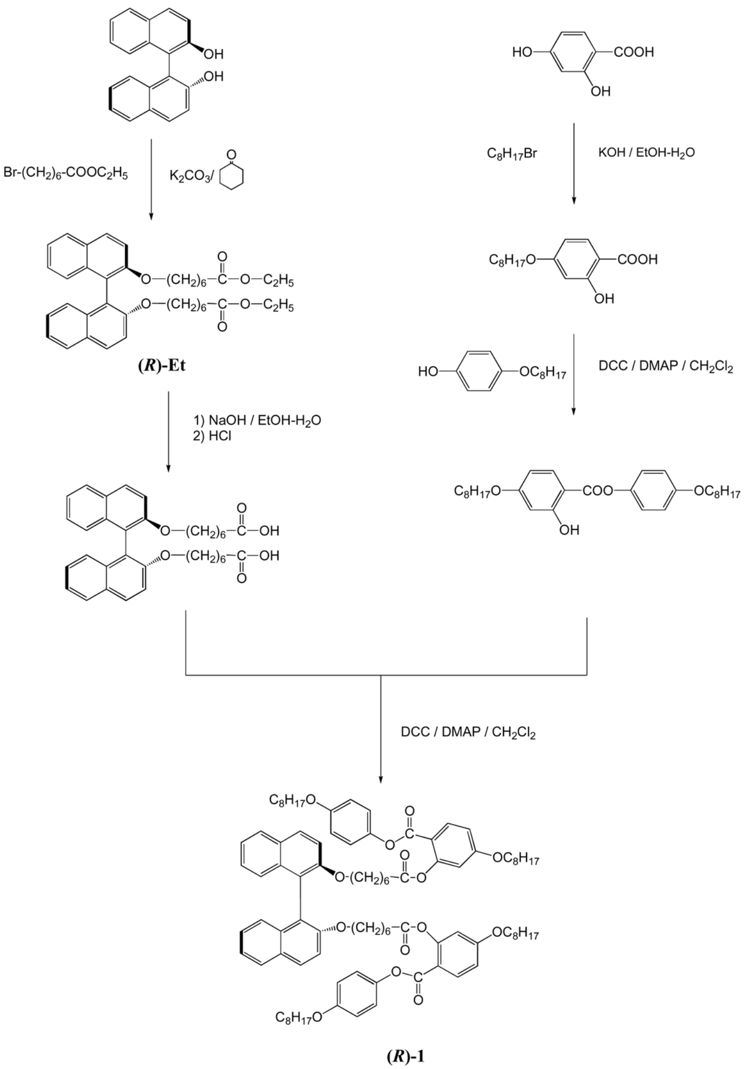
2.2. Preparation of Materials

Compound (***R***)-**1** was prepared by the synthesis outlined in Scheme 1. Preparation of (*R*)-**2**, 2′-bis[6-(ethyloxycarbonyl)hexyloxy]-1,1′-binaphthyl [(***R***)-Et-6] and (*R*)-2, 2′-bis(6-carboxyhexyloxy)-1, 1′-binaphthyl was already reported [13].

2.2.1. *(R)-2, 2′-Bis{6-[2-(4-octyloxyphenyloxycarbonyloxy)-5-octyloxyphenyloxycarbonyl]hexyloxy}-1,1′-binaphthyl [(R)-1]*

To a solution of 2, 4-dihydroxybenzoic acid (7.7 g, 50 mmol) and 1-bromooctane (10.4 g, 53 mmol) in ethanol (70 ml) was added a solution of KOH (10.3 g, 184 mmol) in water (40 ml). The mixture was stirred at 95°C for 10 h. After the solvent was removed, the residue was acidified with aq. HCl. The solution was extracted with diethylether (3×50 ml). The organic layers were combined, dried over anhydrous magnesium sulfate, filtered and evaporated to give 2-hydroxy-4-octyloxybenzoic acid; yield 1.23 g (9%).

To a solution of 2-hydroxy-4-octyloxybenzoic acid (1.0 g, 3.8 mmol) and 4-octyloxyphenol (0.84 g, 3.8 mmol) in dichloromethane (30 ml), *N, N′*-dicyclohexylcarbodiimide (0.8 g, 4 mmol), and 4-(*N,N*-dimethylamino)pyridine (0.05 g, 0.4 mmol) were added. The resulting solution was stirred at room temperature for 3 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 hexane and ethyl acetate (15/1) mixture as the eluent. Recrystallization gave 4-octyloxyphenyl 2-hydroxy-4-octyloxyphenylcarboxylate; yield 0.71 g (40%).



