

Host-guest effect on chirality transfer from a binaphthyl derivative to a host nematic liquid crystal

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Electronic Supplementary Information

1. Synthetic procedure for (*R, R*)-BM

Spectroscopic analysis

Purification of final products was carried out using column chromatography over silica gel (63-210 μ m) (KANTO CHEMICAL Co., INC.) using a toluene-ethyl acetate mixture as the eluent, followed by the recrystallization from ethanol. The purities of compounds were checked by thin layer chromatography (TLC, aluminum sheets, silica gel 60 F254 from Merck). A toluene-ethylacetate mixture was used as the solvent. Detection of products was achieved by UV irradiation ($\lambda = 254$ and 365 nm). The purity of the final compound was checked by HPLC (Japan Analytical Industry Co., Ltd., LC9101, JAIGEL-1H column). Chloroform was used as eluent. Detection of products was achieved by UV irradiation ($\lambda = 254$ nm).

The structures of the final products were elucidated by infrared (IR) spectroscopy (BIO RAD FTS-30) and proton nuclear magnetic resonance (^1H NMR) spectroscopy (JEOL JNM-GX270 or JEOL JNM-A400).

Preparation of materials

(*S*)-2-Octanol was purchased from Aldrich Chemical Company. (*R*)-1, 1'-Bi(2-naphthol) was purchased from Tokyo Kasei Kogyo Co., Ltd.

(*R, R*)-4-[4-(1-Methylheptyloxycarbonyl)phenyl]phenyl 7-[(1, 1'-binaphthalene)-2-hydroxy-2'-yloxy]heptanoate, (*R, R*)-BM

(*R*)-1-Methylheptyl 4-methoxycarbonyloxybiphenyl-4'-carboxylate

To a solution of 4-methoxycarbonyloxybiphenyl-4'-carboxylic acid (2.2 g, 8.0 mmol), (*R*)-2-octanol (1.04 g, 8.0 mmol) and diethylazodicarboxylate (3.5 g, 8.0 mmol) in

tetrahydrofuran (THF, 120 ml) was added triphenylphosphine (2.4 g, 9.0 mmol) in THF (40 ml). The reaction mixture was stirred at room temperature for 24 h. After the filtration of particulate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with dichloromethane. The desired product was obtained. Yield: 1.94 g (68%).

¹H NMR (270MHz, solvent CDCl₃, standard TMS) δ_H/ppm: 8.10(d, 2H, Ar-H, J=8.4Hz), 7.62(d, 4H, Ar-H, J=8.4Hz), 7.28(m, 2H, Ar-H), 5.17(m, 1H, -C*H(CH₃)), 3.93(s, 3H, -OCH₃), 1.79-1.28(m, 13H, aliphatic-H), 0.88(t, 3H, -CH₃, J=6.8Hz)

Ref. E-1. O. Mitsunobu, *Synthesis*, 1981, 1.

(R)-1-Methylheptyl 4-hydroxybiphenyl-4'-carboxylate

To a solution of (R)-1-methylheptyl 4-methoxycarbonyloxybiphenyl-4'-carboxylate (1.94 g, 5.0 mmol) in ethanol (75 ml) was added an aqueous ammonia solution (28~30%, 12.5 ml). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by evaporation. To the residue was added water, and the solution was extracted with diethylether (100 ml). The combined organic layers were dried over anhydrous sodium sulfate. After the drying agent and the solvent were removed, the desired product was obtained without further purification. Yield: 1.50 g (91%)

¹H NMR (270MHz, solvent CDCl₃, standard TMS) δ_H/ppm: 8.06(d, 2H, Ar-H, J=8.4Hz), 7.60(d, 2H, Ar-H, J=8.4Hz), 7.51(d, 2H, Ar-H, J=8.6Hz), 6.95(d, 2H, Ar-H, J=8.6Hz), 5.17(m, 1H, -C*H(CH₃)), 3.93(s, 3H, -OCH₃), 1.78-1.29(m, 11H, aliphatic-H), 0.88(t, 3H, -CH₃, J=6.8Hz)

(R)-7-[(1, 1'-Binaphthalene)-2-hydroxy-2'-yloxy]heptanoic acid

To a solution of (R)-1, 1'-bi(2-naphthol) (0.86g, 3.0 mmol) and ethyl 7-bromoheptanoate (1.4 g, 6.0 mmol) in acetone (60 ml) was added potassium carbonate (0.83 g, 6.0 mmol). The reaction mixture was stirred under reflux for 7 h. After the filtration of particulate, the solvent was removed by evaporation. The residue was purified by column chromatography on silica gel with a toluene-ethylacetate (7:1) mixture as the eluent. The intermediate product, (R)-ethyl 7-[(1, 1'-binaphthalene)-2-hydroxy-2'-yloxy]heptanoate, was obtained. Yield: 0.95 g (72%).

