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Liquid Crystals

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Non-symmetrical bent-shaped liquid crystals with five ester groups

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In this study a new series of bent-core liquid crystals based on laterally substituted 7-hydroxynaphthalene-2-carboxylic acid is presented. All compounds exhibit broken-layer type columnar phases. For CH₃ laterally substituted compounds with a longer chain we found a smectic A above a columnar phase on cooling from the isotropic phase. Additionally, for CH₃-substituted compounds with the longest chains (C₁₄H₂₉) two switchable columnar phases (B_{1RevT}) occurred below the SmA phase. Two columnar phases were also found for Cl-substituted homologues with the long chain C₁₂H₂₅ and C₁₄H₂₉. For the Cl-substituted materials we found significant lowering of transition temperatures and a very steady columnar phase in a broad temperature interval of up to 130 K.

Keywords: bent-shaped liquid crystals; ester linkage orientation; naphthalene; mesomorphic properties

1. Introduction

In recent years, bent-core materials have raised considerable interest in the field of liquid crystal research due to their ability to form new mesophases [1–8]. Among others, it was shown that the direction of linking ester groups is an important factor influencing polarity and bending of the banana-shaped molecules and thus their mesomorphic behaviour [9–16]. In a series of resorcinol-based compounds, where orientation of the linking ester group was systematically changed [16], the calculated dipole moments, the bending angle, the molecular length and the electrostatic potential distribution on the centres of the rings were correlated with the mesophase properties. It was demonstrated [17] that the conformational flexibility of the wings is essentially determined by the arrangement of the polar ester groups. In isomers with high flexibility of the wings, lower electron density on the central ring and a lower dipole moment can be related to lower clearing temperatures and preference to form smectic phases. On the contrary, compounds with lower conformational freedom show higher mesophase stability and tend to form columnar phases. It was also shown that symmetrical materials with carboxylate groups [18–20] located in the terminal chains exhibited smectic phases and switching behaviour.

Previously we investigated symmetrical and non-symmetrical bent-shaped materials with the naphthalene-2,7-diol central core [21–24]. In a series of materials with the same orientation of both ester groups [22] we documented varying mesomorphic behaviour. The type of the mesophases formed depended both on the character of the lateral substituent and the length of the

terminal alkoxy chain. In our preceding paper [25] we studied materials with one ester group between the central and the neighbouring ring in reversed position. Depending on the length of the terminal chain, more oriented polar columnar phases made of broken smectic layer fragments with either orthogonal or tilted molecule arrangements (B_{1Rev} and B_{1RevT}, respectively) were observed, as well as the lamellar B₂ phase. In some compounds the nematic–B_{1Rev} phase sequence was also established. The structural character of switchable columnar phases (B_{1Rev}) is described elsewhere [26–28]. In our follow-up study of naphthalene-based mesogens herein we present three series of non-symmetrical bent-core materials with five ester linkages in lengthening arms pointing in the same direction. Furthermore, the mesomorphic properties of the new materials were tuned by the introduction of methyl and chloro substituents into the central core.

2. Experimental details

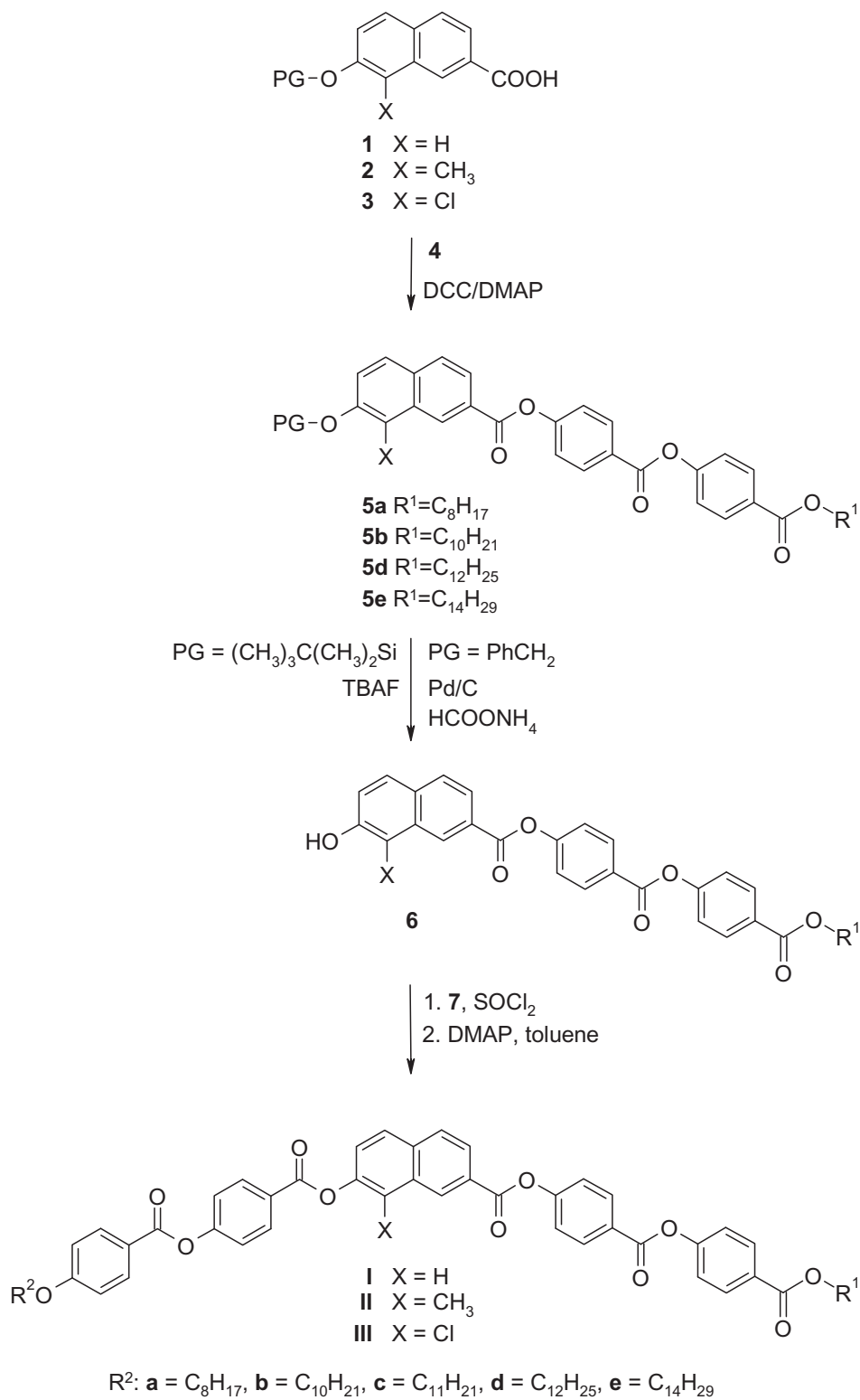
2.1 Synthesis

Syntheses of the central cores and their protected derivatives **1–3** have been published recently [25]. The lengthening arms of the target materials, alkyl 4-[(4-hydroxybenzoyl)oxy]benzoates (**4a,b,d,e**) (**a** octyl, **b** decyl, **d** dodecyl and **e** tetradecyl) and 4-[(4-alkoxybenzoyl)oxy]benzoic acids (**7a–e**) (**a** octyl, **b** decyl, **c** undec-10-enyl, **d** dodecyl and **e** tetradecyl) were obtained by known methods [22, 29, 30]. The bent-shaped liquid crystals (series **I–III**) with structurally different arms were synthesised in three steps. The protected acids **1–3** were esterified with

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the corresponding phenol **4** in the presence of *N,N'*-dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) (Scheme 1) to form an ester of

general formula **5**. The benzylic protecting group in **5** was removed by palladium-catalysed transfer-hydrogenation, and the silyl protecting group was removed



Scheme 1. The synthetic route and designation of compounds.

using tetrabutylammonium fluoride. The obtained hydroxy esters **6** were finally acylated with acid chlorides derived from acids **7** *in situ*. The acid chloride method turned out to be more advantageous than the standard DCC mediated coupling. The procedures for the synthesis of representative intermediates and target compounds of series **I–III** are summarised below.