SCHEME 1 Synthesis of (***R***)-**1**.

To a solution of (*R*)-2, 2′-bis(6-carboxyhexyloxy)-1,1′-binaphthyl (0.16 g, 0.3 mmol) and 4-octyloxyphenyl 2-hydroxy-4-octyloxyphenylcarboxylate (0.29 g, 0.6 mmol) in dichloromethane (15 ml), *N,N′*-dicyclohexylcarbodiimide (0.17 g, 0.8 mmol), and 4-(*N,N*-dimethylamino)pyridine (0.01 g, 0.06 mmol) were added. The resulting solution was stirred at room temperature for 7 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 toluene and ethyl acetate (15/1) mixture as the eluent to give the desired product: yield 0.24 g (55%). ^{1}H NMR (400 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.17 (d, 2H, Ar-**H**, $J = 8.8$ Hz), 7.94 (d, 2H, Ar-**H**, $J = 8.8$ Hz), 7.84 (d, 1H, Ar-**H**, $J = 8.3$ Hz), 7.39 (d, 2H, Ar-**H**, $J = 8.8$ Hz), 7.32–7.16 (m, 6H, Ar-**H**), 7.05 (d, 4H, Ar-**H**, $J = 9.3$ Hz), 6.92–6.86 (m, 6H, Ar-**H**), 6.64 (d, 2H, Ar-**H**, $J = 2.4$ Hz), 4.04 (t, 4H, -O-C$\mathbf{H}_2$, $J = 6.3$ Hz), 3.98–3.82 (m, 8H, -OC$\mathbf{H}_2$-), 2.38 (t, 4H, -OCOC$\mathbf{H}_2$-, $J = 7.8$ Hz), 1.86–1.74 (m, 8H, -OCH$_2$C$\mathbf{H}_2$-), 1.46–1.31 (m, 48H aliphatic-**H**), 1.01–0.81 (m, 20H aliphatic-**H**); IR (neat) ν_{max}/cm^{-1}: 2929, 1767, 1736, 1245, 1132; HPLC: 100%.

2.2.2. *(R)-2, 2′-Bis{6-[4-(4-octyloxyphenyloxycarbonyl)phenyloxycarbonyl]hexyloxy}-1,1′-binaphthyl [(R)-2]*

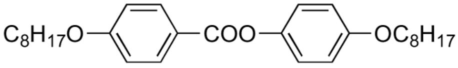
To a solution of 4-methoxycarbonyloxybiphenyl-4′-carboxylic acid (1.2 g, 6.1 mmol) and diethylazodicarboxylate (1.0 g, 6.0 mmol) in tetrahydrofuran (THF, 80 ml) was added triphenylphosphine (1.9 g, 7.1 mmol) in THF (28 ml). The reaction mixture was stirred at room temperature for 24 h. After the filtration of participate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a toluene and ethyl acetate (15/1) mixture to give 4-octyloxyphenyl 4-methoxycarbonyloxybenzoate; yield 0.48 g (20%).

To a solution of 4-octyloxyphenyl 4-methoxycarbonyloxybenzoate (0.28 g, 0.7 mmol) in ethanol (30 ml) was added an aqueous ammonia solution (28~30%, 1.6 ml). The reaction mixture was stirred at room temperature for 3 h. The solvent was removed by evaporation. To the residue was added water and the solution was extracted with diethylether (60 ml). The combined organic layers were dried over anhydrous magnesium sulfate. After the drying agent and the solvent were removed, 4-octyloxyphenyl 4-hydroxybenzoate was obtained without further purification; yield 0.24 g (99%).

