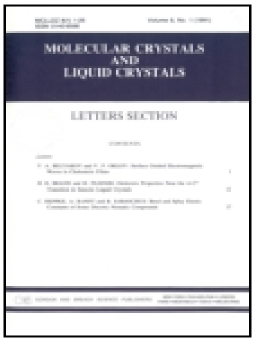


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Biphenyl Based Non-symmetrical Bent-Core Mesogens Containing a Chiral Moiety and an Olefinic End Group

Hale Ocak & Belkiz Bilgin-Eran

To cite this article: Hale Ocak & Belkiz Bilgin-Eran (2015) Biphenyl Based Non-symmetrical Bent-Core Mesogens Containing a Chiral Moiety and an Olefinic End Group, Molecular Crystals and Liquid Crystals, 609:1, 19-30, DOI: 10.1080/15421406.2014.953746

To link to this article: http://dx.doi.org/10.1080/15421406.2014.953746

Mol. Cryst. Liq. Cryst., Vol. 609: pp. 19–30, 2015
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.953746

Taylor & Francis
Taylor & Francis Group

Biphenyl Based Non-symmetrical Bent-Core Mesogens Containing a Chiral Moiety and an Olefinic End Group

HALE OCAK* AND BELKIZ BILGIN-ERAN

Department of Chemistry, Yildiz Technical University, Davutpaşa Yerleşim
Birimi, Esenler, Istanbul, Turkey

New nonsymmetrical bent-core compounds consisting of a biphenyl-3,4′-diol central unit, a chiral terminal chain and an olefinic end group at the other terminus have been synthesized and characterized to study the influence of a chiral moiety, the length of terminal alkenyl chain, and the number of aromatic rings in the rod-like wings which are substituted at the 3- and 4-position of central biphenyl core on mesophase properties of bent-core mesogens. The liquid crystalline properties of the compounds were investigated by differential scanning calorimetry, optical polarizing microscopy, and electro-optic methods. Depending on the length of the olefinic chain and the number of aromatic rings in the rod-like wings, the bent-core compounds with a chiral moiety show B_1 *type mesophase, polar smectic C phase (SmCP) or nonmesomorphic behavior.*

Keywords Bent-core mesogens; chiral moiety; liquid crystals; olefinic end group; rod-like wings

1. Introduction

Bent-core molecules have attracted considerable attention as they can form polar switchable (ferroelectric and antiferroelectric) smectic mesophases with a unique combination of layer chirality and polarity [1]. Bent-core mesogens are formed by covalently linking two rod-like segments to a central bent unit. A minor structural modification on these segments of bent-core molecules can strongly alter the mesomorphic behavior or even leads to the loss of the liquid crystalline properties. For example, the number of rings as well as the diversity of the terminal alkyl chains in the rod-like wings plays a crucial role for the emergence of polar-ordered mesophases [2].

Symmetrical bent-core molecules which are composed of a bent-core unit substitute two identical linear rod-like mesogenic units generally exhibit higher transition temperatures than nonsymmetrical bent-core molecules [3–5]. This means that the phase transition temperatures can be lowered by introducing some nonsymmetry into the molecular structure [6, 7]. The nonsymmetry in the bent-core molecules can be provided by different

---

*Address correspondence to Hale Ocak, Department of Chemistry, Yildiz Technical University, Davutpaşa Yerleşim Birimi, TR-34220, Esenler, Istanbul, Turkey. E-mail: hocak@yildiz.edu.tr

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

rod-like wings at the two sides of the central core or arises from differences in the terminal alkyl(oxy) chain length [8–10].

Chirality is also known to have a major influence on the material properties of liquid crystals. Molecular chirality can be incorporated into the bent-core molecules by the introduction of asymmetric carbon centers at the chiral alkyl chains [11–16]. It is remarkable that from some studies that molecular chirality has a pronounced effect on determining the mesomorphism of bent-core molecules as in calamitic compounds [17–19].

As reported in some studies [8], bent-core molecules with terminal double bonds may show a lower transition temperatures than the similar compounds with the saturated terminal alkyl tails. In addition, the olefin-terminated bent-core compounds having polymerisable functional groups are promising materials for the preparation of oligomeric or polymeric liquid crystal systems with unique polar properties [20–22].

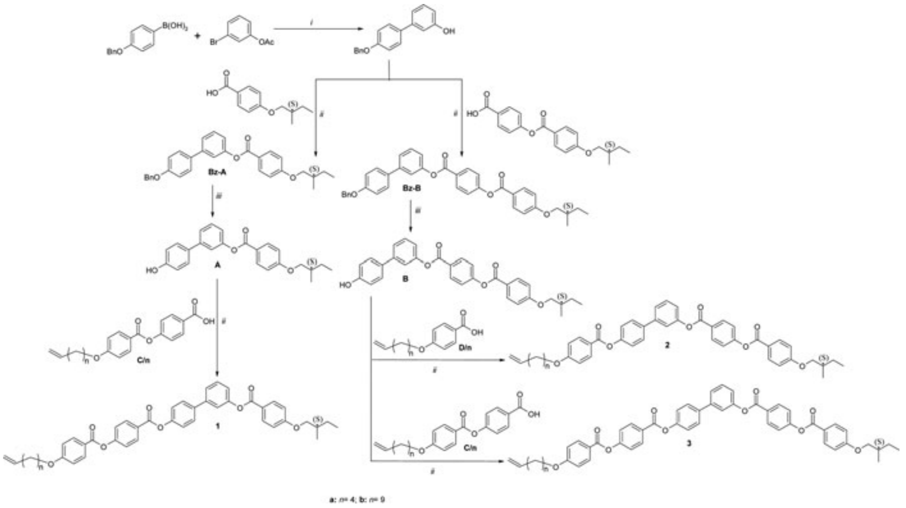
Herein, the synthesis and characterization of nonsymmetrical bent-core compounds consisting of a biphenyl-3,4′-diol central unit, a chiral terminal chain, and an olefinic end group at the other terminus are reported. We have been specifically focused on studying the influence of alkenyl chain length, molecular chirality, and the number of aromatic rings in the rod-like wing groups on the mesomorphic properties of biphenyl-based nonsymmetric bent-core compounds here.

