

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Study on the helical twisting behaviour of chiral 1,2-propanediol derivatives inducing chiral nematic liquid crystals with a helix inversion and controllable pitch variation

Xiaoguang Zhang^{ab}; Wei Huang^a; Zhenyu Bian^a; Guangda Yang^b; Xiaojuan Wu^a; Xiuting Zhao^a; Guojing Ma^a; Haiquan Zhang^c; Huai Yang^a

^a Department of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing, People's Republic of China ^b National Laboratory of Electro-Optics System Technology, Sanhe, Hebei, People's Republic of China ^c State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, Hebei, People's Republic of China

Online publication date: 05 November 2010

To cite this Article Zhang, Xiaoguang , Huang, Wei , Bian, Zhenyu , Yang, Guangda , Wu, Xiaojuan , Zhao, Xiuting , Ma, Guojing , Zhang, Haiquan and Yang, Huai(2009) 'Study on the helical twisting behaviour of chiral 1,2-propanediol derivatives inducing chiral nematic liquid crystals with a helix inversion and controllable pitch variation', *Liquid Crystals*, 36: 5, 531 – 540

To link to this Article: DOI: 10.1080/02678290903039133

URL: <http://dx.doi.org/10.1080/02678290903039133>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Study on the helical twisting behaviour of chiral 1,2-propanediol derivatives inducing chiral nematic liquid crystals with a helix inversion and controllable pitch variation

Xiaoguang Zhang^{a,b}, Wei Huang^a, Zhenyu Bian^a, Guangda Yang^b, Xiaojuan Wu^a, Xiuting Zhao^a, Guojing Ma^a, Haiquan Zhang^c and Huai Yang^{a*}

^aDepartment of Materials Physics and Chemistry, School of Materials Science and Engineering, University of Science and Technology Beijing, Beijing 100083, People's Republic of China; ^bNational Laboratory of Electro-Optics System Technology, Sanhe, Hebei 065201, People's Republic of China; ^cState Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao, Hebei 066004, People's Republic of China

(Received 13 April 2009; final form 12 May 2009)

In this study, a novel series of chiral dopants were synthesised via the esterification reaction between optically active (S)-1,2-propanediol and mesogenic carboxylic acids. The phenomenon of a helix inversion with temperature variation could be observed in the chiral nematic liquid crystals (N*-LCs) by doping the chiral dopants into a nematic liquid crystal host. The results show that the inversion temperature varies only slightly with terminal alkyl chain length, but can be influenced by the structural rigidity and molecular shape of the chiral dopants, while the molecular twisting power has an apparent dependence on terminal alkyl chain length and the number of chiral centres. Depending on the composition proportion of binary chiral mixtures prepared by the synthesised chiral dopants and the commercially-available chiral compounds, induced N*-LCs with controllable pitch variation could be easily achieved.

Keywords: liquid crystal; chiral dopant; helix inversion; molecular twisting power

1. Introduction

A chiral nematic liquid crystal (N*-LC) is formed when a nematic liquid crystal (LC) host is doped with a chiral dopant guest. The longitudinal axes of the host molecules rotate about a helix under the influence of the handedness of the chiral guest molecules. The N*-LC so obtained is characterised by pitch and helical twisting sense. The pitch, P , of the helix corresponding to a 2π molecular rotation is inversely proportional to the concentration of the chiral dopant. The helical twisting sense describes the direction in which helical twisting occurs. Depending on the chiral nature of the perturbation, both left- and right-handed helices (the M- and P-helix) are possible (1).

The twisting sense of the helical structure of N*-LCs could be changed with temperature variation when a helix inversion occurs, leading to a nematic director configuration (infinite-pitch N*-LC) at the inversion temperature (2). This phenomenon has been observed in single component thermotropic chiral LCs (3, 4), mixtures of thermotropic chiral LCs (5, 6) and mixtures of mesogenic (7–11) and non-mesogenic (12, 13) chiral dopants in a nematic LC host. Two general explanations for the helix inversion have been suggested (14). In one, the statistical distribution of the many molecular conformations shifts with changing temperature (15). In the other, the competition between the different temperature

dependences and the opposite handedness of multiple chiral centres causes the helix inversion (3, 16). Generally speaking, the first explanation is preferable in nematic systems with chiral dopants that have been supported experimentally (17, 18).

In pursuit of a clearer understanding between the molecular structure and helical twisting behaviour of chiral dopants inducing N*-LCs with a helix inversion, a series of chiral dopants derived from optically active (S)-1,2-propanediol were synthesised and characterised. The chiral dopants with only one kind of chiral centre induced the N*-LCs exhibiting a helix inversion at a certain temperature. In this study, the effects of terminal alkyl chain length, ring structure and number of chiral centres on the helical twisting behaviour of the chiral dopants were investigated. Furthermore, a simple method to achieve the N*-LCs with controllable pitch variation was devised and realised.

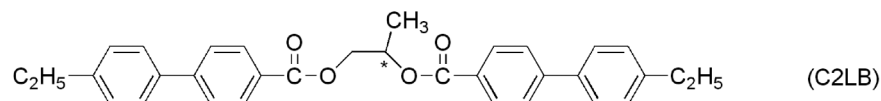
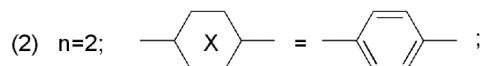
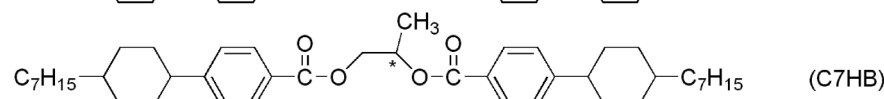
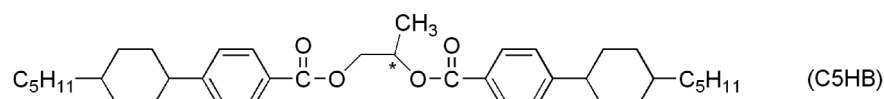
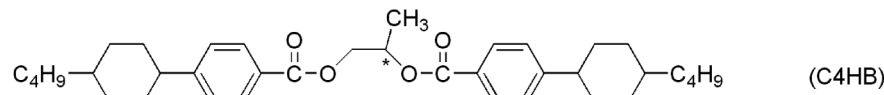
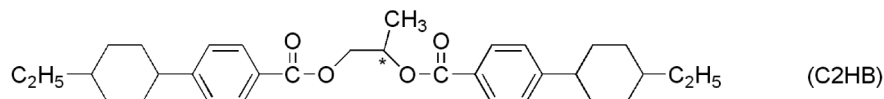
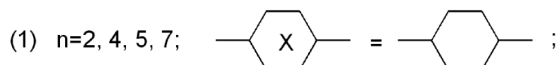
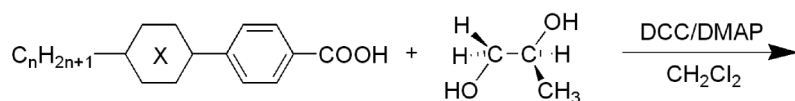
2. Experiments

