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## Liquid Crystals

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### Novel polymerizable bent-shaped monomeric molecules

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# Novel polymerizable bent-shaped monomeric molecules

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Novel bent-shaped mesogens based on substituted naphthalene-2,7-diol, possessing a double bond at the end of terminal branches, have been synthesized and characterized. A variety of banana-mesophases has been found, depending on the type of lateral substitution. Increasing the length of the alkyl chain leads to the appearance of the  $\text{SmC}_A\text{P}_A$  phase for two of the compounds synthesized. Under an electric field a transition into the  $\text{SmC}_S\text{P}_F$  phase takes place and a tilt angle close to  $45^\circ$  has been found. These materials are appropriate for the preparation of polymeric materials.

## 1. Introduction

Due to their unique properties liquid crystals (LCs) have been the subject of considerable interest for many decades. Polymeric liquid crystals or liquid crystalline polymers (LCPs) have become attractive for their practical significance. They are particularly unique in their combination of the properties of low mass liquid crystals (anisotropy of electrical, mechanical and magnetic properties) with the properties of polymers (stability, processability, mechanical integrity, high flexibility, elasticity). Thus, there is an enormous fundamental interest in these materials, which is complemented by a huge potential for ‘high technology’ applications in photonics, spanning ferroelectricity/antiferroelectricity to non-linear optics, or broad band telecommunications. To date, the design of LCPs has been oriented largely to main chain and side chain materials, whose molecular structure is based on the rod-like molecular structure of monomers [1].

Recently, new liquid crystalline phases have been discovered, where mirror symmetry is broken spontaneously, when the molecules are not classical rods but banana-shaped [2] (‘bent-shaped liquid crystals’). Such materials consist of achiral molecules packed in chiral layers in various ways, which produces a diversity of so-called B mesophases [3]. In the most frequently investigated  $\text{B}_2$  phase, the banana-shaped molecules are packed within the layers giving rise to an in-layer

polar axis and therefore to ferro- or antiferro-electric properties. In fact, polymers from banana monomers may combine the properties of polymers with those peculiar to banana molecules, giving rise to chiral phases without the existence of chiral centres in the constituent molecules.

Whilst several classes of banana molecules have been synthesized in recent years [3–16], only a limited number of banana-type liquid crystalline monomers for polymeric liquid crystals have been reported [17–21]. The substances studied possessed a double bond in both terminal chains. Recently a bent core molecule with one terminal double bond was also reported [22]. However, only two materials exhibited the formation of a monotropic  $\text{B}_2$  phase [18, 22], the others tend rather to form nematic and smectic C phases. Two examples of LCPs derived from monomeric banana LCs have also been reported: a crosslinked polyacrylate [17] and a polysiloxane-based side chain LC with a bent core mesogenic unit, showing ferroelectric switching and chiral domains [23].

Recently, we have introduced laterally substituted naphthalene-2,7-diol-based Schiff’s bases and esters, exhibiting various B-type mesophases [24, 25]. Here we report the synthesis, physical properties and phase transition behaviour of two new series of naphthalene-2,7-diol-based monomeric mesogens, possessing two (series I) or one (series II) polymerizable sites in their molecule, as prototypes for the design of main chain or side chain polymeric LCs respectively. Having in mind potential application, the acquisition of a switchable  $\text{B}_2$

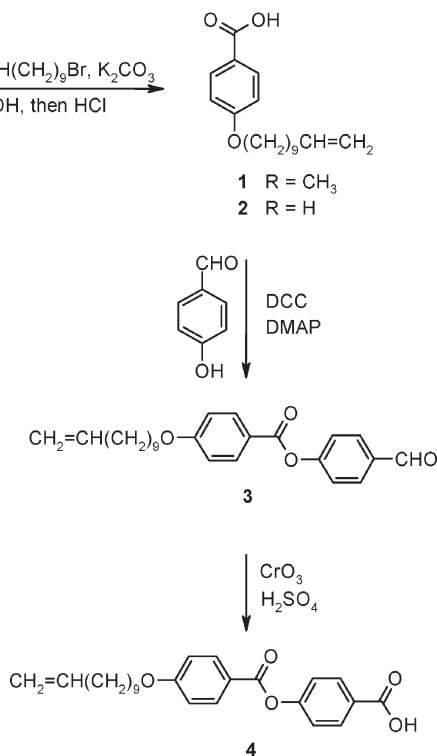
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phase in these new compounds is an aim of this study. As it is well known that lengthening the terminal alkyl chain in banana-type LCs favours the formation of the B<sub>2</sub> phase, we have synthesized as selected compounds from series **II** two homologues with different lengths of the alkyl chain. Within the series **I** and **II** we have also studied the effect variation of the lateral substituent in the molecular core on mesomorphic properties.