2. Results and Discussion

2.1. Synthesis

The bent-core compounds **1–3** with a terminal double bond were synthesized as shown in Scheme 1. First, the synthesis of *4′-Benzyloxybiphenyl-3-ol* [23–26] was carried out according to known procedures. Then, *4-[(S)-2-Methylbutoxy]benzoic acid* [27] or *4-[4-(S)-2-Methylbutoxybenzoyloxy]benzoic acid* [17, 28, 29] were attached to the *4′-Benzyloxybiphenyl-3-ol* by esterification using dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as catalyst [30] to yield the benzylated intermediates **Bz-A** and **Bz-B** [18], respectively. The chiral moiety of these benzoic acids were introduced by an etherification reaction of ethyl 4-hydroxybenzoate with the *(S)-2-Methylbutyltosylate* which was prepared from the commercially available chiral alcohol by tosylation [31]. After hydrolysis, *4-[(S)-2-Methylbutoxy]benzoic acid* [27] was obtained. The DCC esterification of the *chiral benzoic acid* with 4-hydroxybenzaldehyde*,* followed by oxidation using sodium chlorite as oxidizing agent yields to the *4-[4-(S)-2-Methylbutoxybenzoyloxy]benzoic acid.* The spectroscopic data for *4-[4-(S)-2-Methylbutoxybenzoyloxy]benzoic acid* are given in Ocak et. al. [17].

As shown in Scheme 1, the hydrogenolytic deprotection [26] of the benzyl group of the intermediates **Bz-A** and **Bz-B** [18] leads to *3′-[4-((S)-2-Methylbutoxy)benzoyloxy]biphenyl-4-ol* **A** and *3′-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy]biphenyl-4-ol* **B** [18], respectively. In the final step, the esterification of deprotected intermediates **A** and **B** [18] with the appropriate *4-[4-(alkenyloxy)benzoyloxy]benzoic acid* **C/n** [8, 32] or *4-(alkenyloxy)benzoic acid* **D/n** [33, 34] by using dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as catalyst [30] in dichloromethane yield to the target compounds **1-3**. The synthesis of *4-[4-(alkenyloxy)benzoyloxy]benzoic acid* **C/n** [8, 32] or *4-(alkenyloxy)benzoic acid* **D/n** [33, 34] which are attached to on the one sides of the biphenyl central unit were carried out according to similar procedures described in ref. [35, 36]



Scheme 1. Reagents and conditions: (i) cat. [Pd(PPh$_3$)$_4$], NaHCO$_3$,H$_2$O, glyme, reflux 9 h;[23,24,25,26] (ii) DCC, DMAP, CH$_2$Cl$_2$, r.t.;[30] (iii) H$_2$, Pd/C, THF, 40°C, 18 h[26].

Due to the this fact that the stereogenic center of the chiral alcohol (*S*)-(-)-2-Methyl-1-butanol was not touched throughout the synthesis as observed previously in our studies, [17, 18, 37, 38] it can be assumed that the final products have approximately equal optical purity as the starting material. Purification of final compounds **1**-**3** was carried out by column chromatography on silica gel and crystallization from ethanol. The molecular structures were characterized by spectroscopic methods (^{1}H-NMR, ^{13}C-NMR, and MS) and also by elemental analysis. The spectroscopic and analytic data of the materials are consistent with the proposed structures (see Experimental Details).

2.2. Liquid Crystalline Properties

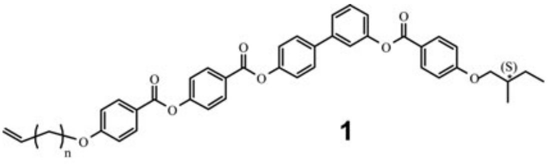
The mesomorphic properties of the obtained compounds **1**-**3** were investigated by polarized light optical microscopy (PM), differential scanning calorimetry (DSC), and one of them by electro-optical studies. The transition temperatures, corresponding enthalpy values and mesophase type observed for these compounds are summarized in Table 1.

Depending on terminal chain length and the number of aromatic rings in the rod-like wings which are attached of the 3′- or 4-position of biphenyl unit, bent-core compounds **1**-**3** show liquid crystalline mesophases such as SmCP and B$_1$ or nonmesomorphic behavior (see Table 1).

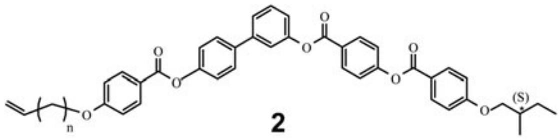
On cooling from the isotropic state, Compound **1a** containing five aromatic rings exhibit monotropic polar SmCP that can be detected by the typical Schlieren texture having multiple brushes (see Fig. 1).

Figure 2 shows the current response of compound **1a** under a triangular wave voltage. When the sample was cooled under an applied field of 200 V$_{pp}$, two current peaks per half period of the applied triangular voltage were detected at a temperature of 94.6°C. No further investigations such as direct current (DC) field were possible due to rapid crystallization during experiment. Hence, the mesophase of compound **1a** is assigned as a monotropic SmCP phase without giving more detailed information about the type of switching (af/fe).

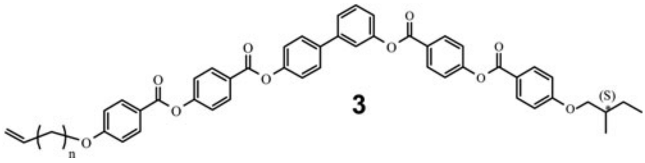
Table 1. Mesophases, phase transition temperatures and transition enthalpies of the olefins **1-3**[a]



1



2



3

Compound	*n*	T/°C [ΔH/kJ mol^{-1}]
1a	9	Cr_1 85 [7.7] Cr_2 116 [38.0] (SmCP 95 [5.3]) *Iso*
1b	4	*Cr* 118 [32.8] *Iso*
2a	9	*Cr* 103 [32.7] (B_1 86 [13.7]) *Iso*
2b	4	*Cr* 92 [19.5] *Iso*
3a	9	*Cr* 143 [55.8] (B_1 136 [14.5]) *Iso*
3b[b]	4	Cr 143 [*22.3*] B_1 166 [*11.1*] Iso

[a] Perkin-Elmer DSC-7; heating/cooling rates 10 K min^{-1}; enthalpy values are given in italics in square parentheses; abbreviations: Cr = crystalline; B_1 = rectangular columnar phase, SmCP = polar smectic C phase and Iso = isotropic liquid phase; monotropic transitions are indicated by parentheses.