2.1 Materials

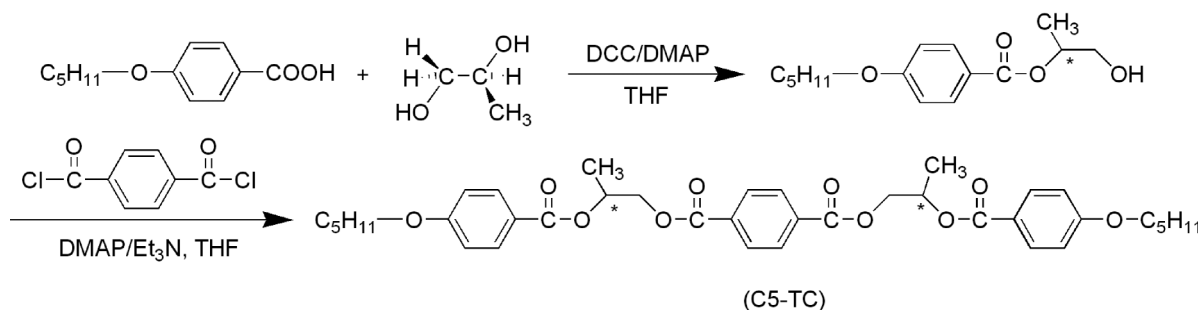
The nematic LC host SLC-1717 ($T_{N-I} = 91.8^\circ\text{C}$) from the Shijiazhuang Yongsheng Huatsing Liquid Crystal Material Co., Ltd. and the chiral compounds S811 and R811 ($T_{C-I} = 47.0^\circ\text{C}$) from the Merck Co., Ltd. were used.

*Corresponding author. Email: yanghuai@mater.ustb.edu.cn

A



B



Scheme 1. The synthetic routes to chiral 1,2-propanediol derivatives.

2.2 Synthesis and characterisation of chiral dopants

To synthesise the expected chiral dopants, tetrahydrofuran (THF) was heated under reflux over sodium and then distilled. Methylene chloride (CH_2Cl_2) was heated over calcium hydride and then distilled. All other chemicals were commercially available and used without further purification. The synthetic routes to chiral 1,2-propanediol derivatives are outlined in Scheme 1.

2.2.1 C2HB: 1,2-di-(4-(4-ethylcyclohexyl)benzoyloxy) propane

Optically active (S)-1,2-propanediol (0.76 g, 10 mmol) and dimethylaminopyridine (DMAP) (0.49 g, 4.0 mmol) were dissolved in 50 mL CH_2Cl_2 , and then added dropwise to a solution of excessive 4-(4-ethylcyclohexyl) benzoic acid (5.11 g, 22 mmol) and dicyclohexylcarbodiimide (DCC) (4.54 g, 22 mmol) in 50 mL CH_2Cl_2 . The reaction mixture was continuously stirred at room temperature

for 40 h. After the precipitate was filtered off, the resulting solution was washed with dilute hydrochloric acid and deionised water and dried with anhydrous magnesium sulphate overnight. 3.95 g of white crystals was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 12/1), following recrystallisation from ethanol twice. The yield was 78.3%.

Fourier transform-infrared (FT-IR) (KBr, cm^{-1}): 2963, 2922, 2850 ($-\text{CH}_3$, $-\text{CH}_2-$), 1716 ($\text{C}=\text{O}$), 1610, 1510 (Ar-). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.24–7.97 (8H, Ar-H), 5.50–5.52 (1H, C^*H), 4.46–4.47 (2H, $\text{C}^*-\text{CH}_2-\text{O}-$), 2.49–2.52 (2H, cyclohexyl-CH-Ar), 1.21–1.29, 1.44–1.50, 1.87–1.89 (21H, cyclohexyl-H, C^*-CH_3), 0.89–0.93, 1.03–1.09 (10H, alkyl-H).

2.2.2 C4HB: 1,2-di-(4-(4-butylcyclohexyl) benzoyloxy) propane

C4HB was synthesised by the analogous procedure used for C2HB in the yield of 74.5%. FT-IR (KBr, cm^{-1}): 2956, 2919, 2849 ($-\text{CH}_3$, $-\text{CH}_2-$), 1713 ($\text{C}=\text{O}$), 1609, 1510 (Ar-). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.24–7.97 (8H, Ar-H), 5.49–5.53 (1H, C^*H), 4.46–4.47 (2H, $\text{C}^*-\text{CH}_2-\text{O}-$), 2.48–2.51 (2H, cyclohexyl-CH-Ar), 1.30–1.31, 1.44–1.49, 1.86–1.89 (29H, cyclohexyl-H, C^*-CH_3 , alkyl-H), 0.89–0.92, 1.00–1.09 (10H, alkyl-H).

2.2.3 C5HB: 1,2-di-(4-(4-pentylcyclohexyl) benzoyloxy) propane

C5HB was synthesised by the analogous procedure used for C2HB in the yield of 77.2%. FT-IR (KBr, cm^{-1}): 2953, 2923, 2849 ($-\text{CH}_3$, $-\text{CH}_2-$), 1716 ($\text{C}=\text{O}$), 1610, 1510 (Ar-). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.25–7.97 (8H, Ar-H), 5.49–5.53 (1H, C^*H), 4.43–4.49 (2H, $\text{C}^*-\text{CH}_2-\text{O}-$), 2.48–2.51 (2H, cyclohexyl-CH-Ar), 1.21–1.34, 1.44–1.55, 1.86–1.89 (33H, cyclohexyl-H, C^*-CH_3 , alkyl-H), 0.88–0.91, 1.03–1.06 (10H, alkyl-H).

2.2.4 C7HB: 1,2-di-(4-(4-heptylcyclohexyl) benzoyloxy) propane

C7HB was synthesised by the analogous procedure used for C2HB in the yield of 71.8%. FT-IR (KBr, cm^{-1}): 2951, 2919, 2850 ($-\text{CH}_3$, $-\text{CH}_2-$), 1716 ($\text{C}=\text{O}$), 1611, 1510 (Ar-). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.25–7.97 (8H, Ar-H), 5.50–5.51 (1H, C^*H), 4.46–4.47 (2H, $\text{C}^*-\text{CH}_2-\text{O}-$), 2.48–2.54 (2H, cyclohexyl-CH-Ar), 1.24–1.28, 1.40–1.54, 1.86–1.89 (37H, cyclohexyl-H, C^*-CH_3 , alkyl-H), 0.87–0.90, 1.00–1.03, 1.06–1.09 (14H, alkyl-H).

