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Katsuhiko Kanazawa [a], Isao Higuchi [a] & Kazuo Akagi [a]

[a] Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, 305-8573, Japan

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Synthesis of Liquid Crystalline Binaphthyl Derivatives

KATSUHIKO KANAZAWA, ISAO HIGUCHI and KAZUO AKAGI

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305–8573, Japan

We present the first liquid crystalline (LC) binaphthyl derivatives, in which the rigid rod-like substituents containing phenylcyclohexyl mesogenic cores are introduced into the 2, 2′, 6, and 6′ positions of the chiral binaphthyl rings. The binaphthyl derivatives show enantiotropic smectic A phase, but neither chiral nematic nor chiral smectic phase. The present quadri-substituted binaphthyl derivatives gave larger values in twisting power (β_M), compared with the non-substituted and di-substituted binaphthyl derivatives.

Keywords: binaphthyl derivatives; liquid crystallinity; axial chirality; chiral dopant; fluorescence

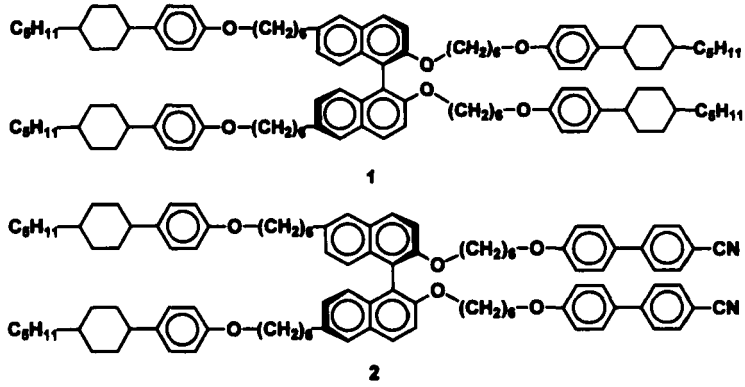
INTRODUCTION

It is well known that chiral binaphthyl derivatives are thermally stable and hardly racemized. This is because there exist large nuclear repulsions between hydrogens of 2 and 2' positions and that of 8 and 8' positions of naphthyl rings. Such nuclear repulrious cause a spatially restricted internal rotation in term of two

naphthyl rings. Thus, the chiral binaphthyl derivatives have been extensively used as chiral reagents[1], chiral dopants[2, 3], and chiral ligands of metal complexes[4].

Although various binaphthyl deriveatives have been synthesized so far, none of them exhibit meso phase. If the binaphthyl derivative shows liquid crystalline (LC) phase, it should have novel properties due to the strong chirality. Only a few examples of axially chiral compounds with meso phase have been reported[5].

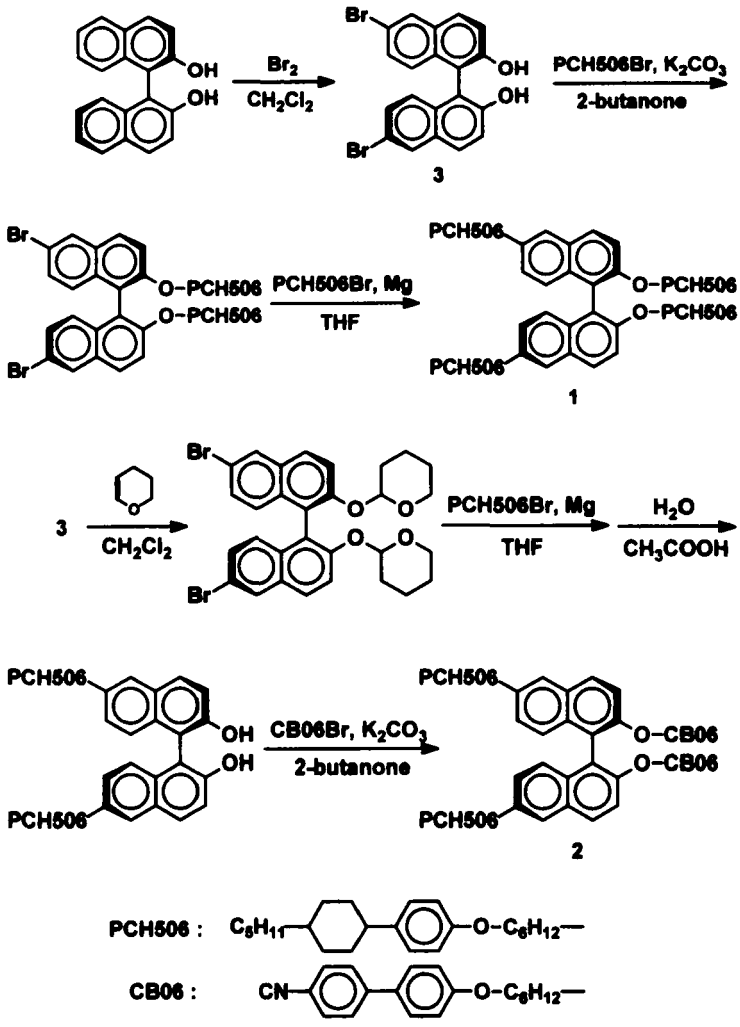
In the present study, novel LC binaphthyl derivatives **1** and **2**, as shown in Scheme 1, were synthesized. Measurements of polarizing optical microscope, differential scanning calorimeter, and X-ray diffraction showed that the mesophase observed for **1** and **2** is an enantiotropic smectic phase.