2.2 Characterisation

Structures of intermediates and products were confirmed by ^1H nuclear magnetic resonance (NMR) spectroscopy (Varian Gemini 300 HC instrument); deuteriochloroform was used as solvent and signals of the solvent served as internal standard, and J values are given in Hz. Elemental analyses were carried out on a Perkin-Elmer 2400 instrument. Purity of all final compounds was confirmed by high-performance liquid chromatography (HPLC) analysis (Tessek C18 25 \times 4.5 RP column) and found to be 99.8%. Column chromatography was carried out using Merck Kieselgel 60 (60–100 μm). Procedures for the synthesis of representative intermediates **5** and **6** and target compounds of series **I**, **II** and **III** are summarised below.

2.2.1 Octyl 4-{4-((7-benzyloxynaphthalene-2-carbonyl]oxy)benzoyl)oxy}benzoate (**5a**)

To a solution of acid **1** (0.3 g; 1.08 mmol), hydroxy ester **4a** (0.42 g; 1.13 mmol) and catalytic amount of DMAP (50 mg) in dry dichloromethane (40 ml), DCC (0.24 g; 1.14 mmol) was added and the reaction mixture was stirred at room temperature for 3 h. It was decomposed with water (0.2 ml), filtered and the filtrate evaporated. The crude product was purified by crystallisation from a toluene/ethanol mixture. 0.57 g (84%) of ester **5a** was isolated, m.p. 164.5–166°C. ^1H NMR: 0.89 (t, 3 H), 1.30 (m, 8 H), 1.42 (m, 2 H), 1.77 (m, 2 H), 4.33 (t, 2 H, COOCH₂), 5.22 (s, 2 H, CH₂O), 7.32 (d, 2 H), 7.35–7.54 (m, 9 H, 7 \times CH, H-6, H-8), 7.85 (d, 1 H, $J = 8.8$, H-5), 7.90 (d, 1 H, $J = 8.5$, H-4), 8.07 (dd, 1 H, $^3J = 8.5$, $^4J = 1.5$, H-3), 8.14 (d, 2 H, 8.32 (d, 2 H), 8.68 (s, 1 H, H-1). Elemental analysis: for C₄₀H₃₈O₇ (630.74), calculated C 76.17, H 6.07; found C 75.84, H 6.12%.

Analogously, derivatives **5b** (R = C₁₀H₂₁, yield 89%, m.p. 164–165°C), **5d** (R = C₁₂H₂₅, yield 92%, m.p. 161.5–163°C), **5e** (R = C₁₄H₂₉, yield 90%, m.p. 163–164°C) were obtained.

In the same way, the reaction of **2** with hydroxy ester (**4a**, **4b**, **4d** or **4e**) yielded methyl derivatives **5f–5i**. Octyl 4-(4-((7-benzyloxy-8-methylnaphthalene-2-carbonyl]oxy)-benzoyl)oxy)benzoate (**5f**) was purified by

crystallisation from a toluene/ethanol mixture, yield 87%, m.p. 78–81°C. ^1H NMR: 0.90 (t, 3 H), 1.27 (m, 8 H), 1.40 (m, 2 H), 1.79 (m, 2 H), 2.72 (s, 3 H, CH₃), 4.35 (t, 2 H, COOCH₂), 5.25 (s, 2 H, CH₂O), 7.34 (d, 2, 7.37–7.56 (m, 9 H, 7 \times CH, H-6, H-8), 7.77 (d, 1 H, $J = 9.1$, H-5), 7.90 (d, 1 H, $J = 8.5$, H-4), 8.08 (dd, 1 H, $^3J = 8.5$, $^4J = 1.5$, H-3), 8.16 (d, 2 H), 8.32 (d, 2 H), 8.95 (s, 1 H, H-1). Elemental analysis: for C₄₁H₄₀O₇ (644.77), calculated C 76.38, H 6.25; found C 76.25, H 6.17%.

The other 8-methyl derivatives **5g** (R = C₁₀H₂₁, yield 76%, m.p. 80.5–82°C), **5h** (R = C₁₂H₂₅, yield 76%, m.p. 76–77.5°C) and **5i** (R = C₁₄H₂₉, yield 78%, m.p. 78–80°C) were prepared by the same procedure.

2.2.2 Octyl 4-{4-((7-(tert-butyldimethylsilyloxy)-8-chloronaphthalene-2-carbonyl]oxy)benzoyl)oxy}benzoate (**5j**)

Analogously as for **5a**, acid **3** (0.2 g; 0.59 mmol) reacted with hydroxy ester **4a** (0.24 g; 0.65 mmol) in the presence of DCC (0.13 g; 0.63 mmol) and a catalytic amount of DMAP (30 mg) in dry CH₂Cl₂ (35 ml). Purification by column chromatography (silica gel, hexane/ethyl acetate, 12:1) afforded 0.29 g (72%) of silyl derivative **5j**, m.p. 84–85°C. ^1H NMR: 0.30 (s, 6 H, (CH₃)₂Si), 0.88 (t, 3 H), 1.09 (s, 9 H, (CH₃)₃CSi), 1.24 (m, 8 H), 1.45 (m, 2 H), 1.78 (m, 2 H), 4.33 (t, 2 H, COOCH₂), 7.29 (d, 1 H, $J = 8.8$, H-6), 7.32 (d, 2 H), 7.46 (d, 2 H), 7.75 (d, 1 H, $J = 8.8$, H-5), 7.92 (d, 1 H, $J = 8.5$, H-4), 8.13 (dd, 1 H, $^3J = 8.5$, $^4J = 1.8$, H-3), 8.14 (d, 2 H), 8.32 (d, 2 H), 9.15 (s, 1 H, H-1). Elemental analysis: for C₃₉H₄₅ClO₇Si (689.33), calculated C 67.96, H 6.58, Cl 5.14; found C 68.23, H 6.73, Cl 4.98%.

Analogously, esters **5k** (R¹ = C₁₀H₂₁, yield 67%, m.p. 80–81°C), **5l** (R¹ = C₁₂H₂₅, yield 66%, m.p. 77.5–79°C) and **5m** (R¹ = C₁₄H₂₉, yield 65%, m.p. 82–83.5°C) were obtained.