2.2.5 C2LB: 1,2-di-(4-(4-ethylphenyl) benzoyloxy) propane

C2LB was synthesised by the analogous procedure used for C2HB in the yield of 73.3%. FT-IR (KBr, cm^{-1}): 2965, 2938, 2849 ($-\text{CH}_3$, $-\text{CH}_2-$), 1714 ($\text{C}=\text{O}$), 1606 (Ar-). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.29–7.31, 7.53–7.56, 7.63–7.66, 8.08–8.13 (16H, Ar-H), 5.53–5.57 (1H, C^*H), 4.53–4.55 (2H, $\text{C}^*-\text{CH}_2-\text{O}-$), 1.50–1.52 (3H, C^*-CH_3), 1.26–1.30, 2.68–2.73 (10H, alkyl-H).

2.2.6 2-Hydroxypropyl 4-(pentyloxy) benzoate

4-(pentyloxy) benzoic acid (2.08 g, 10 mmol) and DMAP (0.25g, 2.0 mmol) were dissolved in 10 mL THF, and then added dropwise to a solution of (S)-1,2-propanediol (0.76 g, 10 mmol) and DCC (2.48 g, 12 mmol) in 20 mL THF. The reaction mixture was continuously stirred at room temperature for 24 h. After the precipitate was filtered off, the resulting solution was evaporated under reduced pressure to remove the solvent. A solution of the residue in CH_2Cl_2 was then washed with deionised water by stirring for 6 h. The 1.23 g of colourless liquid was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 3/1). The yield was 46.2%.

FT-IR (KBr, cm^{-1}): 3445 ($-\text{OH}$), 2957, 2872 ($-\text{CH}_3$, $-\text{CH}_2-$), 1709 ($\text{C}=\text{O}$), 1607, 1508 (Ar-). $^1\text{H-NMR}$ (CDCl_3 , δ , ppm): 7.98–8.00 (4H, Ar-H), 4.32–4.34 (1H, C^*H), 4.01–4.18, 0.93–1.84 (16H, C^*-CH_3 , $\text{C}^*-\text{CH}_2-\text{O}-$, alkyl-H), 2.03–2.17 (1H, $-\text{OH}$).

2.2.7 Terephthaloyl dichloride

Terephthalic acid (33.22 g, 0.2 mol) was reacted at 70.0°C with 50 mL of thionyl chloride containing a few drops of *N,N*-dimethylformamide for 6 h, and then the excess thionyl chloride was removed under reduced pressure to give the corresponding acid chloride.

2.2.8 C5-TC: bis(1-(4-(pentyloxy) benzoyloxy) propan-2-yl) terephthalate

Terephthaloyl dichloride (0.51 g, 2.5 mmol) was dissolved in 20 mL THF, and then added dropwise to a solution of 2-hydroxypropyl 4-(pentyloxy) benzoate (1.33 g, 5 mmol), DMAP (0.12 g, 1 mmol) and triethylamine (Et_3N) (1 mL) in 20 mL THF under dry nitrogen. The reaction mixture was continuously stirred in an ice-water bath for 12 h with the reaction progress monitored by thin layer chromatography. After the removal of the solvent under reduced pressure, the residue in CH_2Cl_2 solution was successively washed

with dilute hydrochloric acid, 5% aqueous NaHCO₃ and deionised water. After drying with anhydrous magnesium sulphate overnight, the 0.96 g of white crystals was obtained by column chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 5/1). The yield was 58.1%.

FT-IR (KBr, cm⁻¹): 2931, 2871 (–CH₃, –CH₂–), 1721 (C=O), 1605, 1510 (Ar–). ¹H-NMR (CDCl₃, δ, ppm): 8.05–8.09, 7.94–7.98, 6.86–6.90 (12H, Ar–H), 5.51–5.55 (2H, C*H), 4.46–4.51 (4H, C*–CH₂–O–), 1.37–1.41 (6H, C*–CH₃), 3.97–4.00, 1.77–1.81, 1.44–1.48, 0.91–0.94 (22H, alkyl–H).

2.3 Preparation of binary chiral mixtures

Binary chiral mixtures prepared by the synthesised chiral dopants and the commercial available chiral compounds were dissolved in acetone with different weight ratios from 1:9 to 9:1. After the acetone was evaporated completely, the mixtures were milled and ground using an agate mortar and pestle for at least 30 min to ensure that an even mixture was obtained.

2.4 Preparation of N*-LCs

The nematic LC host of SLC1717 and the desired chiral dopant or binary chiral mixtures were dissolved in acetone with a concentration of chiral substance of about 2.0 wt%, and then sonicated for at least 2.0 h to ensure that an even N*-LC mixture was obtained after removing the solvent.

2.5 Characterisation of twisting power of N*-LCs

The pitch P of the N*-LCs was measured by the Cano wedge technique (19). In this measurement, a wedge-shaped cell with a wedge angle, α , was used and the inner surfaces of its two glass substrates were treated to provide a homogeneous orientation of LC molecules. After the sample was filled into the cell in the isotropic phase and then cooled to the N* phase, at some temperature a Grandjean–Cano texture formed with disclination lines separated by a distance L . The pitch P is determined from $P = 2\alpha L$ at that temperature.

The twisting power is a measure of the ability of a chiral dopant to induce a N* phase in a nematic host. To characterise the twisting power of the synthesised chiral dopants, either the product PC (C is the concentration of the chiral dopant in wt%) or the molecular twisting power $\beta = 1/PN_v$ was used (N_v is the number density of the chiral dopant in mol m⁻³). The values of β were calculated assuming a density of the LC solution of 1 g cm⁻³ (10).

2.6 Determination of helical twisting sense of N*-LCs

All of the N*-LCs induced by the synthesised chiral dopants were studied using the contact method (20) and their helical twisting senses were established. As standards for the experiments, N*-LCs induced by S811 (left-handed) and R811 (right-handed) were used.

When the interface of two N* phases with the same helical senses was observed microscopically, no discontinuity in the texture was visible. However, when the helical senses were opposite, a narrow band of nematic texture was observed separating the two N* phases regions.

2.7 Treatments of substrate surfaces

To obtain homogeneous alignment of the LC molecules, a 3.0 wt% polyvinyl alcohol (PVA) aqueous solution was coated onto the inner surfaces of the substrates by spinning casting. The deposited film was dried at 80.0°C for about 30 min, and subsequently rubbed with a textile cloth under a pressure of 2.0 g cm⁻² along one direction. In order to induce homeotropic alignment of the LC molecules, the inner surfaces of the substrates were treated with *N,N*-dimethyl-*N*-octadecyl-3-aminopropyltrimethoxysilyl chloride (DMOAP) solution (0.1% by volume in water) (21).