SCHEME 1 Liquid crystalline binaphthyl derivatives **1** and **2**.

RESULTS AND DISCUSSION

Synthesis: The syntheses of the binaphthyl derivatives **1** and **2** are shown in Scheme 2. The bromination[6] of (*R*)-2, 2'-dihydroxy-1, 1'-binaphtyl in CH_2Cl_2



SCHEME 2 Syntheses of **1** and **2**.

gave the dibromide **3** as white solid in 77 % yield. Williamson etherification between **3** and PCH506Br, [*p*-(*trans*-4-*n*-pentylcyclohexyl)-phenoxy]-1-bromohexane], gave the compound **4** as pale yellow oil in 86 % yield. The Grignard reaction between **4** and PCH506Br gave the compound **1** as pale yellow solid in 80 % yield.

The hydroxy groups of **3** were protected[7] to give the compound **5**, white solid in 75 % yeild. Similar proceduer using Grignard reaction was adopted, and followed by the hydrosis in acetic acid, THF and H_2O. Thus the compound **6** was obtained as pale yellow solid in 17 % yield. Williamson etherification between **6** and CBO6, [6-(4'-cyano-1, 1'-biphenylyl-4-oxy)-1-bromohexane], gave the compound **2** as pale yellow solid in 42 % yield.

Mesomorphic Properties : Mesomorphic properties of **1** and **2** were investigated by polarized optical microscopy and differential scanning calorimetry (Fig. 1). The transition temperatures of **1** were as follows ; G→ 51→ S_A → 66 → I, G ← 50 ← S_A ← 63 ← I in heating and cooling processes, respectively.

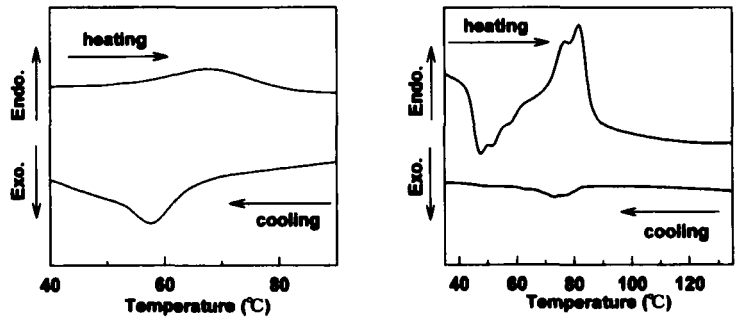


FIGURE 1 Differential scanning calorimetry thermographs of **1** and **2**.

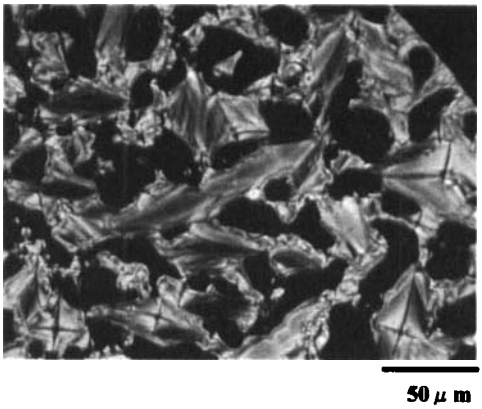


FIGURE 2 Polarizing optical micrograph of **1** (62℃) in the cooling process. See Color Plate XXIX at the back of this issue.