2.2.3 Octyl 4-{4-((7-hydroxynaphthalene-2-carbonyl]oxy)benzoyl)oxy}benzoate (**6a**)

To a solution of benzyl derivative **5a** (0.50 g; 0.79 mmol) in acetone (50 ml), 10% Pd/C (50 mg) was added, followed by ammonium formate (0.20 g; 3.17 mmol). The reaction mixture was heated to boiling for 3 h. The hot mixture was filtered and the filtrate was evaporated. The crude product was purified by column chromatography (silica gel, toluene/*tert*-butyl methyl ether, 20/1). 0.22 g (51%) of ester **6a** was obtained, m.p. 161–162°C. ^1H NMR: 0.89 (t, 3 H), 1.29 (m, 8 H), 1.45 (m, 2 H), 1.78 (m, 2 H), 4.34 (t, 2 H, COOCH₂), 5.29 (s, 1 H, OH), 7.30 (m, 4 H, 2 \times CH, H-6, H-8), 7.45 (d, 2 H), 7.85 (d, 1 H, H-5), 7.90 (d, 1 H,

H-4), 8.05 (dd, 1 H, $^3J = 8.5$, $^4J = 1.5$, H-3), 8.14 (d, 2 H), 8.32 (d, 2 H), 8.64 (s, 1 H, H-1). Elemental analysis: for $C_{33}H_{32}O_7$ (540.62) calculated C 73.32, H 5.97; found C 73.01, H 6.29%.

In the same way, esters **6b** ($R = C_{10}H_{21}$, yield 62%, m.p. 159.5–161°C), **6d** ($R = C_{12}H_{25}$, yield 74%, m.p. 154–155.5°C), **6e** ($R = C_{14}H_{29}$, yield 75%, m.p. 154.5–156°C) were obtained.

Deprotection of benzyl derivatives **5f–5i** yielded the corresponding hydroxy esters **6f–6i**. Octyl 4- $\{4-((7\text{-hydroxy-8-methylnaphthalene-2-carbonyl})\text{oxy})\text{-benzoyl}\text{oxy}\}$ benzoate (**6f**) was purified by column chromatography (silica gel, toluene/*tert*-butyl methyl ether, 20/1), yield 79%, m.p. 114–116°C. ^1H NMR: 0.89 (t, 3 H), 1.28 (m, 8 H), 1.39 (m, 2 H), 1.78 (m, 2 H), 2.64 (s, 3 H, CH_3), 4.34 (t, 2 H, COOCH_2), 5.15 (s, 1 H, OH), 7.23 (d, 1 H, $J = 8.8$, H-6), 7.32 (d, 2 H), 7.39 (d, 2 H), 7.71 (d, 1 H, $J = 8.8$, H-5), 7.89 (d, 1 H, $J = 8.5$, H-4), 8.07 (dd, 1 H, $^3J = 8.5$, $^4J = 1.5$, H-3), 8.15 (d, 2 H), 8.32 (d, 2 H), 8.89 (s, 1 H, H-1). Elemental analysis: for $C_{34}H_{34}O_7$ (554.65), calculated C 73.63, H 6.18; found C 73.58, H 6.07%.

Analogously, 8-methyl derivatives **6g** ($R = C_{10}H_{21}$, yield 79%, m.p. 110–113°C), **6h** ($R = C_{12}H_{25}$, yield 89%, m.p. 109.5–112°C) and **6i** ($R = C_{14}H_{29}$, yield 88%, m.p. 111–113°C) were prepared.

2.2.4 Octyl 4- $\{4-([8\text{-chloro-7-hydroxynaphthalene-2-carbonyl}] \text{oxy})\text{benzoyl}\text{oxy}\}$ benzoate (**6j**)

To a solution of silyl derivative **5j** (0.16 g; 0.23 mmol) in THF (30 ml), TBAF (0.02 mg; 0.06 mmol) was added. The reaction mixture was stirred at room temperature for 1.5 h, diluted with water (30 ml) and ethyl acetate (25 ml). Layers were separated and the aqueous layer was extracted with ethyl acetate (2×20 ml). The combined organic solution was washed with water (30 ml) and dried with anhydrous magnesium sulphate. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, hexane/ethyl acetate, 6/1). 0.12 g (92%) of ester **6j** was obtained, m.p. 124–125.5°C. ^1H NMR: 0.88 (t, 3 H), 1.26 (m, 8 H), 1.47 (m, 2 H), 1.78 (m, 2 H), 4.33 (t, 2 H, COOCH_2), 6.01 (s, 1 H, OH), 7.32 (d, 2 H), 7.43 (d, 1 H, $J = 8.8$, H-6), 7.45 (d, 2 H), 7.81 (d, 1 H, $J = 8.8$, H-5), 7.94 (d, 1 H, $J = 8.5$, H-4), 8.14 (d, 3 H, $2 \times \text{CH}$, H-3), 8.33 (d, 2 H), 9.01 (s, 1 H, H-1). Elemental analysis for $C_{33}H_{31}ClO_7$ (575.06) calculated C 68.93, H 5.43, Cl 6.17; found C 68.54, H 4.45, Cl 6.23%.

By the same procedure compounds **6k** ($R^1 = C_{10}H_{21}$, yield 95%, m.p. 122.5–123.5°C), **6l** ($R^1 = C_{12}H_{25}$, yield 97%, m.p. 117–119.5°C) and **6m**

($R^1 = C_{14}H_{29}$, yield 83%, m.p. 120–121.5°C) were prepared.

2.2.5 Octyl-4- $\{([4-((7-([4-((4\text{-octyloxybenzoyl})\text{oxy})\text{benzoyl})\text{oxy})\text{naphthalene-2-carbonyl})\text{oxy})\text{benzoyl})\text{oxy}\}$ benzoate (**1a**)

A mixture of acid **7a** (0.14 g; 0.38 mmol), thionyl chloride (0.2 ml; 2.8 mmol) and pyridine (0.25 ml; 3.1 mmol) in dry toluene (15 ml) was stirred and heated to boiling for 2 h. The solvent and unreacted thionyl chloride were evaporated and the residue dried at reduced pressure. The crude acid chloride was dissolved in dry toluene (7.5 ml) and added to a hot solution of hydroxy ester **6a** (0.16 g; 0.30 mmol) and DMAP (0.07 g; 0.56 mmol) in toluene (30 ml). After cooling to room temperature, the reaction mixture was diluted with 5% hydrochloric acid (30 ml) and chloroform (30 ml). Layers were separated and the aqueous layer was washed with chloroform (2×15 ml). The combined organic solution was washed with water (2×25 ml), saturated solution of NaCl (30 ml), and dried with anhydrous magnesium sulphate. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, dichloromethane). 0.23 g (68%) of **1a** was obtained. ^1H NMR: 0.89 (t, 3 H), 1.28 (m, 16 H), 1.47 (m, 4 H), 1.81 (m, 4 H), 4.06 (t, 2 H, CH_2O), 4.33 (t, 2 H, COOCH_2), 7.00 (d, 2 H), 7.32 (d, 2 H), 7.41 (d, 2 H), 7.47 (d, 2 H), 7.55 (dd, 1 H, $^3J = 9.1$, $^4J = 2.2$, H-6), 7.89 (d, 1 H, $J = 2.2$, H-8), 8.02 (d, 2 H, H-4, H-5), 8.14 (d, 2 H), 8.17 (d, 2 H), 8.22 (dd, 1 H, $^3J = 8.5$, $^4J = 1.5$, H-3), 8.33 (d, 2 H), 8.34 (d, 2 H), 8.81 (s, 1 H, H-1). Elemental analysis: for $C_{55}H_{56}O_{11}$ (893.05), calculated C 73.97, H 6.32; found C 73.63, H 6.55%.