To a solution of (*R*)-2, 2′-bis(6-carboxyhexyloxy)-1,1′-binaphthyl (0.11 g, 0.2 mmol) and 4-octyloxyphenyl 4-hydroxybenzoate (0.14 g, 0.4 mmol) in dichloromethane (30 ml), *N,N*′-dicyclohexylcarbodiimide (0.12 g, 0.6 mmol), and 4-(*N,N*-dimethylamino)pyridine (0.01 g, 0.06 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 toluene and ethyl acetate (15/1) mixture, and then washed with etanol to give the desired product: yield 0.10 g (41%). ^{1}H NMR (500 MHz, solvent $CDCl_3$, standard TMS) δ_H/ppm: 8.22 (d, 2H, Ar-**H**, $J = 9.2$ Hz), 7.94 (d, 2H, Ar-**H**, $J = 9.2$ Hz), 7.86 (d, 1H, Ar-**H**, $J = 8.0$ Hz), 7.42 (d, 2H, Ar-**H**, $J = 8.0$ Hz), 7.33–7.16 (m, 10H, Ar-**H**), 7.10 (d, 4H, Ar-**H**, $J = 9.2$ Hz), 6.93 (d, 4H, Ar-**H**, $J = 8.6$ Hz), 4.03–3.99 (m, 2H, -OC**H**$_2$-), 3.96 (t, 4H, -O-C**H**$_2$, $J = 6.6$ Hz), 3.93–3.88 (m, 2H, -OC**H**$_2$-), 2.35 (t, 4H, -OCOC**H**$_2$-, $J = 7.5$ Hz), 1.86–1.76 (m, 4H, -OCH$_2$C**H**$_2$-), 1.47–1.23 (m, 28H aliphatic-**H**), 1.09–0.88 (m, 14H aliphatic-**H**); IR (neat) $\nu_{max}/\mathrm{cm}^{-1}$: 2928, 1761, 1736, 1270, 1247; 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 aluminum 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, 4-pentyloxyphenyl 4-octyloxybenzoate (**5P-8-PA**) and 2 wt% of each chiral additive. Molecular structure and phase transition temperatures of **5P-8-PA** are shown in Figure 2. 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 [14] and (*S*)-2-methylbutyl 4-(4-decyloxybenzylideneamino)cinnamate (**DOBAMBC** [15]). The helical pitch in the SmC* phase was obtained directly by measuring the distance between the lines corresponding to the full pitch under polarized light microscopy for a homogeneously aligned sample in a cell with 300 μm spacing. The helical twist senses in the SmC* phase were measured by



5P-8-PA: Cry 56 °C SmC 62 °C SmA 64 °C N 85 °C Iso

FIGURE 2 Molecular structure and phase transition temperatures of the host liquid crystal.

using the contact method. The helical twist definition used in this report is identical to that used by Goodby [16].

3. RESULTS AND DISCUSSION

On cooling, (***R***)-**1** exhibited a glass transition at −15°C, whereas (***R***)-**2** showed the following phase sequence: isotropic liquid 28°C (2.3 $\mathrm{kJmol^{-1}}$) unidentified mesophase I 24°C (8.7 $\mathrm{kJmol^{-1}}$) unidentified mesophase II; the melting temperature was 42°C.

We investigated the chirality transfer from each binaphthyl derivative to the host liquid crystal. A macroscopic measure of this chirality transfer is the helical pitch or helical twisting power (HTP). We observed the helical sense and pitch induced by each chiral dopant in the host **5P-8-PA**. Figure 3 shows the temperature dependence of chiral nematic (N^*) helical pitch values induced by 2 wt% of (***R***)-**1** in **5P-8-PA**. (***R***)-**1** was found to induce left-handed (LH) helical structures. The helical pitch value at 72.2°C was 24.6 μm. The helical pitch is independent of the temperature. On the other hand, a dechiralization line in the chiral smectic C (SmC^*) was not observed, indicating that helical structure in the SmC^* phase is incomplete.

Figure 4 shows the temperature dependence of N^* and SmC^* helical pitch values induced by 2 wt% of (***R***)-**2** in **5P-8-PA**. (***R***)-**2** was found to induce right-handed (RH) helical structures in the N^* and

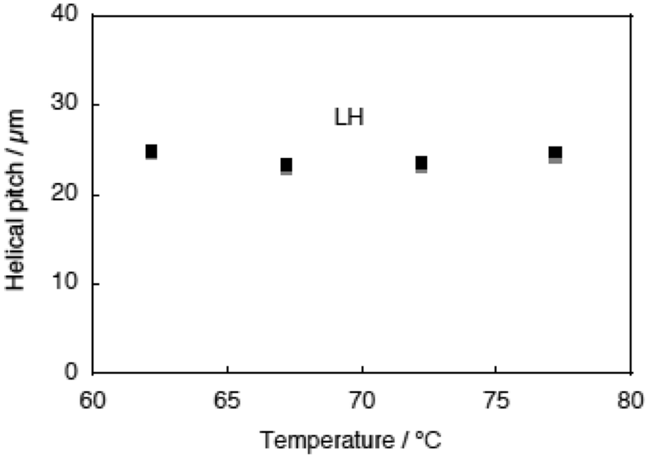


FIGURE 3 Temperature dependence of N^* helical pitch values induced by 2 wt% of (***R***)-**1** in **5P-8-PA**.