[b] The transition temperatures and mesomorphic properties of compound **3b** have already been reported in Ref. 18.

The SmCP phase obtained for bent-core compound **1a** containing five aromatic rings shows a high value of spontaneous polarization. $\mathrm{P_s}$ was calculated to $\approx$ 896 nC cm^{-2}.

When compared with compound **1a** which exhibits SmCP phase, compound **1b** with a shorter terminal chain is nonmesomorphic. This must be related to the fact that the shorter terminal chain of compound **1b** containing only five aromatic rings in the bent-core structure leads to relatively strong destabilization of the mesophase.

Compound **2a** comprising a one aromatic ring in the olefine terminated rod-like wing attached to the 4-position of biphenyl unit exhibit monotropic B_1 mesophase. On cooling from the isotropic liquid, a dendritic growth texture was observed which is a characteristic of the B_1 mesophase (see Fig. 1).

Compound **2b** with shorter terminal chain behaves similar to compound **1b** which has the same terminal chain length. Increasing or decreasing in the number of the aromatic rings

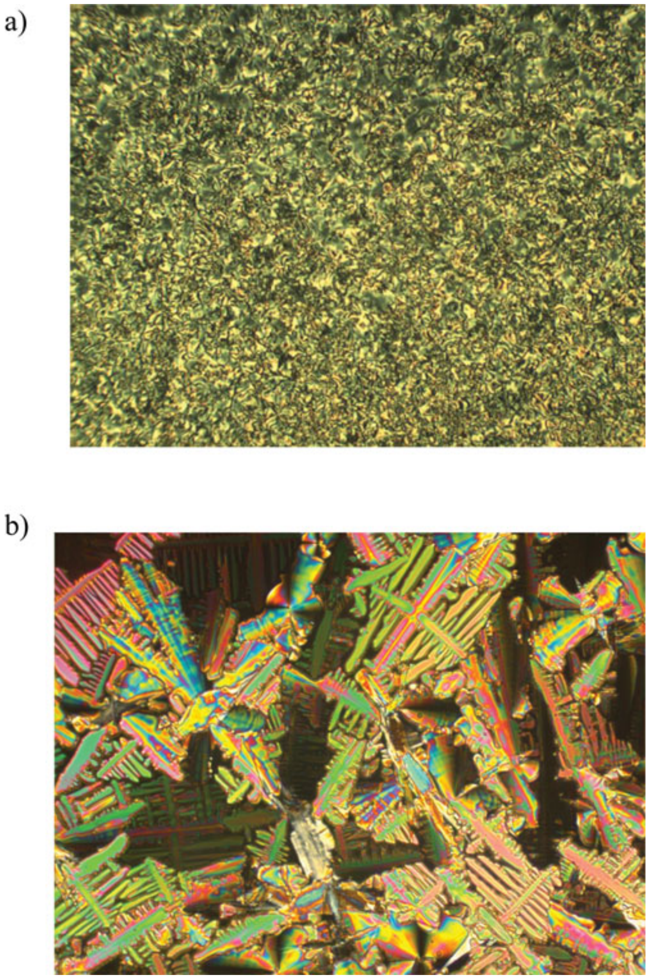


Figure 1. The textures obtained between crossed polarizers as observed during cooling just below the isotropic phase: (a) SmCP phase at 88.8°C and (b) B_1 phase at 85.0°C for the bent-core molecules **1a** and **2a**, respectively.

in the rod-like wings which are substituted at the 3- or 4-position of central biphenyl core does not change the mesomorphic properties as we expected. This leads us to conclude that the length of terminal chains plays a key role in the emergence of mesogenity for bent-core compounds comprising five aromatic rings reported here.

Compounds **1** and **2** comprising five aromatic rings in the structure of bent-core molecule have a lower melting point than compound **3** carrying two aromatic rings in each rod-like wings. Compound **3a** shows a monotropic B_1 mesophase with a dendritic growth texture (see Fig. 3) whereas compound **1a** which have one aromatic ring in the chiral moiety terminated rod-like wing attached to the 3-position of biphenyl central unit exhibits SmCP phase.

Compound **3b** which is previously reported in Ocak et al. [18] shows enatiotropic B_1 mesophase. A comparison of the mesomorphic properties of the compound **3a** and **3b** shows that thermal stability of B_1 mesophase of compound **3b** carrying a shorter alkenyl chain