Materials **1b** ($R^1 = R^2 = C_{10}H_{21}$, yield 56%), **1c** ($R^1 = C_{12}H_{25}$, $R^2 = C_{11}H_{21}$, yield 65%), **1d** ($R^1 = R^2 = C_{12}H_{25}$, yield 60%) and **1e** ($R^1 = R^2 = C_{14}H_{29}$, yield 58%) were obtained by the same method.

Analogously, by acylation of hydroxy esters **6f–6i** with acid chlorides of acids **7a–7e** materials **1la–1le** were prepared. The crude octyl-4- $\{([4-((7-([4-((4\text{-octyloxybenzoyl})\text{oxy})\text{benzoyl})\text{oxy})\text{benzoyl})\text{oxy})\text{benzoyl})\text{oxy}\}$ benzoate (**1la**) was purified by column chromatography (silica gel, eluent dichloromethane), yield 75%. ^1H NMR: 0.88 (t, 6 H), 1.20 (m, 16 H), 1.46 (m, 4 H), 1.81 (m, 4 H), 2.68 (s, 3 H, CH_3), 4.06 (t, 2 H, CH_2O), 4.33 (t, 2 H, COOCH_2), 7.00 (d, 2 H), 7.33 (d, 2 H), 7.42 (d, 2 H), 7.47 (d, 2 H), 7.48 (d, 1 H, $J = 9.1$, H-6), 7.87 (d, 1 H, $J = 9.1$, H-5), 8.01 (d, 1 H, $J = 8.8$, H-4), 8.15 (t, 4 H), 8.24 (dd, 1 H, $^3J = 8.5$, $^4J = 1.6$, H-3), 8.33 (d, 2 H), 8.37 (d, 2 H), 9.01 (s, 1 H, H-1). Elemental analysis: for $C_{56}H_{58}O_{11}$

(907.08), calculated C 74.15, H 6.45; found C 74.01, H 6.62%.

In the same way materials **IIa** ($R^1 = R^2 = C_8H_{17}$, yield 75%), **IIb** ($R^1 = R^2 = C_{10}H_{21}$, yield 79%), **IIc** ($R^1 = C_{12}H_{25}$, $R^2 = C_{11}H_{21}$, yield 72%), **IIId** ($R^1 = R^2 = C_{12}H_{25}$, yield 58%) and **IIe** ($R^1 = R^2 = C_{14}H_{29}$, yield 87%) were prepared.

2.2.6 Octyl 4-{4-([7-((4-(4-decyloxy)benzoyl)oxy)benzoyl)oxy-8-chloronaphthalene-2-carbonyl]oxy)benzoyl}oxy}benzoate (**IIIa**)

A mixture of acid **7a** (0.18 g; 0.49 mmol), thionyl chloride (0.2 ml; 2.8 mmol) and pyridine (0.25 ml; 3.1 mmol) in dry toluene (15 ml) was stirred and heated to boiling for 2 h. The solvent and unreacted thionyl chloride solution were evaporated and the residue dried at reduced pressure. The crude acid chloride was dissolved in dry toluene (10 ml) and added to a hot solution of hydroxy ester **6j** (0.22 g; 0.38 mmol) and DMAP (0.07 g; 0.57 mmol) in toluene (30 ml). After cooling to room temperature the reaction mixture was diluted with 5% hydrochloric acid (35 ml) and chloroform (50 ml). Layers were separated and the aqueous layer was washed with chloroform (2 × 15 ml). The combined organic solution was washed with water (2 × 25 ml), saturated solution of NaCl (30 ml), and dried with anhydrous magnesium sulphate. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, dichloromethane). Yield 0.31 g (68%) of **IIIa**. 1H NMR: 0.88 (t, 6 H), 1.28 (m, 16 H), 1.46 (m, 4 H), 1.81 (m, 4 H), 4.06 (t, 2 H, OCH₂), 4.33 (t, 2 H, COOCH₂), 7.00 (d, 2 H), 7.33 (d, 2 H), 7.43 (d, 2 H), 7.48 (d, 2 H), 7.60 (d, 1 H, $J = 8.8$, H-6), 7.95 (d, 1 H, $J = 8.8$, H-5), 8.05 (d, 1 H, $J = 9.1$, H-4), 8.16 (d, 2 H), 8.17 (d, 2 H), 8.29 (dd, 1 H, $^3J = 9.1$, $^4J = 1.5$, H-3), 8.33 (d, 2 H), 8.38 (d, 2 H), 9.25 (s, 1 H, H-1). Elemental analysis: for C₅₅H₅₅ClO₁₁ (927.50), calculated C 71.23, H 5.98, Cl 3.82; found C 70.98, H 6.17, Cl 4.02%.

Materials **IIIb** ($R^1 = R^2 = C_{10}H_{21}$, yield 65%), **IIIc** ($R^1 = C_{12}H_{25}$, $R^2 = C_{11}H_{21}$, yield 62%), **IIId** ($R^1 = R^2 = C_{12}H_{25}$, yield 71%) and **IIIe** ($R^1 = R^2 = C_{14}H_{29}$, yield 66%) were obtained by the same method.

2.3 Measurement set-ups and conditions

Sequence of phases and phase transition temperatures were determined from textures and their changes observed on planar cells of different thickness in the polarising optical microscope (Nikon Eclipse E600Pol). The LINKAM LTS E350 heating/cooling

stage with TMS 93 temperature programmer was used for the temperature control, which enabled temperature stabilisation within ± 0.1 K. The planar samples for texture observation and electrooptic studies were made from glasses with ITO transparent electrodes (5×5 mm²) separated by mylar sheets defining the cell thickness. They were filled with studied compounds in the isotropic phase by capillary action.

Phase transition temperatures were determined by differential scanning calorimetry (DSC) using a Pyris Diamond Perkin-Elmer 7 calorimeter. The samples of about 2–5 mg hermetically sealed in aluminium pans were placed in a nitrogen atmosphere. Temperature and enthalpy change value were calibrated on extrapolated onset temperatures and enthalpy changes of melting points of water, indium and zinc. Calorimetric measurements were performed on cooling/heating runs at a rate of 5 K min⁻¹.

Switching studies were performed using driving voltage from a Phillips generator PM 5191 accompanied by a linear amplifier providing a maximum amplitude of about ± 120 V. A LeCroy 9304 memory oscilloscope gives information about the switching current profile versus time.

The X-ray diffraction studies were performed using Bruker Nanostar system (CuK α radiation, Vantec 2000 area detector, MRI TCPU H heating stage) working in transmission mode and Bruker GADDS system (CuK α radiation, HiStar area detector) working in reflection mode. In both systems the temperature stability was 0.1 K. Powder samples (for Nanostar) were prepared in thin-walled glass capillaries (1.5 mm diameter); partially oriented samples for experiments in reflection were prepared as droplets on heated surface.