The corresponding enthalpy changes between S_A and isotropic phases in **1** were 9.3 and 6.4 J/g in heating and cooling processes, respectively. The transition temperature of **2** were clearly observed in only cooling process ; G ← 69 ← S_{X1} ← 81 ← S_{X2} ← 87 ← I. The X-ray diffraction of **1** showed two peaks in the small angle region and a broud one in the wide angle region. Polarizing optical micrograph of **1** showed a fan-shaped texture characterisitic of smectic A (S_A) phase (Fig. 2), and that of **2** showed an optical texture assignable to smectic phase.

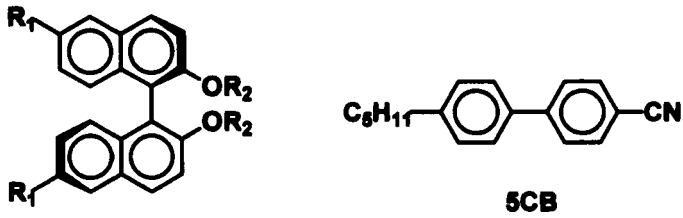
Binaphthyl Derivatives as Chiral Dopants

Inductinon of Chiral Nematic Phase from Nematic Phase : Addition of the chiral binaphthyl derivative to 4-cyano-4'-pentyl biphenyl (5CB), a representative nematic liquid crystal (Scheme 3), induced the chiral nematic phase. In Table I are shown chiral nematic phases induced by **1**, **2** and other kinds of dopants[8].

TABLE I Helical pitch and twisting power (β_M) in mixtures of 5CB and binaphthyl derivatives

Chiral dopant	R_1	R_2	c[a] (10^{-3} mol_D/mol_{LC})	pitch (μ m)	β_M (μm^{-1})
1	PCH506	PCH506	3.48	3.8	76
2	PCH506	CB06	3.32	3.5	85
	H	PCH506	7.73	5.2	25
	H	CB06	6.06	6.2	27
	H	H	22.3	2.6	17

a; c is a mole ratio; mol_D and mol_{LC} represent moles of chiral dopant and 5CB, respectively.



SCHEME 3 Chiral dopant and LC.

The LC mixture was placed in a Cano's wedge-type glass cell[9] (tan θ : 8.3 x 10^{-3}) at 25℃. The helical pitch was determined by measuring intervals of Cano's lines appearing on the surface of wedge-type LC cells (Fig. 3).

The absolute values of twisting power (β_M)[10] were calculated as the reciprocal of the product of helical pitch (μ m) and the concentration ratio of the chiral dopant and liquid crystal.

For example, the addition of **2** to 5CB under the condition of 3.32 x 10^{-3} mol_D/mol_{LC} at 25℃ generated the induced chilal nematic phase, whose helical pitch was 3.5 μ m. The efficiency of the chiral dopant was evaluated by β_M,

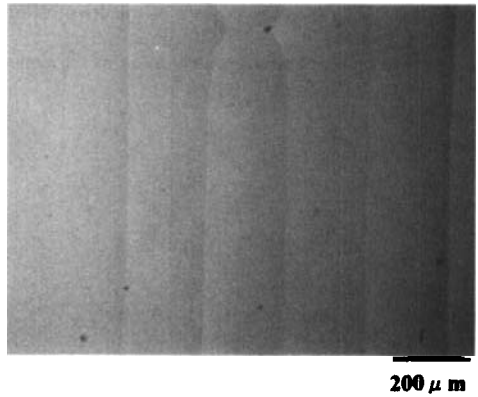


FIGURE 3 Polarized optical micrograph of the Cano's lines of a mixture of 5CB and **2** at 25℃. c is 3.32 x 10^{-3} (mol_D/mol_{LC}). See Color Plate XXX at the back of this issue.

which represents the twisting power of the chiral nematic phase. It is evident from Table I that the twisting power of the LC mixture increases with an increase of the number of substituent in the binaphthyl derivatives; The present quadri-substituted binaphthy derivatives gave larger values in β_M, compared with the non-substituted and di-substituted binaphthyl derivatives.

Besides, among the quadri-substituted ones, the compound of **2** showed the largest twisting power. This may be due to the ability of intermolecular electrostatic interactions between cyano moieties in the CB06 type substituents of **2**.

CONCLUSION

We have synthesized the first LC chiral binaphthyl derivatives. The present binaphthyl derivatives induced chiral nematic LC phases when they were doped in

a nematic liquid crystal. The twisting powers of quadri-substituted binaphthyl derivatives were found to be much stronger than those of the non-substituted and di-substituted ones.