(*R*)-ethyl 7-[(1, 1'-binaphthalene)-2-hydroxy-2'-yloxy]heptanoate (0.94 g, 2.1 mmol) was added to a solution of NaOH (0.14 g, 3.5 mmol) in an ethanol-water (4:1) mixture. The resulting solution was stirred under reflux for 6 h. After removal of the ethanol by evaporation, the residue was acidified with aq. HCl. The solution was extracted with dichloromethane (3 x 50 ml). The organic layers were combined, dried over magnesium sulfate, filtered and evaporated. Yield: 0.78 g (90%).

¹H NMR (270MHz, solvent CDCl₃, standard TMS) δ_H/ppm: 8.04(d, 1H, Ar-**H**, J=8.8Hz), 7.91(d, 2H, Ar-**H**, J=8.8Hz), 7.87(d, 1H, Ar-**H**, J=7.8Hz), 7.47(d, 1H, Ar-**H**, J=8.8Hz), 7.41-7.20 (m, 6H, Ar-**H**), 7.07(d, 1H, Ar-**H**, J=8.3Hz), 4.07-3.93(m, 2H, -OCH₂-), 2.17(t, 2H, -OCOCH₂-, J=7.6Hz), 1.51-1.34(m, 4H, aliphatic-**H**), 1.10-0.95(m, 4H, aliphatic-**H**).

Ref. E-2. J. Lu, S-Z, Kang, S-L, Xu, Q-D, Zeng, C. Wang, L-J, Wan and C-L, Bai, *Chem. Commun.*, 2003, 1498.

(*R*, *R*)-4-[4-(1-Methylheptyloxy)phenyl]phenyl 7-[(1, 1'-binaphthalene)-2-hydroxy-2'-yloxy]heptanoate, (*R*, *R*)-BM