3. Results

3.1 Calorimetric studies and texture observation

DSC studies were performed for all compounds; the phase transition temperatures and associated enthalpy changes are summarised in Table 1. Based on the substitution at the central naphthalene ring, compounds are divided into three groups: non-substituted **I**, methyl-substituted **II** and chloro-substituted **III**. For non-substituted **I** and methyl-substituted compounds **II** with short aliphatic chain (**Ia**, **Ib**, **Ic**, and **IIa**, **IIb**) and all chlorine-substituted compounds **III**, one columnar phase was observed (**B**_{1RevT} type, see below). Methyl-substituted materials **II** with longer chain exhibited the SmA-columnar phase sequence on cooling from the isotropic phase. The richest polymorphism was found for **IIe** with the longest chain ($R = C_{14}H_{29}$), which exhibited two switchable

Table 1. Melting point (m.p.) phase transition temperatures, T_{tr} , and temperature of crystallisation, T_{cr} , in °C and corresponding enthalpy changes, ΔH in kJ mol⁻¹, detected on the second temperature run at a rate of 5 K min⁻¹ are in brackets at the corresponding temperature.

Comp.	R ¹	R ²	m.p. (ΔH)	T_{cr} (ΔH)	M ₃	T_{tr} (ΔH)	M ₂	T_{tr} (ΔH)	M ₁	T_{tr} (ΔH)	Iso
Ia	C ₈ H ₁₇	C ₈ H ₁₇	115 (+24.0)	108 (-27.1)	-	-	-	-	B_{1RevT}	205 (-16.7)	•
Ib	C ₁₀ H ₂₁	C ₁₀ H ₂₁	114 (+18.5)	105 (-13.8)	-	-	-	-	B_{1RevT}	202 (-15.9)	•
Ic	C ₁₂ H ₂₅	C ₁₁ H ₂₁	113 (+12.1)	106 (-13.3)	-	-	-	-	B_{1RevT}	190 (-11.3)	•
Id	C ₁₂ H ₂₅	C ₁₂ H ₂₅	114 (+10.9)	105 (-14.6)	-	-	B_{1RevT}	188 (-0.55)	B_{1RevTx}	199 (-12.0)	•
Ie	C ₁₄ H ₂₉	C ₁₄ H ₂₉	114 (+12.4)	109 (-14.1)	-	-	B_{1RevT}	173 (-0.25)	B_{1RevTx}	197 (-12.3)	•
IIa	C ₈ H ₁₇	C ₈ H ₁₇	150 (+8.2)	148 (-10.3)	-	-	-	-	B_{1RevT}	179 (-0.55)	•
IIb	C ₁₀ H ₂₁	C ₁₀ H ₂₁	154 (+10.2)	149 (-12.0)	-	-	-	-	B_{1RevT}	181 (-10.5)	•
IIc	C ₁₂ H ₂₅	C ₁₁ H ₂₁	148 (+12.0)	145 (-10.5)	-	-	B_{1RevT}	175 (-0.65)	SmA	179 (-5.6)	•
IId	C ₁₂ H ₂₅	C ₁₂ H ₂₅	150 (+10.7)	148 (-12.0)	-	-	B_{1RevT}	181 (-1.1)	SmA	184 (-5.1)	•
IIE	C ₁₄ H ₂₉	C ₁₄ H ₂₉	147 (+12.5)	145 (-14.8)	B_{1RevT}	175 (-0.32)	B_{1RevTx}	179 (-1.4)	SmA	187 (-8.2)	•
IIIa	C ₈ H ₁₇	C ₈ H ₁₇	70 (+10.5)	57 (-10.1)	-	-	-	-	B_{1RevT}	189 (-32.8)	•
IIIb	C ₁₀ H ₂₁	C ₁₀ H ₂₁	64 (+8.2)	52 (-9.0)	-	-	-	-	B_{1RevT}	188 (-44.0)	•
IIIc	C ₁₂ H ₂₅	C ₁₁ H ₂₁	69 (+13.0)	66 (-8.6)	-	-	-	-	B_{1RevT}	184 (-38.7)	•
IIId	C ₁₂ H ₂₅	C ₁₂ H ₂₅	62 (+11.4)	56 (-18.9)	-	-	-	-	B_{1RevT}	184 (-40.0)	•
IIIe	C ₁₄ H ₂₉	C ₁₄ H ₂₉	132 (+9.9)	86 (-30.5)	-	-	-	-	B_{1RevT}	185 (-17.5)	•

columnar phases below the smectic A phase. The phase sequence of two **B_{1RevT}** type columnar phases was observed for non-substituted **Id** and **Ie**. Typical DSC plots are presented for compounds **Ia**, **IIE** and **IIIc** in Figures 1(a), 1(b) and 1(c), respectively. The inset in Figure **IIE** enlarges the area of thermograph in the vicinity of the phase transition between two columnar tilted phases **B_{1RevT}**, which will be discussed later in detail.

In those compounds in series **II** with longer chains, the **SmA** phase appeared above the columnar phase. A fan-shaped texture was observed in the **SmA** phase (Figure 2(a)) as well as in both columnar phases (Figures 2(b) and (c) and Figures 3(a) and (b)). In the **SmA** phase there is no evidence on switching in current as well as in electrooptical response. On the other hand, the electric field of approximately 20 V μm^{-1} applied in the **SmA** phase very often induces irreversible transformation of the planar fan-shaped texture to the homeotropic one. On cooling, the homeotropic texture persists also within the columnar phases. Comparison of the planar texture and the homeotropic one, created in the electrode part of the sample under the electric field, can be seen in Figure 2. The homeotropic texture in the **SmA** phase is homogeneously black, without schlierens or other defects (the right-hand part of Figure 2(a)).

Two different columnar tilted **B_{1RevT}**-type phases were observed in compounds **IIE**, **Id** and **Ie**. The general structure of switchable columnar phases (**B_{1Rev}**) is described elsewhere [26–28]. We have used an additional subscript x for the columnar phase appearing just below the **SmA** or isotropic phase (**B_{1RevTx}**) due to X-ray measurements results (see later) as well as textural studies showing similar features. On cooling

from the **SmA** phase for compound **IIE**, a homeotropic part of the texture transforms into a domain-like type in the **B_{1RevTx}** phase (the right-hand side of Figure 2(b)). In the lower temperature **B_{1RevT}** phase, other modification of the homeotropic part of texture occurs (the right-hand side of Figure 2(c)). On the contrary, only a slight change occurs in the planar fan-shaped texture between the **B_{1RevTx}** and **B_{1RevT}** phases (compare the left parts of Figures 2(b), (c) for compound **IIE** and in more detail in Figures 3(a), (b) for compound **Id**). After heating up to the isotropic phase and subsequent cooling down without the influence of the electrical field, the fan-shaped texture is restored in the whole sample area. Application of the electric field in the columnar phases does not transform the planar texture into the homeotropic one, in contrast to the **SmA** phase behaviour. In the **B_{1RevTx}** as well as in the **B_{1RevT}** phase, a polarisation current with two distinct peaks was detected in a half-cycle, which evidences their antiferroelectric character (see Figure 4 with polarisation current profile in the **B_{1RevT}** phase for **IId**). Nevertheless, the peaks in polarisation current are rather weak in both studied columnar phases corresponding to the spontaneous polarisation of approximately 100 nC cm⁻².

