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Helical twisting properties of new chiral dopants with double (S)-1,2-propanediol units for nematic liquid crystals

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Abstract

A novel series of chiral dopants synthesized from (S)-1,2-propanediol and mesogenic carboxylic acids were characterized by FT-IR, ¹H NMR, elemental analysis and their helical twisting properties were investigated by doping the chiral dopants into a nematic liquid crystal host (SLC-1717). The results show that, the helical pitch of N*-LC mixture exhibited a terminal alkyl chain length dependence and the molecular twisting power β also exhibited a temperature dependence (increasing β with increasing temperature).

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The thermotropic liquid crystals have attracted the keenest interest of scientists for their important technological applications [1–3], and chiral nematic liquid crystals having macro helical structure are currently used in liquid crystal display (LCD) devices [4–5]. The induction of chirality in mesophases of non-chiral mesogens can be achieved by adding a small quantity of chiral dopant (up to 10%) to non-chiral liquid-crystalline hosts [6], and molecular chirality is transferred to macroscopic chirality resulting in the formation of new phases with helical ordering. The N*-LC so obtained is characterized by pitch and helical twisting sense. Nowadays, many more investigation on the temperature dependence of the pitch of the chiral nematic phase and structural design of the chiral molecule has been conducted on, but the category of chiral dopants is almost amino chiral compound [6–9]. Recently, Mitov and Dessaud have investigated the polymorphism and optical behavior of chiral dopants with single (S)-1,2-propanediol unit [10] and we have also researched the helical twisting behavior of chiral dopants containing single chiral centre ((S)-1,2-propanediol derivatives) [11,12].

In this paper, in pursuit of a clearer understanding between molecular structure and helical twisting behavior of chiral dopants inducing N*-LCs, a new kind of chiral dopants with double chiral centres (optically active (S)-1,2-propanediol) were synthesized and investigated.

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Scheme 1. The synthetic routes to CnTC: (a) DCC/DMAP, THF, rt; (b) p-phthaloyl chloride, Et₃N/DMAP, THF, 0 °C.

The synthesis of the chiral dopants is outlined in Scheme 1. First, compound Cn was synthesized by esterification of the commercially available corresponding 4-alkyloxybenzoic acid added dropwise and (S)-1,2-propanediol with dicyclohexyl carbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). Further, a series of *Cn*TC were synthesized by acylation of terephthaloyl dichloride and Cn with DMAP and triethylamine (Et₃N). The results of FT-IR, ¹H NMR and elemental analyses [FT-IR (KBr, cm⁻¹): 2931, 2871 (–CH₃, –CH₂–), 1721 (C=O), 1605, 1510; ¹H NMR (CDCl₃): δ 8.05–8.09, 7.94–7.98, 6.86–6.90 (m, 12H, Ph–H), 5.51–5.55 (m, 2H, C*H), 4.46–4.51 (d, 4H, C*–CH₂–O–), 1.37–1.41 (d, 6H, C*–CH₃), 3.97–4.00, 1.77–1.81, 1.44–1.48, 0.91–0.94 (m, 22H, alkyl-H); elemental analysis (%) for C₃₈H₄₆O₁₀: calcd: C 68.86, H 7.00, O 24.14; found: C 68.91, H 7.06, O 24.03] indicated that the chemical structure was found to be consistent with the structure *Cn*TC. (Electronic Supplementary Information (ESI) available: general experimental procedure, synthesis and characterization.)

The nematic LC host of SLC-1717 ($T_{N-I} = 91.8$ °C) and chiral dopant (CnTC) were dissolved in acetone with the concentration of chiral substance in 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. The Cano wedge technique [13] was employed to measure the pitch lengths of the N*-LC mixture at different temperatures.

Fig. 1 shows the dependence of helical pitch on the terminal alkyl chain length at 30 °C. It could be seen clearly that the pitch decreased with terminal alkly chain length increasing. Besides, an odd–even effect could be observed in the helical pitches of N*-LC doping by the chiral dopants with different terminal alkyl chain length. For the even-member terminal alkyl chain, a weaker chirality transfer to nematic LC molecules might suggest a larger pitch.