2.8 Other measurements

The FT-IR spectra were recorded on a Nicolet-510P spectrometer at frequencies ranging from 400 to 4000 cm⁻¹. The ¹H-NMR experiments were performed at 400 MHz on a Bruker DMX-300 spectrometer while CDCl₃ was used as the deuterated solvent for the compounds. The optical textures were observed by polarised optical microscopy (POM, Olympus BX51) equipped with a hot stage calibrated to an accuracy of ±0.1°C (Linkam LK-600PM). The phase transition temperatures of the compounds were investigated by differential scanning calorimetry (DSC, Perkin Elmer Pyris 6) at a heating rate of 10.0°C min⁻¹ under a dry nitrogen purge.

3. Results and discussion

3.1 Terminal alkyl chain length dependence of helical twisting behaviour

Figure 1 shows the POM photos of the N*-LC induced by C2HB at different temperatures in the wedge-shaped cell. It can be seen that the distance of parallel disclination lines increases with temperature increasing in the

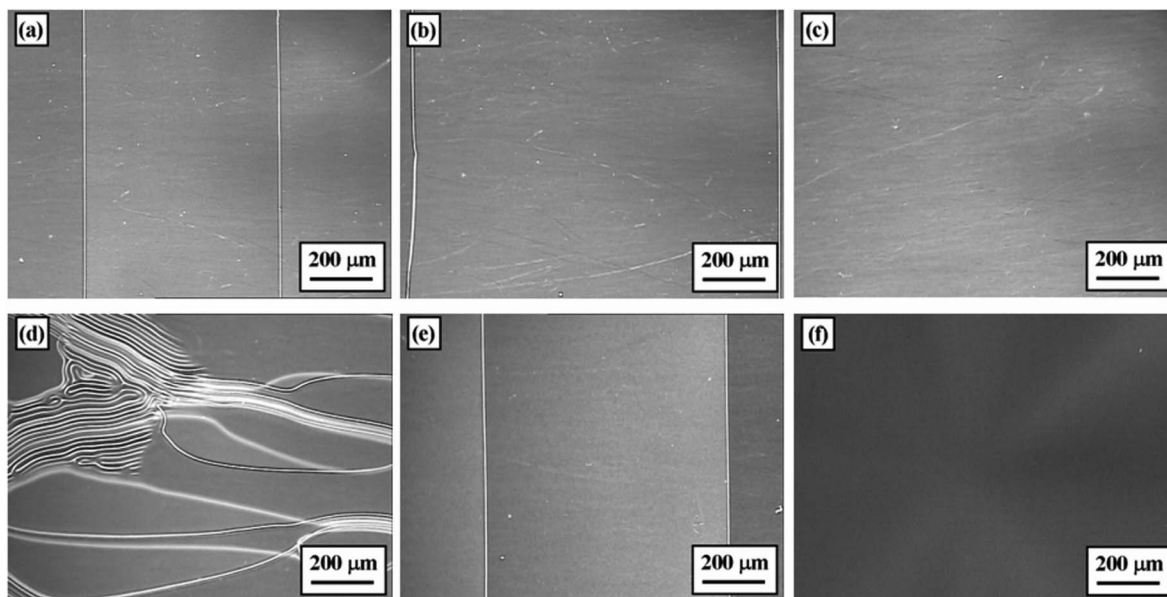


Figure 1. The POM photos of the N*-LCs induced by C2HB at different temperatures in the wedge-shaped cell: 25.0°C (a); 45.0°C (b); 60.0°C (c); 64.0°C (d); 85.0°C (e) and 95.0°C (f).

temperature range from 20.0°C to 60.0°C. The homogeneous alignment of nematic LCs can be observed at about 60.0°C, with the transmitted light intensity of the cell changing periodically while rotating between the polariser and analyser. That is to say, the pitch P increases accordingly, and becomes infinite at about 60.0°C. Then, a helix inversion with temperature variation occurs. With the temperature increasing further, the distance of parallel disclination lines decreases in the temperature range from 65.0°C to the temperature of the clearing point. This represents the pitch P with the opposite twisting sense decreasing with temperature increasing further.

Figure 2 shows the optical textures of the contact region between the standard N*-LC induced by S811 or R811 and the test N*-LC induced by C5HB. As shown in Figure 2(a) and (b), a narrow band of nematic texture separating the N*-LC induced by R811 and the N*-LC induced by C5HB appears at room temperature, while a continuous texture can be found in the contact region between the N*-LC induced by S811 and the N*-LC induced by C5HB with substrates treated for homogeneous orientation. Figure 2(c)–(h) shows the POM photos of the contact region between the N*-LC induced by R811 and the N*-LC induced by C5HB with increasing temperature. The dark contact region of pseudo-isotropic texture shows a homeotropic nematic phase at 25.0°C with substrates treated for homeotropic orientation. As the temperature increases, the pitch of the N*-LC induced by C5HB increases and LC molecules tend to align themselves homeotropically, which illustrates

the expansion of the dark area. With temperature increasing further, the bright area of the N*-LC induced by R811 diffuses directly and then a continuous fingerprint texture of right-handed N*-LC comes out. This demonstrates that the helical twisting sense of the N*-LC induced by C5HB changes from left-handed to right-handed with increasing temperature.

Figure 3 shows the temperature dependence of the PC -product of C2HB, C4HB, C5HB and C7HB. It can be seen that the pitches of the N*-LCs induced by the chiral dopants mentioned above show a much stronger increase with increasing temperature. The pitches diverge at about 60.0°C, which is in agreement with textural observations of the N*-LCs. Above this temperature of a helix inversion, the pitches of the N*-LCs decrease strongly.

Figure 4 shows the temperature dependence of the molecular twisting power β of C2HB, C4HB, C5HB and C7HB. It can be seen that the chiral dopants with different terminal alkyl chain lengths exhibit a similar temperature dependence of the induced helical structure, for example, increasing β with increasing temperature. The helix inversion temperatures (T_{HI}) extrapolated from the β curves were 60.1°C for C2HB, 60.8°C for C4HB, 60.6°C for C5HB and 59.5°C for C7HB. This demonstrates that the T_{HI} varies only slightly with terminal alkyl chain length. Furthermore, it should be noted that the absolute values of β increase with increasing terminal alkyl chain length. Typically, the β values at 20.0°C were $-953.4 \text{ m}^2 \text{ mol}^{-1}$ for C2HB, $-971.4 \text{ m}^2 \text{ mol}^{-1}$ for C4HB, $-1131.6 \text{ m}^2 \text{ mol}^{-1}$ for C5HB and $-1149.4 \text{ m}^2 \text{ mol}^{-1}$ for C7HB. Here the