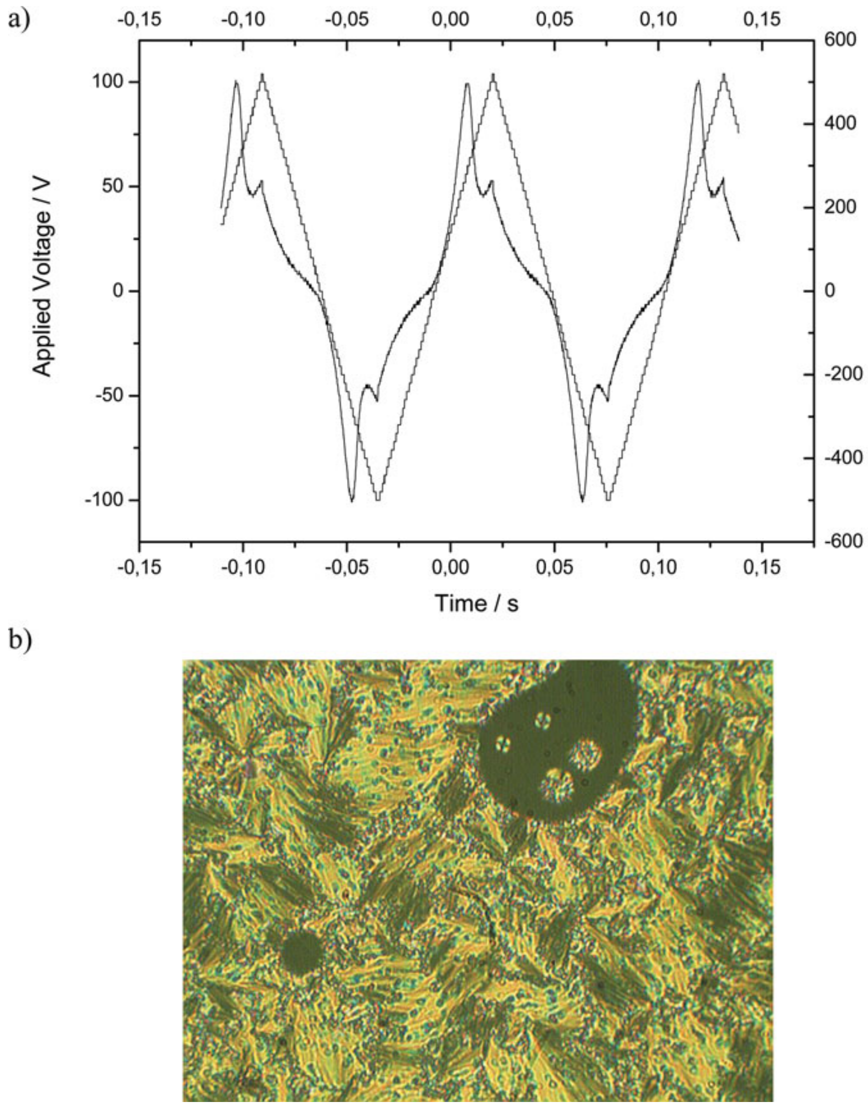


Figure 2. Switching current response on applying a triangular wave field (94.6°C, 200 Vpp, 9 Hz, 5 kΩ, 6 μm noncoated ITO cells) in the SmCP phase of compound **1a**; (b) the texture observed under the same conditions.

at terminus is greater than that of compound **3a.** Nevertheless, the melting points of both compounds are nearly the same. Compounds **3a** and **3b** also exhibits wider mesomorphic temperature range in comparison with compounds **1** and **2** having a shorter wing at one of the sides of the central biphenyl core. No polar switching could be observed for the mesophases of neither compound **2a** nor compounds **3a** and **3b** in the electro-optical studies, which is also in line with B_1 phases reported in refs. [2, 18, 39].

The presence of molecular chirality for compounds **2** and **3** has clearly no effect on the formation of B_1 phases as previously reported bent-core compounds [18, 19, 37]. In addition, the emergence of SmCP phase for compound **1a** are more related to the structural

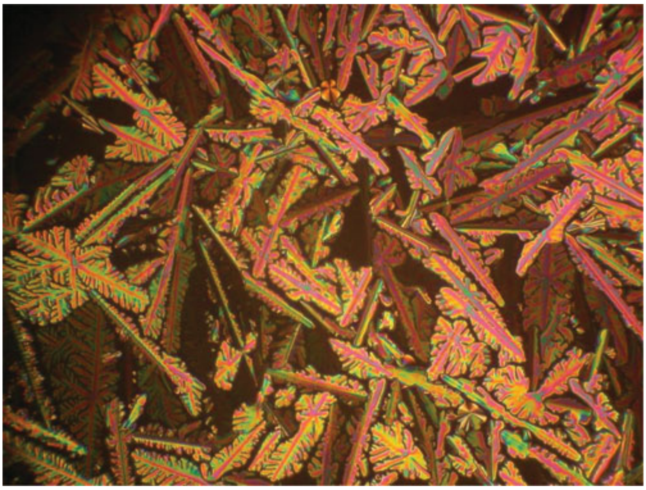


Figure 3. The dendritic growth texture obtained between crossed polarizers as observed for the B_1 phases of compound **3a** at 130°C.

modifications in this bent-core molecule such as the number of aromatic rings and terminal chain length in the rod-like units attached to the 3′- and 4-positions of biphenyl unit than the presence of a chiral terminal group according to the obtained mesomorphic properties of the compounds with (S)-2-methylbutoxy group reported here.

3. Experimental Details

3.1. Characterization Methods

The characterization of the synthesized compounds are based on ^{1}H-, ^{13}C-NMR (Varian Unity 500 and Varian Unity 400 spectrometers, in $CDCl_3$ solutions, with tetramethylsilane as internal standard), MS [AMD 402 (electron impact, 70 eV), and Thermo Finnigan LCQ Advantage Max (electrospray ionization)]. Microanalysis was performed using a Leco CHNS-932 elemental analyzer.

Transition temperatures were measured using a Mettler FP-82 HT hot stage and control unit in conjunction with a Leica polarizing microscope. The associated enthalpies were obtained from DSC-thermograms which were recorded on a Perkin-Elmer DSC-7, heating and cooling rate: 10°C min^{-1}.

Electro-optical investigation of compound **1a** was carried out by using a commercially available 6 μm noncoated indium tin oxide (ITO) cell (E.H.C. Japan) with a measuring area of 1 cm^2.

3.2. Synthesis and Analytical Data

Materials: (*S*)-(-)-2-Methyl-1-butanol (Fluka, 95.0%, $[\alpha]_D^{20}$ $-6.3 \pm 0.5°$, $c = 10$ in EtOH), was purchased commercially.

3.2.1. Synthesis of the 4′-Benzyloxy-3-[4-((S)-2-methylbutoxy)benzoyloxy]biphenyl Bz-A and 4′-Benzyloxy-3-[4-((S)-2-methylbutoxy)benzoyloxy]benzoyloxy]biphenyl Bz-B. The synthesis of the 4′-Benzyloxy-3-[4-((S)-2-methylbutoxy)benzoyloxy]biphenyl **Bz-A** and 4′-Benzyloxy-3-[4-((S)-2-methylbutoxy)benzoyloxy]benzoyloxy]biphenyl **Bz-B** [18] was carried out by the esterification of 4′-benzyloxybiphenyl-3-ol [23–26] with the 4-[(S)-2-Methylbutoxy]benzoic acid[27] or 4-[4-(S)-2-Methylbutoxybenzoyloxy]benzoic acid [17, 28, 29], respectively, according to known procedures. The crude products were purified by column chromatography on silica gel, elution with dichloromethane and crystallized from ethanol. The preparation procedures and spectroscopic data for compound **Bz-B** are given in Ocak et al. [18].