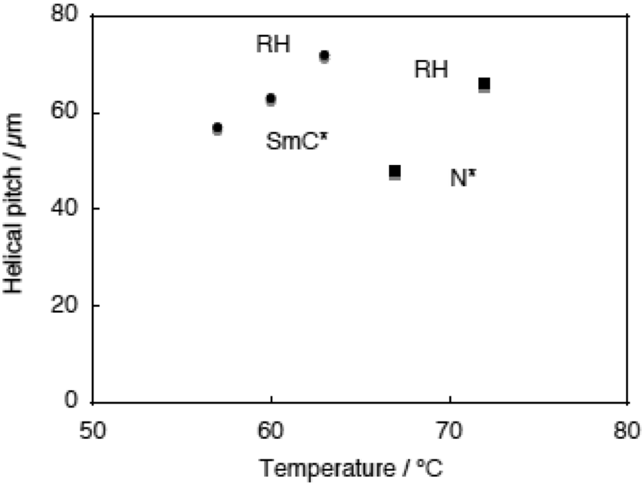
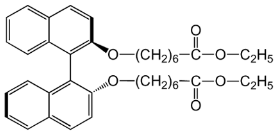


FIGURE 4 Temperature dependence of N* and SmC* helical pitch values induced by 2 wt% of (***R***)-**2** in **5P-8-PA**.

SmC* phases. Both N* and SmC* pitches shorten with decreasing the temperature.

To clarify the effects of the binaphthyl group on twisting power, we investigated a helical structure induced by a binaphthyl derivative without an attached mesognic group, (***R***)-**Et**. Figure 5 shows the temperature dependence of N* helical pitch values induced by 2 wt% of (***R***)-**Et** in **5P-8-PA**. (***R***)-**Et** was found to induce a LH helical structure. The helical pitch is independent of the temperature. In the SmC* phase, a dechiralization line was not observed, indicating that helical structure in the SmC* phase is incomplete.

The present results are explainable in terms of two origins for twisting power of a binaphthyl derivative [13]. The binaphthyl derivative possessing terminally attached biphenyl moieties has two origins for the twisting power: an asymmetric axis of the binaphthyl unit and a twist conformation of the two biphenyl moieties. Both (***R***)-**1** and (***R***)-**Et** induce a LH helical structure in the N* phase, and the helical pitches are independent of the temperature. Then, the twisting power of each chiral compound is too weak to form a helix in the SmC* phase. Therefore, the twisting power of (***R***)-**1** in the N* and SmC* phases can result from an asymmetric axis of the binaphthyl unit. The two phenylbenzoate moieties are thought to be far from each other, thus, they cannot form a twist conformation. On the other hand, (***R***)-**2** induces a RH helical structure in the N* and SmC* phases, and the helical pitch shortens as decreasing the temperature. Twisting power of (***R***)-**2** is



(*R*)-Et

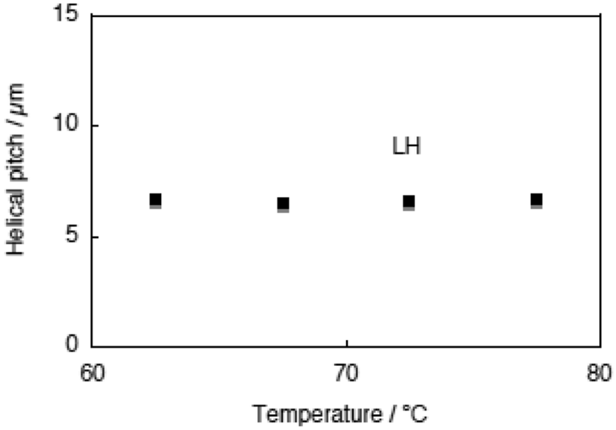


FIGURE 5 Temperature dependence of N* helical pitch values induced by 2 wt% of (***R***)-**Et** in **5P-8-PA**.

thought to attributed to a twist conformation of the terminally attached phenyl benzoate moieties.

4. CONCLUSION

We prepared two binaphthyl derivatives, i.e., (***R***)-**1** possessing laterally attached phenyl benzoate moieties and (***R***)-**2** possessing terminally attached phenyl benzoate moieties. They were found to induce different helical structures, i.e., opposite twist senses and distinct temperature dependence of helical pitch in the N* phase in the mixture with a host liquid crystal, **5P-8-PA**. These results are consistent with our reported chirality transfer mechanism of a binaphthyl derivative possessing laterally attached mesogenic moieties [13].

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