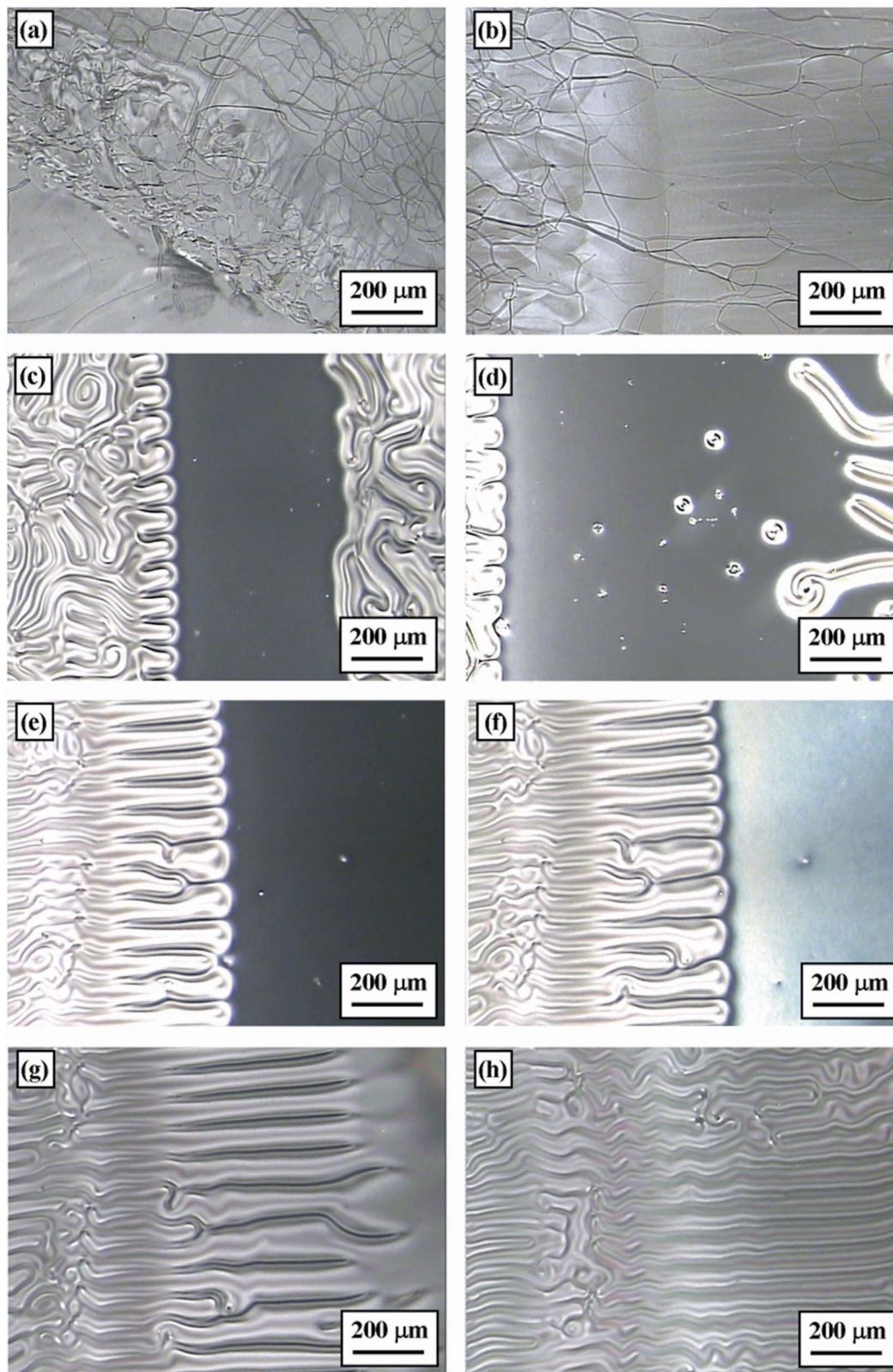


Figure 2. (Colour online). The optical textures of the contact region between the standard N*-LC induced by S811 or R811 and the test N*-LC induced by C5HB: R811 (upper right) and C5HB (lower left) (a); S811 (right) and C5HB (left) (b); at room temperature with substrates treated for homogeneous orientation, R811 (left) and C5HB (right) at 25.0°C (c); 40.0°C (d); 74.5°C (e); 78.2°C (f); 79.3°C (g) and 85.0°C (h) at a heating rate of 10.0°C min⁻¹ with substrates treated for homeotropic orientation.

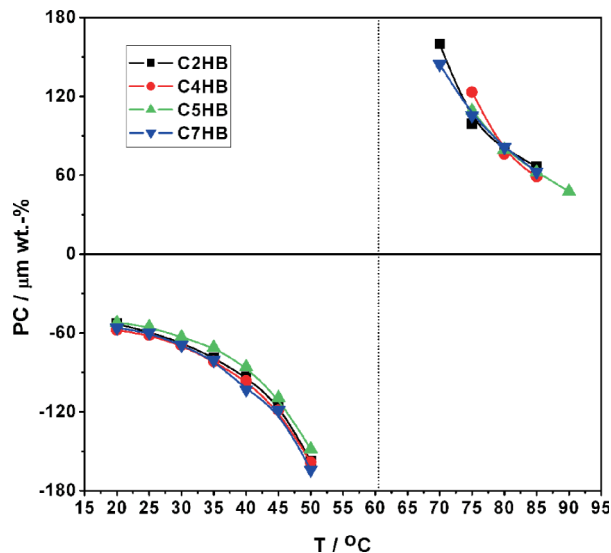


Figure 3. The temperature dependence of the PC -product of C2HB, C4HB, C5HB and C7HB.

signs + and – indicate right-handed and left-handed helices, respectively. It was found that the twisting power is weakly dependent on the nature of the aliphatic chiral centre (22, 23); the increasing β values from C2HB to C7HB may result from greater anisometry of the molecular structure.

3.2 Rigid ring structure dependence of helical twisting behaviour

Figure 5 represents the temperature dependence of the molecular twisting power β of C2HB and C2LB. As

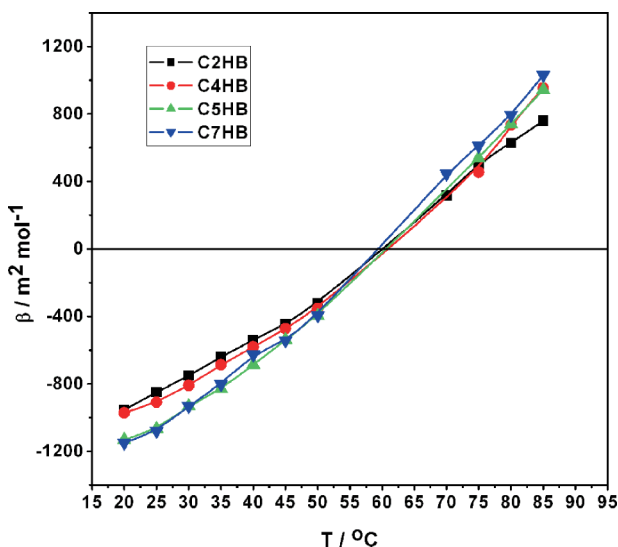


Figure 4. The temperature dependence of the molecular twisting power β of C2HB, C4HB, C5HB and C7HB.