4′-Benzyloxy-3-[4-((S)-2-methylbutoxy)benzoyloxy]biphenyl ($C_{31}H_{30}O_4$; 466.57 g/mol)

Bz-A: Yield: 78%, white crystals; m.p.: 110°C. **^{1}H-NMR**: δ (ppm) = 8.12 (d, $J \approx 9.1$ Hz; 2 Ar-H), 7.50 (d, $J \approx 8.9$ Hz; 2 Ar-H), 7.45–7.41 (m, 4 Ar-H), 7.39–7.30 (m, 4 Ar-H), 7.12–7.09 (m, 1 Ar-H), 7.01 (d, $J \approx 8.9$ Hz; 2 Ar-H), 6.95 (d, $J \approx 9.1$ Hz; 2 Ar-H), 5.08 (s, 2H, OCH_2Ph), 3.88, 3.80 (2dd, $J \approx 9.0$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.92–1.85 (m, 1H, CH), 1.60–1.19 (m, 2H, CH_2), 1.02 (d, $J \approx 6.6$ Hz; 3H, CH_3), 0.94 (t, $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR**: δ (ppm) = 163.64 (CO), 158.56, 151.45, 142.34, 136.89, 133.06, 121.59 (Ar-C), 132.21, 129.56, 128.55, 128.20, 127.93, 127.42, 123.95, 120.06, 119.95, 115.20, 114.35 (Ar-CH), 73.22, 70.22 (OCH_2), 34.79 (CH), 26.25 (CH_2), 16.63, 11.42 (CH_3). **MS (EI):** *m/z* (%) = 466 (16) [M^+], 191 (100) [M^+-$C_{19}H_{15}O_2$], 121 (80) [C_5H_{11}], 91 (37) [C_2H_6].

3.2.2. Synthesis of the 3′-[4-((S)-2-Methylbutoxy)benzoyloxy]biphenyl-4-ol A and 3′-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy]biphenyl-4-ol B. The deprotection of the benzyl group of the **Bz-A** and **Bz-B** to obtain *3′-[4-((S)-2-Methylbutoxy)benzoyloxy]biphenyl-4-ol* ***A*** *and 3′-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy]biphenyl-4-ol* ***B*** [18] was carried out under catalytic hydrogenation conditions (H_2, Pd/C in THF) according to procedures described in ref.[26] The compounds were purified by column chromatography on silica gel using dichloromethane as eluent.

The preparation procedures and spectroscopic data for compound ***B*** are given in Ocak et al. [18].

3′-[4-((S)-2-Methylbutoxy)benzoyloxy]biphenyl-4-ol ($C_{24}H_{24}O_4$; 376.45 g mol^{-1})

A: Yield: 47%, yellowish crystals; m.p.: 99°C. **^{1}H-NMR**: δ (ppm) = 8.14 (d, $J \approx 8.7$ Hz; 2 Ar-H), 7.45–7.39 (m, 4 Ar-H), 7.37–7.35 (m, 1 Ar-H), 7.13–7.10 (m, 1 Ar-H), 6.96 (d, $J \approx 8.7$ Hz; 2 Ar-H), 6.86 (d, $J \approx 8.3$ Hz; 2 Ar-H), 3.89, 3.81 (2dd, $J \approx 8.9$ Hz and $J \approx 6.2$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 1.93–1.85 (m, 1H, CH), 1.60–1.20 (m, 2H, CH_2), 1.03 (d, $J \approx 6.6$ Hz; 3H, CH_3), 0.95 (t, $J \approx 7.3$ Hz; 3H, CH_3). **^{13}C-NMR**: δ (ppm) = 163.74 (s; CO), 155.46, 151.43, 142.39, 132.90, 121.46 (Ar-C), 132.26, 129.62, 128.41, 123.99, 120.07, 119.93, 115.65, 114.33 (Ar-CH), 73.10 (OCH_2), 34.62 (CH), 26.06 (CH_2), 16.46, 11.26 (CH_3). **MS (EI):** *m/z* (%) = 376 (36) [M^+], 191 (100) [M^+-$C_{12}H_9O_2$], 121 (77) [C_5H_{11}].

3.2.3. Synthesis of the Olefins 1-3. Compounds **1-3** with a terminal double bond were obtained by esterification of 3′-[4-((S)-2-Methylbutoxy)benzoyloxy]biphenyl-4-ol **A** (2 mmol) or 3′-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy]biphenyl-4-ol **B** with the appropriate 4-[4-(alkenyloxy)benzoyloxy]benzoic acid **C/n** (2 mmol) or 4-(alkenyloxy)benzoic acid **D/n** (2 mmol), using 2.3 mmol of dicyclohexylcarbodiimide (DCC) as condensation agent and DMAP (0.4 mmol) as catalyst in 20 ml of dry dichloromethane [30]. The reaction mixture was stirred at room temperature under an argon atmosphere for 24 h. The precipitate was filtered, the solvent was evaporated. The crude products were purified by column chromatography on silica gel using dichloromethane as eluent and recrystallized from ethanol. The spectroscopic data for compound **3b** are given in Ocak et al. [18].