3.2 X-ray studies

We performed X-ray diffraction studies for representative compounds: **Ib**, **Ie**, **IIb**, **IIE**, **IIIb**, **IIIc**, and **IIIe**. The X-ray pattern of the **B_{1RevT}** phase can be indexed assuming an oblique primitive crystallographic unit cell. In this case, the signal corresponding to the molecular length is indexed as (01) and is the strongest one, suggesting a high degree of lamellarisation in the

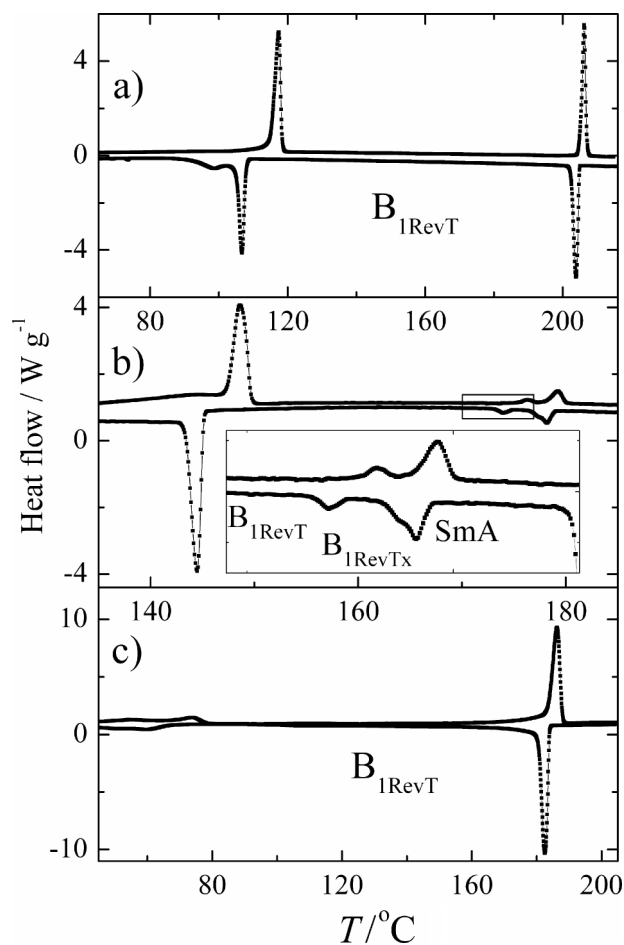


Figure 1. Thermographs taken for compounds (a) **Ia**, (b) **IIe** and (c) **IIIc** during the second heating and cooling runs (the upper and lower curve, respectively, in each figure) at a rate of 5 K min^{-1} . The slopes are adjusted for convenience, phases are indicated.

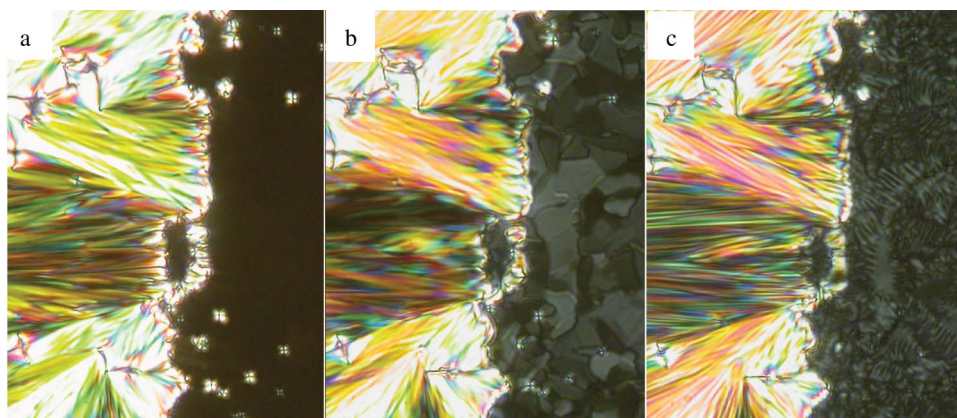


Figure 2. Texture of **IIe** compound in (a) the SmA phase at temperature $T = 185^\circ\text{C}$, (b) the $B_{1\text{RevTx}}$ phase at $T = 178^\circ\text{C}$ and (c) the $B_{1\text{RevT}}$ phase at $T = 170^\circ\text{C}$. The right side of each figure is the area under the ITO electrode, which was treated by an electric field (20 V cm^{-1} , frequency 5–12 Hz, for 1 min at 182°C). The width of figures corresponds to $150 \mu\text{m}$.

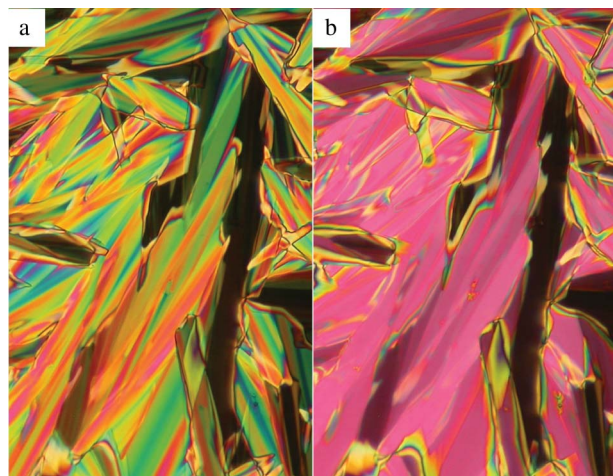


Figure 3. Planar texture of **Id** compound in (a) the B_{1RevT} phase at $T = 190^\circ\text{C}$ and (b) the B_{1RevT} phase at $T = 180^\circ\text{C}$. The width of figures corresponds to 200 μm .

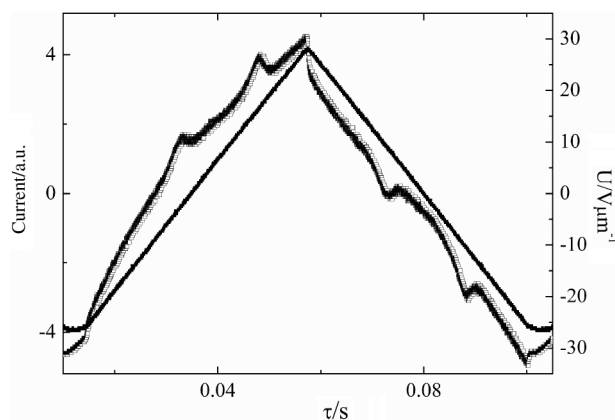


Figure 4. Switching current for compound **Id** at $T = 178^\circ\text{C}$ taken in the B_{1RevT} phase at a triangular field, U , at frequency of 11 Hz.

structure. Cell parameters are summarised in Table 2. In all compounds the c parameter is nearly temperature-independent in contrast to the a parameter, reflecting block length within its cross-section, which changes with temperature. For some compounds (**Ib**, **Ie** and **IIb**), the a parameter grows on cooling; for other compounds it increases (**III** compounds analysed by X-ray). The c parameter grows with increasing length of molecular chain (compare **IIIb**, **IIIc** and **IIIe**). This fact reflects the enlargement of the molecules by the lengthening of alkyl chains. The unit cell inclination angle, β , increases on cooling. We did not succeed in fitting the X-ray data in the B_{1RevTx} phase of **IIe** to determine its crystallographic cell parameters. Nevertheless, the X-ray profile detected in the B_{1RevTx} phase corresponds to a columnar phase of this type. In

Table 2. Parameters of the crystallographic unit cell measured by X-ray in the B_{1RevT} phase for selected compounds at selected temperatures, T . For **IIe** layer spacing in the SmA phase is also given.