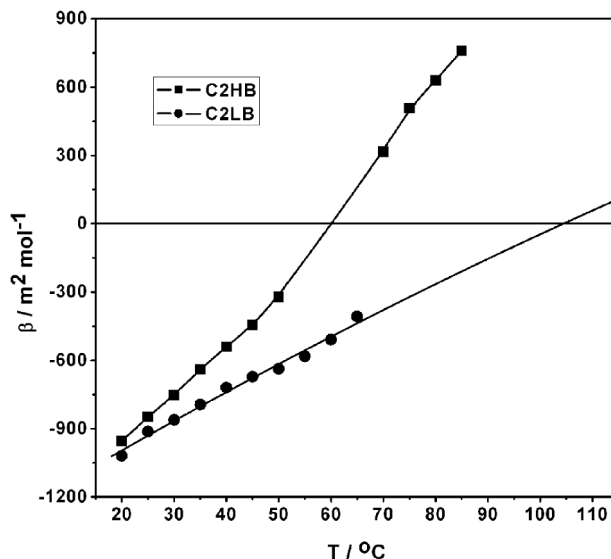


Figure 5. The temperature dependence of the molecular twisting power β of C2HB and C2LB.

shown in Figure 5, C2LB has a higher molecular twisting power than C2HB, and no helix inversion could be found in the investigated temperature range. The T_{HI} extrapolated from the β curve of C2LB is about 104.4 °C, which is well above the clearing temperature of the N*-LC.

Because there is only a single chiral centre in C2HB or C2LB, competition between different chiral centres within the molecule is not possible. Thus, the helix inversion has to result from competition between different molecular conformations. It has been proved that in order for a helix inversion to occur, the chiral centre must be free to rotate to give different conformers (4, 24). Because of the steric effect of the more rigid biphenyl ring structure, conformational changes in C2LB may be hindered, resulting in a change in the equilibrium distribution of different conformations. This might be the reason why the T_{HI} of C2LB shifts to a higher temperature. The improved molecular twisting power of C2LB should be attributed to the enhanced interactions with the nematic LC host (25). It is well known that the structural similarity between the chiral dopant and the nematic LC host tends to increase the twisting power.

3.3 Chiral centre number dependence of helical twisting behaviour

Figure 6 shows the temperature dependence of the molecular twisting power β of C5HB and C5-TC. It can be seen that the molecular twisting power of C5-TC is much higher than that of C5HB due to the higher concentration of chiral centres. The theory of

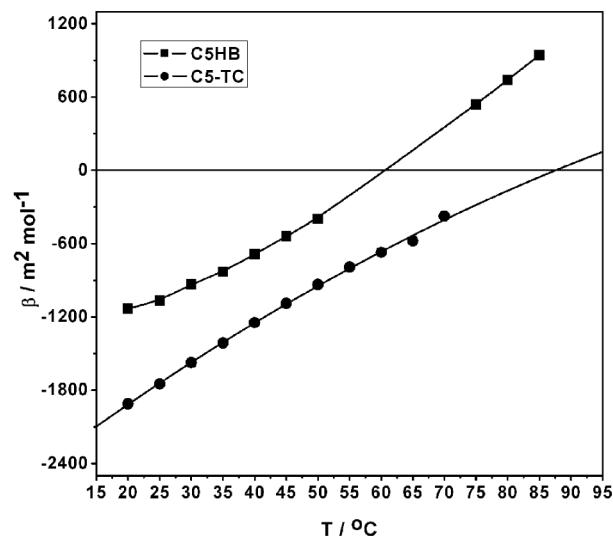


Figure 6. The temperature dependence of the molecular twisting power β of C5HB and C5-TC.

solute–solvent interactions through chiral conformers considers the interactions of the chiral dopant's molecule with a nematic mean-field potential or a uniaxial 'cavity' in analogy to discussion of the chirality transfer mechanisms in LCs (26). The chiral dopants with most elongated molecular shapes best fit the 'cavity', which alters the equilibrium distribution of various molecular conformations. As a result, the T_{HI} extrapolated from the β curve of C5-TC increases at about 87.6°C, which has also exceeded the investigated temperature range of the N*-LC.

The phase transition temperatures, the PC-products, the molecular twisting power β at 20.0°C and the helix inversion temperatures of the synthesised chiral dopants are listed in Table 1. With increasing terminal alkyl chain length, the phase transition temperatures of the chiral dopants decrease. An odd–even effect can be observed in the molecular twisting power of the chiral dopants with different terminal alkyl chain lengths at 20.0°C. Even-membered terminal alkyl chains may possess more conformers, which allow an essentially parallel arrangement of the mesogenic ring structure and enhance the mutual interactions with nematic LC

molecules. The promoted chirality transfer in LCs could well explain the sudden increase of the molecular twisting power of C5HB.

3.4 Phase transition behaviour of binary chiral mixtures

Figure 7 shows the phase transition temperatures of the binary chiral mixtures prepared from C2HB and S811 with composition proportions from 9:1 to 1:9. It is clear that the thermal curve of C2HB:S811 = 9:1 displays pronounced melting peaks of S811 and C2HB. As the weight ratio of S811 increases, the area of the melting peak of S811 increases while that of C2HB decreases. At the same time, the peak shape of C2HB deforms to be a broadening and diffuse peak and the location shifts to a lower temperature due to the increasing impurity. When the weight ratio of S811 increases to the proportion of C2HB:S811 = 3:7 or much more, a eutectic mixture forms as illustrated to be a single sharp peak.

3.5 Control on pitch variation of induced N*-LCs

Figure 8 shows the temperature dependence of the pitch of N*-LCs induced by C2HB, S811 and R811. It can be seen that the pitch of N*-LCs induced by C2HB increases in the temperature range from 20.0°C to 60.0°C and decreases strongly after changing from left-handed to right-handed helical structure. However, the pitch of N*-LCs induced by S811 and R811 increases so slightly as to be considered nearly independent on the temperature.

Figure 9 shows the temperature dependence of the pitch of N*-LCs induced by the binary chiral mixtures with composition proportions from C2HB:S811 = 1:9 to 9:1. It is clear that the pitch increases more drastically with increasing the weight ratio of C2HB. It has been proved that the twisting powers of individual chiral elements can be added up to yield a macroscopic power if the chiral centres are regarded as independent, without any intramolecular coupling between them (2). In the temperature range of 20.0–60.0°C where the helical structure of C2HB is left-handed,

Table 1. The phase transition temperatures, the PC-products, the molecular twisting power β at 20.0°C and the helix inversion temperatures of the synthesised chiral dopants.