3′-[4-((S)-2-Methylbutoxy)benzoyloxy]-4-{4-[4-(10-undecenyloxy)benzoyloxy] benzoyloxy}biphenyl ($C_{49}H_{52}O_8$; 768.95 g/mol)

1a: Yield: 0.87 g (57%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.15 (d; $J \approx 8.9$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.64 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.48-7.47 (m; 2 Ar-H), 7.42 (broad s; 1 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.29 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.21-7.18 (m, 1 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 4 Ar-H), 5.85-5.75 (m; 1H, $CH_2 = C\underline{H}$), 5.00-4.91 (m; 2H, $C\underline{H_2} = CH$), 4.04 (t; $J \approx 6.4$ Hz; 2H, OCH_2), 3.90, 3.82 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain), 2.06-2.00 (m; 2H, $CH_2 = CH\text{-}C\underline{H_2}$), 1.94-1.87 (m; 1H, CH), 1.86-1.77 (m, 2H, CH_2), 1.63-1.24 (m; 7 CH_2), 1.03 (d; $J \approx 6.6$ Hz; 3H, CH_3), 0.96 (t; $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR**: δ (ppm) = 164.83, 164.35, 164.20 (CO), 163.76, 163.69, 155.30, 151.50, 150.57, 141.92, 138.10, 126.84, 121.52, 121.01 (Ar-C), 132.38, 132.26, 131.79, 129.72, 128.28, 124.41, 122.08, 122.01, 120.72, 120.55, 114.45, 114.37 (Ar-CH), 139.12 ($CH_2 = \underline{C}H$), 114.13 ($\underline{C}H_2 = CH$), 73.22, 68.49 (OCH_2), 34.80 (CH), 33.92, 29.83, 29.62, 29.54, 29.47, 29.24, 29.07, 26.26, 26.12 (CH_2), 16.65, 11.45 (CH_3). **MS (EI):** *m/z* (%) = 768 (1) [M^+], 393 (4) [M^+-$C_{24}H_{23}O_4$], 273 (45) [$C_7H_4O_2$], 191 (69) [M^+-$C_{37}H_{37}O_6$], 121 (100) [C_5H_{11}]. **$C_{49}H_{52}O_8$** (768.95); Anal. Calc.: C, 76.53; H, 6.81. Found: C, 76.23; H, 6.67%.

3′-[4-((S)-2-Methylbutoxy)benzoyloxy]-4-{4-[4-(5-hexenyloxy)benzoyloxy] benzoyloxy}biphenyl ($C_{44}H_{42}O_8$; 698.81 g/mol)

1b: Yield: 0.77 g (55%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 2 Ar-H), 8.13 (d; $J \approx 8.9$ Hz; 2 Ar-H), 7.64 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.48-7.47 (m; 2 Ar-H), 7.42 (broad s; 1 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.20-7.17 (m, 1 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 4 Ar-H), 5.87-5.77 (m; 1H, $CH_2 = C\underline{H}$), 5.06-4.97 (m; 2H, $C\underline{H_2} = CH$), 4.05 (t; $J \approx 6.4$ Hz; 2H, OCH_2), 3.90, 3.82 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 2.16-2.11 (m; 2H, $CH_2 = CH\text{-}C\underline{H_2}$), 1.92-1.87 (m; 1H, CH), 1.86-1.80 (m, 2H, CH_2), 1.62-1.24 (m; 2 CH_2), 1.03 (d; $J \approx 6.6$ Hz; 3H, CH_3), 0.96 (t; $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR**: δ (ppm) = 164.84, 164.35, 164.19 (CO), 163.77, 163.68, 155.37, 151.49, 150.56, 141.92, 138.10, 126.85, 121.51, 121.07 (Ar-C), 132.39, 132.25, 131.79, 129.72, 128.28, 124.41, 122.07, 122.00, 120.72, 120.55, 114.90, 114.43 (Ar-CH), 138.26 ($CH_2 = \underline{C}H$), 114.37 ($\underline{C}H_2 = CH$), 73.22, 68.25 (OCH_2), 34.80 (CH), 33.49, 28.67, 26.26, 25.41 (CH_2), 16.65, 11.45 (CH_3). **MS (EI):** *m/z* (%) = 698 (1) [M^+], 203 (59) [M^+-$C_{31}H_{27}O_6$], 191 (58) [$C_{32}H_{27}O_6$], 121 (100) [C_5H_{11}]. **$C_{44}H_{42}O_8$** (698.81); Anal. Calc.: C, 75.62; H, 6.06. Found: C, 75.60; H, 6.05%.

3′-{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}-4-[4-(10-undecenyloxy)benzoyloxy] biphenyl ($C_{49}H_{52}O_8$; 768.95 g/mol)

2a: Yield: 0.71 g (46%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.7$ Hz; 4 Ar-H), 7.63 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.49-7.48 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.27 (d; $J \approx 8.5$ Hz; 2 Ar-H), 7.21-7.18 (m, 1 Ar-H), 6.98 (d; $J \approx 8.7$ Hz; 2 Ar-H), 6.96 (d; $J \approx 8.7$ Hz; 2 Ar-H), 5.79-5.75 (m; 1H, $CH_2 = C\underline{H}$), 5.00-4.90 (m; 2H, $C\underline{H_2} = CH$), 4.03 (t; $J \approx 6.6$ Hz; 2H, OCH_2), 3.90, 3.83 (2dd, $J \approx 9.0$ Hz and $J \approx 5.8$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 2.04-2.00 (m; 2H, $CH_2 = CH\text{-}C\underline{H_2}$), 1.91-1.88 (m; 1H, CH), 1.83-1.79 (m, 2H, CH_2), 1.60-1.24 (m; 7 CH_2), 1.04 (d; $J \approx 6.6$ Hz; 3H, CH_3), 0.96 (t; $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR**: δ (ppm) = 164.84, 164.41, 164.26 (CO), 163.96, 163.55, 155.41, 151.32, 150.85, 142.15, 137.73, 126.87, 121.50, 120.97 (Ar-C), 132.37, 132.27, 131.79, 129.79, 128.20, 124.64, 122.14, 122.08, 120.51, 120.40, 114.45, 114.32 (Ar-CH), 139.14 ($CH_2 = \underline{C}H$), 114.10 ($\underline{C}H_2 = CH$), 73.20, 68.36 (OCH_2), 34.69 (CH), 33.81, 29.51, 29.43, 29.36, 29.13, 28.96, 26.14, 26.01 (CH_2), 16.52, 11.32 (CH_3). **MS (EI):** *m/z* (%) = 768 (10) [M^+], 273 (100) [M^+-$C_{31}H_{27}O_6$], 191 (31) [M^+-$C_{37}H_{37}O_6$], 121 (71) [C_5H_{11}]. **$C_{49}H_{52}O_8$** (768.95); Anal. Calc.: C, 76.54; H, 6.81. Found: C, 76.44; H, 6.64%.