	$T/^\circ\text{C}$	$a/\text{\AA}$	$c/\text{\AA}$	β
Ib	190	94.65	49.65	95.44
	150	110.7	50.26	93.95
	120	128.8	50.73	93.54
Ie	170	85.54	55.48	98.48
	150	91.94	56.15	97.44
	120	107.97	57.11	96.40
IIb	178	131.5	49.39	94.11
	170	137.1	48.47	93.34
	160	147.4	48.59	92.56
	150	159.8	49.69	91.96
IIe	182	SmA	53.75	-
	160	110.6	55.93	97.99
IIIb	180	83.86	49.72	97.19
	160	60.72	50.21	103.7
	140	57.35	50.34	104.8
	100	54.86	50.32	107.4
	40	53.44	50.18	108.9
	175	71.19	52.23	99.06
IIIc	150	57.65	52.89	102.6
	120	55.97	53.20	103.1
	100	55.59	53.31	104.9
	172	70.68	56.14	102.1
IIIe	161	61.31	56.59	103.8
	150	57.98	56.83	104.4

Figure 5 the X-ray profiles acquired in the SmA, B_{1RevTx} and B_{1RevT} phases are compared for compound **IIe**. In the SmA phase of **IIe** the layer spacing value was established as 53.75 \AA at $T = 172^\circ\text{C}$. An evaluation of the molecular length using the Chem3D software yields a higher value of around 59 \AA . We can speculate about the intercalation of molecular chains or their contraction during packing into layers. Miller indices are added to Figure 5(c); this indexing was used for all studied columnar phases.

4. Discussion and conclusions

A series of compounds differing in the type of the substituent at the central naphthalene ring (**I**, $X = \text{H}$, **II**, $X = \text{CH}_3$, **III**, $X = \text{Cl}$) and the length of the terminal alkoxy chain (from C_8H_{17} to $\text{C}_{14}\text{H}_{29}$) were synthesised and their mesomorphic properties were studied. All compounds exhibit the formation of at least one mesophase (Table 1). While the transition temperatures in each series are approximately uniform regardless of the length of the terminal alkyl chains, the presence of a lateral substitution in the central core has a pronounced effect on the transition temperatures and mesomorphic properties (see Figure 6).

The introduction of a methyl group (series **II**) leads to a substantial narrowing of the mesophase

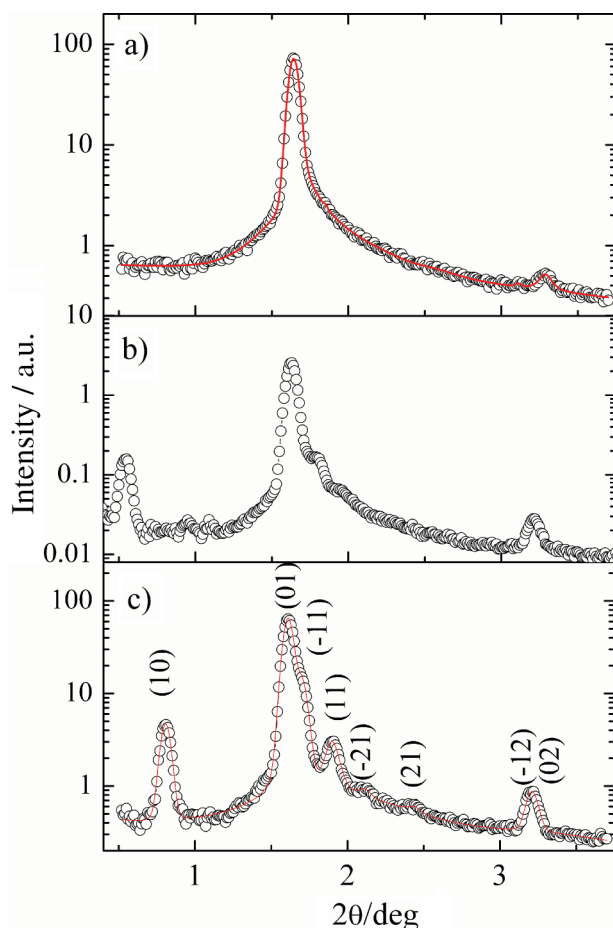


Figure 5. X-ray intensity versus the scattering angle for compound **IIe** in (a) the SmA phase at $T = 182^\circ\text{C}$, (b) $\text{B}_{1\text{RevTx}}$ at $T = 176^\circ\text{C}$ and (c) $\text{B}_{1\text{RevT}}$ at $T = 160^\circ\text{C}$. Red lines show fits assuming (a) lamellar structure with $d = 53.75 \text{ \AA}$ and (c) 2D oblique structure with $a = 110.6 \text{ \AA}$, $c = 55.32 \text{ \AA}$ and $\beta = 97.92^\circ$ (colour version online).

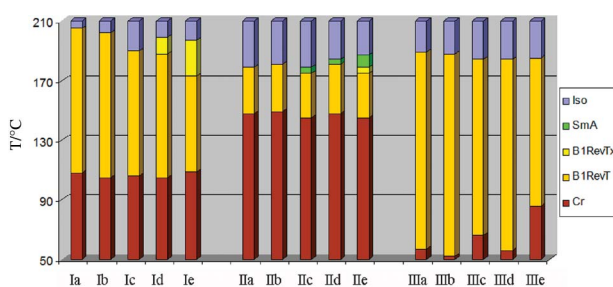


Figure 6. Overview of all compounds studied, comparison of mesomorphic behaviour (colour version online).

stability range, by approximately 50 K in comparison with the non-substituted compounds of series **I**. On the other hand, compound **IIe** exhibits the richest polymorphism: two columnar phases were observed below the SmA phase on cooling from the isotropic

phase. The chloro substituent in the materials of series **III** causes slight lowering of the clearing temperatures but a substantial decrease of melting point, which results in the largest temperature interval of a columnar $\text{B}_{1\text{RevT}}$ phase ($\sim 120 \text{ K}$). From X-ray studies we established the structural parameters of the columnar phases (Table 2).