Chiral dopants	Transition temperatures / °C	PC (20°C) / $\mu\text{m wt.}\%$	β (20°C) / $\text{m}^2 \text{mol}^{-1}$	T_{HI} / °C
C2HB	Cr 153.4 I	-52.9	-953.4	60.1
C4HB	Cr 109.0 I	-57.7	-971.4	60.8
C5HB	Cr 111.8 I	-52.0	-1131.6	60.6
C7HB	Cr 105.1 I	-56.1	-1149.4	59.5
C2LB	Cr 204.5 I	-48.3	-1019.3	104.4
C5-TC	Cr 50.8 I	-34.7	-1911.8	87.6

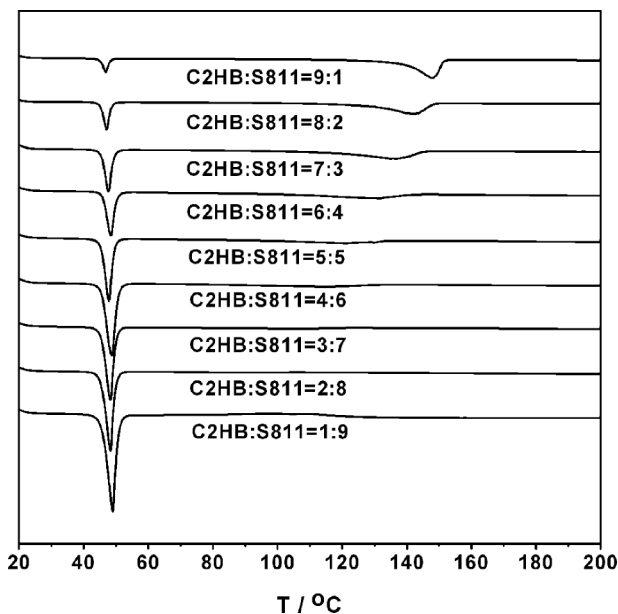


Figure 7. The phase transition temperatures of the binary chiral mixtures prepared from C2HB and S811 with composition proportions from 9:1 to 1:9, respectively.

the pitch increases mildly due to the chiral synergistic effect between C2HB and S811; at temperatures above T_{HI} of 60.1°C where the helical structure of C2HB changes to right-handed, the pitch increases drastically due to the chiral racemisation effect between C2HB and S811.

Figures 10 and 11 show the temperature dependence of the pitch of N*-LCs induced by the binary

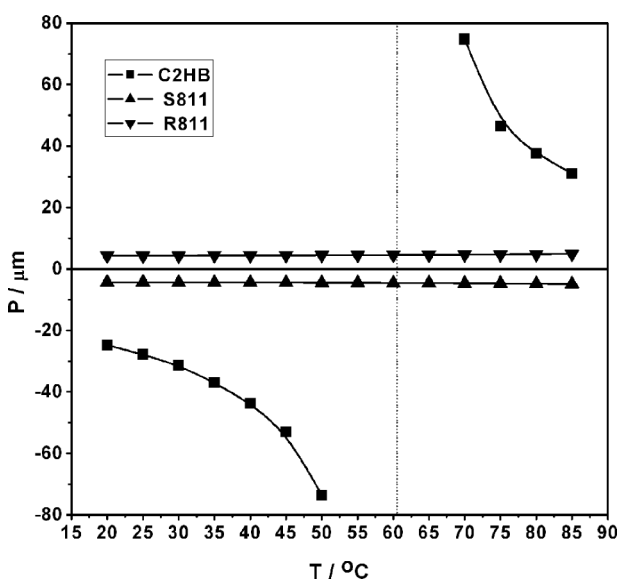


Figure 8. The temperature dependence of the pitch of N*-LCs induced by C2HB, S811 and R811.

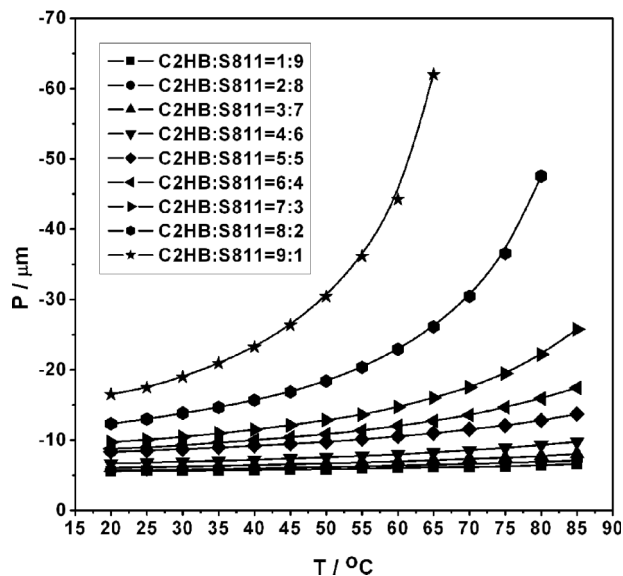


Figure 9. The temperature dependence of the pitch of N*-LCs induced by the binary chiral mixtures with composition proportions from C2HB:S811 = 1:9 to 9:1.

chiral mixtures with composition proportions from C2HB:R811 = 1:9 to 8:2. Taking the slight increase of pitch of N*-LCs induced by R811 with increasing temperature into account, the pitch of N*-LCs induced by the binary chiral mixtures with a relative low weight ratio of C2HB increase accordingly as shown in Figure 10. When the weight ratio of C2HB increases to the proportion of C2HB:R811 = 4:6 or much more, the pitch decreases with increasing

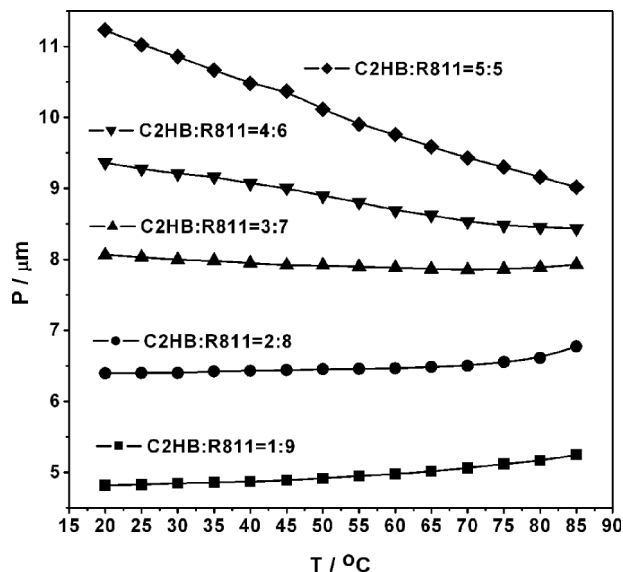


Figure 10. The temperature dependence of the pitch of N*-LCs induced by the binary chiral mixtures with composition proportions from C2HB:R811 = 1:9 to 5:5.