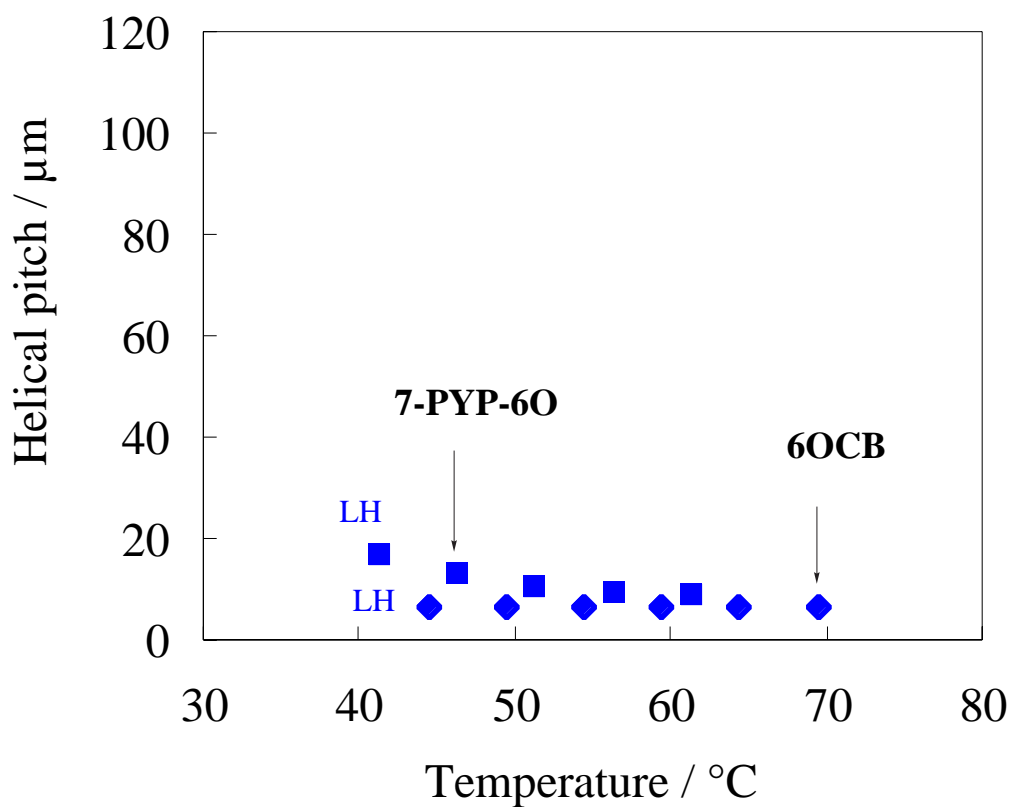
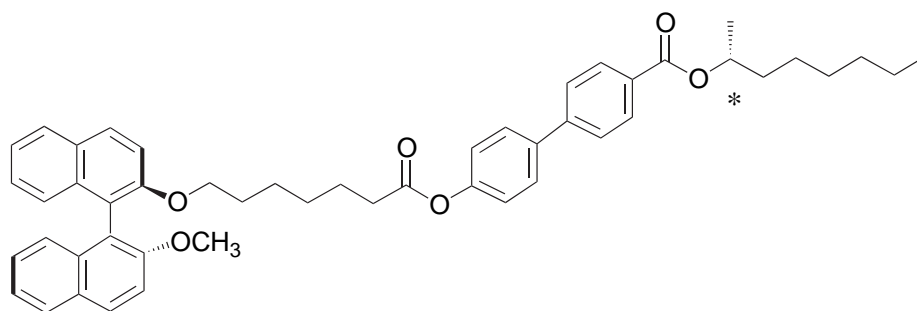
To a solution of (*R*)-7-[(1, 1'-binaphthalene)-2-hydroxy-2'-yloxy]heptanoic acid (0.22g, 0.5mmol) in dichloromethane (10ml), (*R*)-1-Methylheptyl 4-hydroxybiphenyl-4'-carboxylate (0.26g, 0.8mmol), dicyclohexylcarbodiimide (0.21g, 1.0mmol), and 4-(*N,N*-dimethylamino)pyridine (0.10g, 0.08mmol) were added. The resulting solution was stirred at room temperature for 4 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-ethylacetate (30:1) mixture as the eluent and reprecipitated with dichloromethane/ethanol and then dichloromethane / hexane, giving the desired product as colourless liquid. Yield: 0.14 g (39 %).

¹H NMR (400MHz, solvent CDCl₃, standard TMS) δ_H/ppm: 8.13(d, 2H, Ar-**H**, J=8.3Hz), 8.05(d, 1H, Ar-**H**, J=8.8Hz), 7.92(d, 2H, Ar-**H**, J=8.8Hz), 7.92(d, 1H, Ar-**H**, J=8.3Hz), 7.66(d, 2H, Ar-**H**, J=4.9Hz), 7.63(d, 2H, Ar-**H**, J=4.9Hz), 7.49(d, 1H, Ar-**H**, J=8.8Hz), 7.42-7.18(m, 8H, Ar-**H**), 7.08(d, 1H, Ar-**H**, J=8.8Hz), 5.23-5.16(m, 1H, -C***H**(CH₃)), 4.10-3.96(m, 2H, -OCH₂), 2.40(t, 2H, -OCOCH₂-, J=7.6Hz), 1.80-1.01(m, 21H, aliphatic-**H**), 0.91(m, 3H, -CH₃, J=6.8Hz); IR (neat) ν_{max}/cm⁻¹: 3430, 2930, 1757, 1710, 1274; Purity: 100 %.

2. Liquid-crystalline and physical properties

The initial assignments and corresponding transition temperatures for the products were determined by thermal optical microscopy using a Nikon Optiphot POL polarizing microscope equipped with a Mettler FP82 microfurnace and FP80 control unit. The heating and cooling rates were $5^{\circ}\text{Cmin}^{-1}$. 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 $5^{\circ}\text{Cmin}^{-1}$, 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. 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.

Ref. E-3. J. W. Goodby, *J. Mater. Chem.*, 1991, **1**, 307.



ESI Figure 1. Structure of the methylated compound and the temperature dependence of helical pitch values induced by 2 wt% of the compound in each host material.