The most frequent phase observed in these compounds is a columnar $\text{B}_{1\text{RevT}}$ -type of phase, which is stabilised in a very broad temperature range of up to 130 K. For related materials studied earlier [22, 23] with a naphthalene central unit and with uniform orientation of connecting ester groups in molecular arms, a lateral substituent causes much higher diversity of observed mesophases. In compounds with opposite orientation of ester groups in one molecular arm [25], the effect of substitution was also much more pronounced than for compounds studied here. Materials published by Kohout *et al.* [25] exhibited substantial differences in mesomorphic properties, which were induced by substitution and chain length, as well as rich polymorphism with the nematic, switchable columnar $\text{B}_{1\text{RevT}}$ -type and the lamellar B_2 (SmC_APA) phases [25]. Nevertheless, no SmA phase was observed for bent-shaped compounds previously studied [22–25]. In this study, all studied materials with the shorter alkyl chain (C_8H_{17} and $\text{C}_{10}\text{H}_{21}$) exhibit only the formation of a $\text{B}_{1\text{RevT}}$ -type of columnar phase. For series **II**, lengthening of the alkyl chains to $\text{C}_{12}\text{H}_{25}$ leads to the appearance of the SmA phase above the $\text{B}_{1\text{RevT}}$ phase. Due to the lack of polarisation switching and homogeneous texture character, we concluded that the SmA phase has a calamitic character. For **IIe**, with the longest chain $\text{C}_{14}\text{H}_{29}$, the additional switchable columnar $\text{B}_{1\text{RevT}}$ -type phase was observed.

We have successfully prepared new bent-shaped compounds which prefer the formation of columnar phases. The present study confirmed that the introduction of double bonds at the end of the alkyl chains does not significantly influence the mesogenic properties of this type of bent-shaped material. The non-saturated compounds will be used for preparation of side chain polymeric liquid crystals.

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References

- [1] Niori, T.; Sekine, T.; Watanabe, J.; Furukawa, J.; Takezoe, H. *J. Mater. Chem.* **1996**, *6*, 1231–1233.
- [2] Link, D.R.; Natale, G.; Shao, R.; MacLennan, J.E.; Clark, N.A.; Körblöva, E.; Walba, D.M. *Science* **1997**, *278*, 1924–1927.
- [3] Pelzl, G.; Diele, S.; Weissflog, W. *Adv. Mater.* **1999**, *11*, 707–724.
- [4] Weissflog, W.; Nádasi, H.; Dunemann, U.; Pelzl, G.; Diele, S.; Eremin, A.; Kresse, H. *J. Mater. Chem.* **2001**, *11*, 2748–2758.
- [5] Dunemann, U.; Schröder, M.W.; Amarantha Reddy, R.; Pelzl, G.; Diele, S.; Weissflog, W. *J. Mater. Chem.* **2005**, *15*, 4051–4061.
- [6] Amarantha Reddy, R.; Tschierske, C. *J. Mater. Chem.* **2006**, *16*, 907–961.
- [7] Weissflog, W.; Shreenivasa Murthy, H.N.; Diele, S.; Pelzl, G. *Phil. Trans. R. Soc. A*, **2006**, *364*, 2657–2679.
- [8] Takezoe, H.; Takanishi, Y. *Jpn. J. Appl. Phys.* **2006**, *45*, 597–625.
- [9] Shen, D.; Pegenau, A.; Diele, S.; Wirth, I.; Tschierske, C. *J. Am. Chem. Soc.* **2000**, *122*, 1593–1601.
- [10] Amaranatha Reddy, R.; Sadashiva, B.K. *Liq. Cryst.* **2003**, *30*, 1031–1050.
- [11] Rouillon, J.C.; Marcerou, J.P.; Laguerre, M.; Nguyen, H.T.; Achard, M.F. *J. Mater. Chem.* **2001**, *11*, 2946–2950.
- [12] Nguyen, H.T.; Rouillon, J.C.; Marcerou, J.P.; Bedel, J.P.; Barois, P.; Sarmiento, S. *Mol. Cryst. Liq. Cryst.* **1999**, *328*, 177–184.
- [13] Amaranatha Reddy, R.; Schröder, M.W.; Bodyagin, M.; Kresse, H.; Diele, S.; Pelzl, G.; Weissflog, W. *Angew. Chem. Int. Ed.* **2005**, *44*, 774–778.
- [14] Shreenivasa Murthy, H.N.; Sadashiva, B.K. *J. Mater. Chem.* **2005**, *15*, 2056–2064.
- [15] Shreenivasa Murthy, H.N.; Bodyagin, M.; Diele, S.; Baumeister, U.; Pelzl, G.; Weissflog, W. *J. Mater. Chem.* **2006**, *16*, 1634–1643.
- [16] Weissflog, W.; Nauman, G.; Kosata, B.; Schröder, M.W.; Eremin, A.; Diele, S.; Vakhovskaya, Z.; Kresse, H.; Friedmann, R.; Krishnan, S.A.R.; Pelzl, G. *J. Mater. Chem.* **2005**, *15*, 4328–4337.
- [17] Krishnan, S.A.R.; Weissflog, W.; Pelzl, G.; Diele, S.; Kresse, H.; Vakhovskaya, Z.; Friedemann, R. *Phys. Chem. Chem. Phys.* **2006**, *8*, 1170–1177.
- [18] Umadevi, S.; Jákli, A.; Sadashiva, B.K. *Soft Matter* **2006**, *2*, 875–885.
- [19] Bedel, J.P.; Rouillon, J.C.; Marcerou, J.P.; Laguerre, M.; Nguyen, H.T.; Achard, M.F. *Liq. Cryst.* **2001**, *28*, 1285–1292.
- [20] Bedel, J.P.; Rouillon, J.C.; Marcerou, J.P.; Nguyen, H.T.; Achard, M.F. *Phys. Rev. E* **2004**, *69*, 061702.
- [21] Svoboda, J.; Novotná, V.; Kozmík, V.; Glogarová, M.; Weissflog, W.; Diele, S.; Pelzl, G. *J. Mater. Chem.* **2003**, *13*, 2104–2110.
- [22] Kozmík, V.; Kuchař, M.; Svoboda, J.; Novotná, V.; Glogarová, M.; Baumeister, U.; Diele, S. *Liq. Cryst.* **2005**, *32*, 1151–1160.
- [23] Kozmík, V.; Kovářová, A.; Kuchař, M.; Svoboda, J.; Novotná, V.; Glogarová, M.; Kroupa, J. *Liq. Cryst.* **2006**, *33*, 41–56.
- [24] Novotná, V.; Žurek, J.; Kozmík, V.; Svoboda, J.; Glogarová, M. *Liq. Cryst.* **2008**, *35*, 1023–1036.
- [25] Kohout, M.; Svoboda, J.; Novotná, V.; Glogarová, M.; Pocięcha, D.; Gorecka, E. *J. Mater. Chem.* **2009**, *19*, 3153–3160.
- [26] Gorecka, E.; Vaupotic, N.; Pocięcha, D. *Chem. Mater.* **2007**, *19*, 3027–3031.
- [27] Gorecka, E.; Vaupotic, N.; Pocięcha, D.; Cepic, M.; Mieczkowski, J. *ChemPhysChem* **2005**, *6*, 1087–1093.
- [28] Gorecka, E.; Pocięcha, D.; Vaupotic, N.; Cepic, M.; Gomola, K.; Mieczkowski, J. *J. Mater. Chem.* **2008**, *18*, 3044–3049.
- [29] Kimura, T.; Duan, X.-M.; Kato, M.; Yamada, S.; Matsuda, H.; Nakanishi, H. *Polymer* **1998**, *39*, 491–495.
- [30] Kelly, M.S.; Buchecker, R. *Helv. Chim. Acta* **1988**, *71*, 461–466.