EXPERIMENTAL

(*R*)-6, 6'-dibromo-2, 2'-dihydroxy-1, 1'-binaphtyl, (3) : Synthesized according to *Ref. 6*

(*R*)-6, 6'-dibromo-2,2'-di[(*p*-(*trans*-4-*n*-pentyl cyclohexyl)-phenoxy)-1-hexyloxy]-1,1'-binaphthyl, (4) : (*R*)-6, 6'-dibromo dihydroxy-1, 1'-dinaphthyl (4.00 g 9.0 mmol), PCH506Br (8.64 g 18.0 mmol), potassium carbonate (12.6 g 91.2 mmol), potassium iodide and methylethylketone (200 ml) were mixed and stirred for 24 h at 75 ℃. After filtration, the solvent was evaporated in vacuo to yield solid. The purification was carried out using a chromatography of silica gel with an eluent of hexane and $CHCl_3$ in 1 : 1 mole ratio.

(*R*)-6, 6', 2, 2'-tetra[(*p*-(*trans*-4-*n*-pentylcyclohexyl)-phenoxy)-1-hexyloxy]-1,1'-binaphthyl, (1) : Magnesium (0.230 g 9.46 mmol) and THF (10 ml) were stirred, and then PCH506Br (3.72 g 9.08 mmol) was added slowly to them while the temperature was 30 ℃ until the solution become suspension. The suspension was added to the mixture of 4 (0.961 g 0.873 mmol), 1,3-bis(diphenylphosphino) propane nickel (Ⅱ) chloride (0.631 g 1.16 mmol)

and THF (20 ml), and then stirred for 24 h at 65 ℃. The reaction was quenched by adding HCl (5 ml). The organic layer was extracted with diethyl ether. After drying over $MgSO_4$, the solution was filtered and evaporated in vacuo to yield solid. Chromatography over silica gel (hexane) gave **1**. **1** was further washed with ethanol.

(*R*)-6, 6'-dibromo-2, 2'-dihydroxy pyran-1, 1'-binaphthyl, (5) : CH_2Cl_2 (20 ml) was added into a flask containing **3** (2.00 g 4.50 mmol) and 1,2-dihydro pyran (4.0 g 47.6 mmol). The solution was cooled to 0 ℃. *p*-Toluenesulfonic acid (5 mg. cat) was added into the solution. After stirring for 24 hrs, the solution was extracted with diethyl ether. The ether layer was then dried (K_2CO_3), filtered and evaporated in vacuo to yield solid. Chromatography over silica gel ($CHCl_3$) gave a crystalline solid of **5**.

(*R*)-6, 6'-di-((*p*-(*trans*-4-*n*-pentyl cyclohexyl)-phenoxy)-1-hexyloxy)-2,2'-dihydoroxy-1,1'-binaphthyl, (6) : Magnesium (0.500 g 20.8 mmol) and THF (10 ml) were stirred, and then PCH506Br (6.70 g 16.3 mmol) was added slowly to them while the temperature was 30 ℃ until the solution become suspension. The suspension was added to the mixture of **5** (1.00 g 1.63 mmol), 1,3-bis(diphenylphosphino) propane nickel (Ⅱ) chloride (0.631 g 1.16 mmol) and THF (20 ml), and then stirred for 24 h at 65 ℃. The reaction was quenched by adding HCl (5 ml) to the solution. The organic layer was extracted with diethyl ether. After drying over $MgSO_4$, the solution was filtered and evaporated

in vacuo to yield solid.

THF (50 ml), acetic acid (50 ml), H_2O (20 ml) and the solid were mixed and stirred for 24 h. The organic layer was extracted with diethyl ether. After drying over $MgSO_4$, the solution was filtered and evaporated in vacuo to yield solid. Chromatography over silica gel ($CHCl_3$) gave **6**.

(*R*)-6, 6'-di[(*p*-(*trans*-4-*n*-pentylcyclohexyl)-phenoxy)-1-hexyloxy]-2,2'-di[6-(4'-cyano-1,1'-biphenylyl-4-oxy)-1-hexyloxy]-1,1'-binaphthyl, (2) : 6 (0.40 g 0.424 mmol), CB06 (0.86 g 2.40 mmol), potassium carbonate (2.10 g 15.2 mmol), potassium iodide and methylethylketone (10 ml) were mixed and stirred for 24 h at 75 ℃. After filtration, the solvent was evaporated in vacuo to yield solid. Chromatography over silica gel (hexan : $CHCl_3$ = 1 : 1) gave **2**.

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[10] The twisting power β_M is expressed as $\beta_M=(pcr)^{-1}$, where p is the helical pitch length measured in μm, c is the concentration ratio expressed in molar ratio of the chiral dopant and the liquid crystal, and r is the optical purity of the dopant[11].

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