3′-{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}-4-[4-(5-hexenyloxy)benzoyloxy] biphenyl ($C_{44}H_{42}O_8$; 698.81 g/mol)

2b: Yield: 1.05 g (75%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.16 (d; $J \approx 8.5$ Hz; 4 Ar-H), 7.65 (d; $J \approx 8.6$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.45 (broad s; 1 Ar-H), 7.38 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.29 (d; $J \approx 8.6$ Hz; 2 Ar-H), 7.23-7.21 (m, 1 Ar-H), 6.99 (d; $J \approx 8.5$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.5$ Hz; 2 Ar-H), 5.84-5.81 (m; 1H, $CH_2 = C\underline{H}$), 5.07-4.98 (m; 2H, $C\underline{H_2} = CH$), 4.06 (t; $J \approx 6.4$ Hz; 2H, OCH_2), 3.92, 3.84 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 2.17-2.13 (m; 2H, $CH_2 = CH\text{-}C\underline{H_2}$), 1.93-1.88 (m; 1H, CH), 1.86-1.82 (m, 2H, CH_2), 1.63-1.25 (m; 2 CH_2), 1.05 (d; $J \approx 6.8$ Hz; 3H, CH_3), 0.97 (t; $J \approx 7.5$ Hz; 3H, CH_3). **^{13}C-NMR**: δ (ppm) = 164.78, 164.37, 164.22 (CO), 163.92, 163.45, 155.39, 151.30, 150.82, 142.13, 137.73, 126.88, 121.58, 120.98 (Ar-C), 132.37, 132.28, 131.78, 129.79, 128.21, 124.64, 122.14, 122.09, 120.52, 120.40, 114.88, 114.47 (Ar-CH), 138.29 ($CH_2 = \underline{C}H$), 114.33 ($\underline{C}H_2 = CH$), 73.27, 68.20 (OCH_2), 34.80 (CH), 33.50, 28.69, 26.26, 25.42 (CH_2), 16.64, 11.45 (CH_3). **MS (EI):** *m/z* (%) = 698 (1) [M^+], 203 (91) [M^+-$C_{31}H_{27}O_6$], 191 (38) [M^+-$C_{32}H_{27}O_6$], 121 (100) [C_5H_{11}]. **$C_{44}H_{42}O_8$** (698.81); Anal. Calc.: C, 75.62; H, 6.05. Found: C, 75.37; H, 6.00%.

3′-{4-[4-((S)-2-Methylbutoxy)benzoyloxy]benzoyloxy}-4-{4-[4-(10-undecenyloxy) benzoyloxy]benzoyloxy}biphenyl ($C_{56}H_{56}O_{10}$; 889.05 g mol^{-1})

3a: Yield: 1.17 g (66%) of white crystals. **^{1}H-NMR**: δ (ppm) = 8.29 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.28 (d; $J \approx 8.7$ Hz; 2 Ar-H), 8.14 (d; $J \approx 8.9$ Hz; 4 Ar-H), 7.65 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.51-7.50 (m; 2 Ar-H), 7.44 (broad s; 1 Ar-H), 7.37 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.36 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.30 (d; $J \approx 8.7$ Hz; 2 Ar-H), 7.22-7.19 (m, 1 Ar-H), 6.98 (d; $J \approx 8.9$ Hz; 2 Ar-H), 6.97 (d; $J \approx 8.9$ Hz; 2 Ar-H), 5.84-5.77 (m; 1H, $CH_2 = C\underline{H}$), 5.00-4.91 (m; 2H, $C\underline{H_2} = CH$), 4.04 (t; $J \approx 6.6$ Hz; 2H, OCH_2), 3.91, 3.83 (2dd, $J \approx 9.1$ Hz and $J \approx 6.0$ Hz each; 2H, OCH_2, (chiral alkyl chain)), 2.06-2.00 (m; 2H, $CH_2 = CH\text{-}C\underline{H_2}$), 1.93-1.88 (m; 1H, CH), 1.85-1.78 (m, 2H, CH_2), 1.62-1.24 (m; 7 CH_2), 1.04 (d; $J \approx 6.9$ Hz; 3H, CH_3), 0.96 (t; $J \approx 7.3$ Hz; 3H, CH_3). **^{13}C-NMR**: δ (ppm) = 164.42, 164.34, 164.31, 164.20 (CO), 163.92, 163.75, 155.42, 151.33, 150.63, 142.06, 137.98, 126.87, 126.83, 121.02, 120.99 (Ar-C), 132.39, 131.80, 129.83, 128.30, 124.67, 122.09, 122.05, 120.58, 120.42, 114.46, 114.45 (Ar-CH), 139.09 ($CH_2 = \underline{C}H$), 114.12 ($\underline{C}H_2 = CH$), 73.20, 68.42 (OCH_2), 34.69 (CH), 33.81, 30.98, 29.51, 29.43, 29.36, 29.13, 28.96, 26.14, 26.01 (CH_2), 16.52, 11.32 (CH_3). **MS (EI):** *m/z* (%) = 889 (1) [M^+], 393 (5) [M^+-$C_{31}H_{27}O_6$], 273 (45) [M^+-$C_7H_4O_2$], 191 (74) [M^+-$C_{44}H_{41}O_8$], 121 (100) [C_5H_{11}]. **$C_{56}H_{56}O_{10}$** (889.05); Anal. Calc.: C, 75.65; H, 6.35. Found: C, 75.35; H, 6.14%.