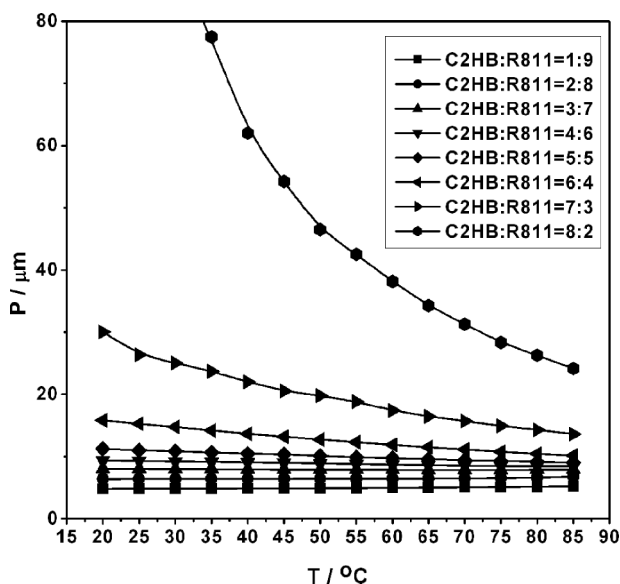


Figure 11. The temperature dependence of the pitch of N*-LCs induced by the binary chiral mixtures with composition proportions from C2HB:R811 = 1:9 to 8:2.

temperature as shown in Figure 11. On the basis of the chiral addition mentioned above, the pitch decreases more drastically with increasing the weight ratio of C2HB.

4. Conclusions

In summary, a novel series of chiral 1,2-propanediol derivatives, inducing N*-LCs with a helix inversion, were synthesised and characterised. The phase transition temperatures, the twisting power and the helix inversion temperatures of the chiral dopants were investigated. The results show that all the chiral dopants exhibit a similar temperature dependence of the helical twisting behaviour, typically increasing molecular twisting power with increasing temperature. As the terminal alkyl chain length increases, the molecular twisting power increases, the helix inversion temperature varies slightly while the phase transition temperature decreases. Rigid molecular structure shows a prominent effect on changing the equilibrium distribution of different conformations, which results in the increase of the helix inversion temperature. Introducing more chiral centres into the molecular structure can be an effective way to improve the molecular twisting power. As the composition proportion of binary chiral mixtures prepared by the chiral dopants and S811 or R811 changes, the pitch of induced N*-LCs increases or decreases with controllable variations.

Acknowledgements

Financial support from the National Science Foundation under Grant No. 20674005, the Flat-Panel Display Special Project of China 863 Plan under Grant No. 2008AA03A318, Projects of Chinese National Science and Technology Tackling Key Problems under Grant No. 2007BAE31B02 and Program of National Laboratory of Electro-Optics System Technology under Grant No. 9140C150102090C1501 is acknowledged.

References

- (1) De Gennes, P.G. *The Physics of Liquid Crystals*; Clarendon: Oxford, 1974; pp 215–237.
- (2) Dierking, I.; Giebelmann, F.; Zugenmaier, P.; Mohr, K.; Zschke, H.; Kuczynski, W. *Z. Naturforsch.* **1994**, *49a*, 1081–1086.
- (3) Stegemeyer, H.; Siemensmeyer, K.; Scurow, W.; Appel, L. *Z. Naturforsch.* **1989**, *44a*, 1127–1130.
- (4) Slaney, A.J.; Nishiyama, I.; Styring, P.; Goodby, J.W. *J. Mater. Chem.* **1992**, *2*, 805–810.
- (5) Sackmann, E.; Meiboom, S.; Snyder, L.C.; Meixner, A.E.; Dietz, R.E. *J. Amer. Chem. Soc.* **1968**, *90*, 3567–3569.
- (6) Baessler, H.; Malya, P.A.G.; Nes, W.R.; Labes, M.M. *Mol. Cryst. Liq. Cryst.* **1970**, *6*, 329–338.
- (7) Finkelmann, H.; Stegemeyer, H. *Z. Naturforsch.* **1973**, *28a*, 799–800.
- (8) Heppke, G.; Oestreicher, F. *Z. Naturforsch.* **1977**, *32a*, 899–901.
- (9) Heppke, G.; Oestreicher, F.; Scherowsky, G. *Z. Naturforsch.* **1982**, *37a*, 1176–1184.
- (10) Heppke, G.; Lotzsch, D.; Oestreicher, F. *Z. Naturforsch.* **1987**, *42a*, 279–283.
- (11) Kirste, B.; Scherowsky, G. *Liq. Cryst.* **1989**, *6*, 17–29.
- (12) Finkelmann, H.; Stegemeyer, H. *Ber. Bunsenges. Phys. Chem.* **1974**, *78*, 869–874.
- (13) Finkelmann, H.; Stegemeyer, H. *Ber. Bunsenges. Phys. Chem.* **1978**, *82*, 1302–1308.
- (14) Mitov, M.; Dessaud, N. *Nat. Mater.* **2006**, *5*, 361–364.
- (15) Styring, P.; Vuijk, J.D.; Slaney, A.J.; Goodby, J.W. *J. Mater. Chem.* **1993**, *3*, 399–405.
- (16) Dierking, I.; Giebelmann, F.; Zugenmaier, P.; Kuczynski, W.; Lagerwall, S. T.; Stebler, B. *Liq. Cryst.* **1993**, *13*, 45–55.
- (17) Kuball, H.G.; Muller, T.; Weyland, H.G. *Mol. Cryst. Liq. Cryst.* **1992**, *215*, 271–278.
- (18) Kuball, H.G.; Muller, T.; Bruning, H.; Schonhofer, A. *Mol. Cryst. Liq. Cryst.* **1995**, *261*, 845–856.
- (19) Cano, R. *Bull. Soc. Fr. Mineral* **1968**, *91*, 20–27.
- (20) Gray, G.W.; McDonnell, D.G. *Mol. Cryst. Liq. Cryst.* **1977**, *34*, 211–217.
- (21) Kahn, F.J. *Appl. Phys. Lett.* **1973**, *22*, 386–388.
- (22) Vashchenko, V.; Drushlyak, T.; Shkolnikova, N.; Kutulya, L. *Mol. Cryst. Liq. Cryst.* **1999**, *328*, 245–253.
- (23) Januszko, A.; Kaszynski, P.; Drzewinski, W. *J. Mater. Chem.* **2006**, *16*, 452–461.
- (24) Styring, P.; Vuijk, J.D.; Nishiyama, I.; Slaney, A.J.; Goodby, J.W. *J. Mater. Chem.* **1993**, *3*, 399–405.
- (25) Eelkema, R.; Feringa, B.L. *Org. Biomol. Chem.* **2006**, *4*, 3729–3745.
- (26) Gottarelli, G.; Mariani, P.; Spada, G.P.; Samori, B.; Forni, A.; Solladie, G.; Hibert, M. *Tetrahedron* **1983**, *39*, 1337–1344.