Fig. 2 shows the temperature dependence of the molecular twisting power β of CnTC (n = 3-8). As seen, the chiral dopants with different terminal alkyl chain length exhibited a similar temperature dependence of the induced helical structure, namely, increasing β values with increasing temperature. However, increasing degree is different slightly. Enhanced mutual interactions with nematic LC molecules and promoted chirality transfer in LCs could well explain the β values increasing [14]. In addition, as can be seen in Fig. 2, compared to C3TC and C4TC with a higher β , C5TC,



Fig. 1. The dependence of helical pitch on the terminal alkyl chain length at 30 °C.



Fig. 2. The temperature dependence of the molecular twisting power β .



Fig. 3. The POM photos of the SLC-1717 and N*-LC induced by C8TC: (a) SLC-1717, 25 °C; (b) N*-LC (C8TC/SLC-1717), 20 °C; (c) N*-LC (C8TC/SLC-1717), 86 °C.

C6TC and C8TC exhibited a lower β values due to much longer alkyl diminishing the "biaxiality" by increasing the conformational flexibility of the molecule according to the reported theory [15]. But C7TC is specific leading to our indepth investigation in the future. Here the signs '+' and '-' indicate right-handed and left-handed helices, respectively. Compared to the former research done [12], this kind of chiral dopants with more higher molecular twisting power were obtained by increasing the amounts of chiral centre. Therefore, introducing more chiral centres into molecular structure could be an effective way to improve the molecular twisting β .

The polarized optical microscopy (POM) photos of the N*-LC mixture and host nematic LC (SLC-1717) are showed in Fig. 3. At room temperature 25 °C, the typical schlieren texture to the nematic phase for the SLC-1717. Fingerprint texture to a chiral nematic phase (N*) at 20 °C and texture of a schlieren defect with twofold brushes to the nematic phase at 86 °C for the N*-LC mixture (C8TC/SLC-1717) could suggest that the helical pitch increases gradually with the increasing temperature.

To sum up, a novel series of chiral dopants with double (S)-1,2-propanediol units were synthesized and the twisting power of chiral dopants was investigated. The results showed that an odd–even effect was observed in the helical pitches with different terminal alkyl chain length, the even ones suggested a larger pitch due to a weaker chirality transfer to nematic LC molecules. Moreover, the chiral dopants exhibited a temperature dependence of the helical twisting behavior, typically increasing molecular twisting power with increasing temperature. And for the compounds with longer alkyl length (C5TC, C6TC, C8TC) showed a lower β values due to the diminishing "biaxiality". At last, this kind of chiral dopants with two chiral centres exhibited more higher β than the one with single chiral centre.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cclet.2009.09.007.

References

- [1] M.R. Huang, X.G. Li, G. Lin, Sep. Sci. Technol. 30 (1995) 449.
- [2] X.G. Li, M.R. Huang, L. Hu, et al. Eur. Polym. J. 35 (1999) 157.
- [3] M.R. Huang, X.G. Li, Gas Sep. Purif. 9 (1995) 87.
- [4] S.S. Choi, S.M. Morris, W.T.S. Huck, Soft Matter 5 (2009) 354.
- [5] R.A. Van Delden, B.L. Feringa, Angew. Chem. Int. Ed. 40 (2001) 3198.
- [6] G.W. Gray, M. Hird, D. Lacey, J. Chem. Soc. Perkin Trans. 2 (1989) 2041.
- [7] R.A. Van Delden, B.L. Feringa, Angew. Chem. 40 (2001) 3198.
- [8] H.G. Kuball, H. Bruning, Chirality 9 (1997) 407.
- [9] N.I. Shkolnikova, L.A. Kutulya, N.S. Pivnenko, Liq. Cryst. 50 (2005) 108.
- [10] M. Mitov, N. Dessaud, Liq. Cryst. 34 (2007) 183.
- [11] X.T. Yuan, H. Cao, H. Yang, Chin. J. Liq. Cryst. Displays 23 (2008) 404.
- [12] W. Huang, H.Q. Zhang, H. Yang, Liq. Cryst. 36 (2009) 531.
- [13] R. Cano, Bull. Soc. Fr. Miner. 91 (1968) 20.
- [14] G. Gottarelli, P. Mariani, G.P. Spada, Tetrahedron 39 (1983) 1337.
- [15] D.J. Earl, M.R. Wilson, J. Chem. Phys. 119 (2003) 10280.