4. Conclusions

We have synthesized and characterized new nonsymmetrical bent-core compounds consisting of a biphenyl-3,4′-diol central unit, a chiral terminal chain and an olefinic end group at the other terminus to study structure—mesogenic property relations of bent-core molecules combining molecular chirality with superstructural chirality. The thermal stability and mesophase type of the non-symmetrical bent-core molecules are significantly influenced by varying the structure of rod-like wings at the two sides of the 3′- or 4-position of biphenyl central core. Depending on the length of the olefinic chain and the number of aromatic rings in the rod-like wings, the studied compounds exhibit liquid crystalline mesophases such as SmCP and B_1 or nonmesomorphic behavior. For one of the five-ring compounds with the chiral moiety at the shorter wing of the bent structure, the SmCP was observed. Decreasing the terminal alkenyl chain length of bent-core compounds comprising five aromatic rings leads to nonmesomorphism. The broader mesomorphic ranges were exclusively obtained for biphenyl based bent-core compounds with the longer wings. From the obtained data, we also conclude that the molecular chirality has no effect on the mesophases of the molecules reported here.

Funding

The work has been supported by the Scientific and Technological Research Council of Turkey (TUBITAK) under Project Number: 107T395.

References

[1] Niori, T., Sekine, T., Watanabe, J., Furukawa, T., & Takezoe, H. (1996). *J. Mater. Chem.*, *6*(7), 1231–1233.
[2] Amaranatha Reddy, R., & Tschierske, C. (2006). *J. Mater. Chem.*, *16*, 907–961.
[3] Prasad, V., Kang, S.-W., & Kumar, S. (2003). *J. Mater. Chem.*, *13*, 1259–1264.
[4] Gomola, K. *et al.* (2009). *J. Mater. Chem.*, *19*, 4240–4247.
[5] Bubnov, A. *et al.* (2011). *Macromol. Chem. Phys.*, *212*, 191–197.
[6] Maksimenko, S. I., Gorecka, E., Novikova, N. S., & Kondratyeva, R. V. (2010). *Liq. Cryst.*, *37*(1), 93–99.
[7] Dunemann, U. *et al.* (2005). *J. Mater. Chem.*, *15*, 4051–4061.
[8] Achten, R., Koudijs, A., Giesbers, M., Marcelis, A. T. M., & Sudhölter, E. J. R. (2005). *Liq. Cryst.*, *32*(3), 277–285.
[9] Balamurugan, S., Kannan, P., Yadupati, K., & Roy, A. (2011). *Liq. Cryst.*, *38*(9), 1199–1207.
[10] Achten, R. *et al.* (2004). *Liq. Cryst.*, *31*(8), 1167–1174.
[11] Kumazawa, K. *et al.* (2004). *J. Mater. Chem.*, *14*, 157–164.
[12] Lee C. K. *et al.* (2003). *Liq. Cryst.*, *30*, 1401.
[13] Lee, S. K. *et al.* (2005). *Liq. Cryst.*, *32*, 1205–1212.
[14] Lee, S. K. *et al.* (2005). *J. Am. Chem. Soc.*, *127*, 11085–11091.
[15] Nishida, K. *et al.* (2006). *Phys. Rev. E*, *74*, 021704.
[16] Thisayukta, J., Niwano, H., Takezoe, H., & Watanabe, J. (2001). *J. Mater. Chem.*, *11*, 2717–2721.
[17] Ocak, H. *et al.* (2011). *Soft Matter*, *7*, 8266–8280.
[18] Ocak, H., Bilgin-Eran, B., Prehm, M., & Tschierske, C. (2012). *Soft Matter*, *8*, 7773–7783.
[19] Reddy, R. A., Sadashiva, B. K., & Baumeister, U. (2005). *J. Mater. Chem.*, *15*, 3303–3316.
[20] Keith, C., Reddy, R. A., & Tschierske, C. (2005). *Chem. Commun.*, *7*, 871–873.
[21] Achten, R. *et al.* (2006). *Liq. Cryst.*, *33*, 681–688.
[22] Novotná, V. *et al.* (2012). *Liq. Cryst.*, *39*(10), 1252–1260.
[23] Miyaura, N., Yanagi, T., & Suzuki, A. (1981). *Synth. Commun.*, *11*, 513–519.
[24] Miyaura, N., & Suzuki, A. (1995). *Chem. Rev.*, *95*, 2457–2483.
[25] Hird, M., Gray, G. W., & Toyne, K. J. (1991). *Mol. Cryst. Liq. Cryst.*, *206*, 187–204.
[26] Keith, C., Reddy, R. A., Hauser, A., Baumeister, U., & Tschierske, C. (2006). *J. Am. Chem. Soc.*, *128*, 3051–3066.
[27] Kaeding-Koppers, A., Zugenmaier, P., & Roman, M. (2008), *Can. J. Chem.*, *86*(6), 525–532.
[28] Xie, M., Qin, J., Hu, Z., & Zhao, H. (1992). *Chin. Chem. Lett.*, *3*, 775–778.
[29] Jun, Q., Ming-Gui, X., Zi-Lun, H., Hua-Ming, Z., & Shi-Kui, L. (1992). *Synth. Commun.*, *22*, 2253–2258.
[30] Tschierske, C., & Zaschke, H. (1989). *J. Prakt. Chem.*, *331*, 365–366.

[31] Otterholm, B., Nilsson, M., Lagerwall, S. T., & Skarp, K. (1987). *Liq. Cryst.*, *2*, 757–769.

[32] Schiewe, B., Hohmuth, A., Weissflog, W., & Kresse, H. (1996). *Mol. Cryst. Liq. Cryst.*, *287*, 115–127.

[33] Hempenius, M. A., Lammertink, R. G. H., & Vancso, G. J. (1997). *Macromolecules*, *30*(2), 266–272.

[34] Bispo, M., Guillon, D., Donnio, B., & Finkelmann, H. (2008). *Macromolecules*, *41*(9), 3098–3108.

[35] Keith, C. *et al.* (2007). *Chem. Eur. J.*, *13*, 2556–2577.

[36] Amaranatha Reddy, R. *et al.* (2007), *Soft. Matter*, *3*, 558–570.

[37] Ocak, H., Bilgin-Eran, B., Prehm, M., & Tschierske, C. (2013). *Soft Matter*, *9*, 4590–4597.

[38] Ocak, H., Bilgin-Eran, B., Tschierske, C., Baumeister, U., & Pelzl, G. (2009). *J. Mater. Chem.*, *19*, 6995–7001.

[39] Takezoe, H., & Takanishi, Y. (2006). *Jpn. J. Appl. Phys.*, *45*, 597–625.