## 2. Synthesis

To introduce the unsaturated arms possessing polymerizable sites in the target liquid crystals, 4-[4-(undec-10-enyloxy)benzoyloxy]benzoic acid (**4**) was prepared by a four-step sequence starting with methyl 4-hydroxybenzoate (scheme 1). Its alkylation with 11-bromoundecene in basic medium afforded methyl 4-(undec-10-enyloxy)benzoate (**1**), which was then hydrolyzed with sodium hydroxide to give 4-(undec-10-enyloxy)benzoic acid (**2**). Coupling acid **2** with 4-hydroxybenzaldehyde [26] provided aldehyde **3**, which was oxidized with the Jones reagent to the desired acid **4**. The known 4-(4-alkoxybenzoyloxy)benzoic acids (**5**,  $n=10, 12$ ) were obtained in an analogous manner.

The monomeric materials with structurally identical arms (series **I**) were prepared by esterification of 1-substituted naphthalene-2,7-diols **6a–e** with acid **4** (scheme 2) in the presence of dicyclohexylcarbodiimide



Scheme 1.

(DCC) and a catalytic amount of 4-dimethylaminopyridine (DMAP) in dry dichloromethane in excellent yields (~90%) after chromatographic purification.

The synthesis of bent-shaped LCs with structurally different arms (series **II**) required stepwise acylation of naphthalene-2,7-diol hydroxyl groups. It was successfully achieved only with the unsubstituted naphthalenediol **6a** ( $X=\text{H}$ ). Its reaction with 4-(4-decyloxybenzoyloxy)benzoyl chloride (**7**) and successive DCC coupling of the obtained intermediate **8** with acid **4** afforded the parent material **IIa** (scheme 3).

This approach was impossible to apply to 1-laterally substituted diols **6b–d**. To avoid the formation of a mixture of regioisomers during the first acylation step, one of the hydroxyl groups was protected with the *tert*-butyldimethylsilyl group (TBDMS), which was easily introduced with TBDMS chloride (scheme 4). While the silylation proceeded regioselectively in position 2 of the naphthalene ring in the 1-chloro and 1-cyano derivatives **6b** and **6d**, silylation of the 1-methyl derivative **6c** showed different selectivity and the protecting group entered at position 7. The structure of the silylated products **9b–d** was unambiguously assigned by <sup>1</sup>H and <sup>13</sup>C NMR spectra and NOE experiments.

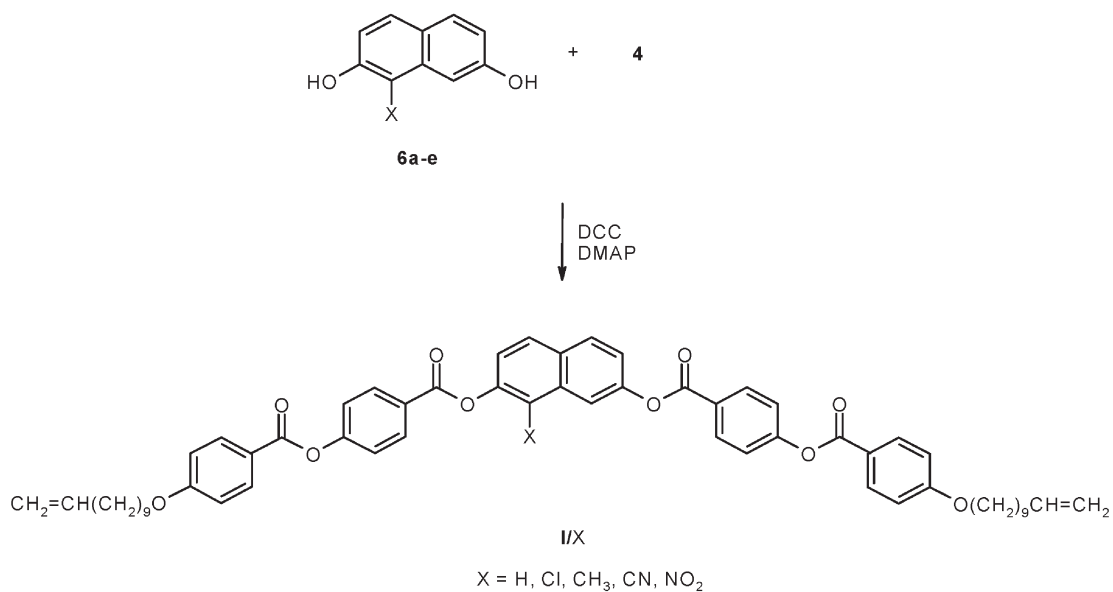
As a consequence of the different silylation regioselectivity, the sequence of successive esterification of silyl derivatives **9b,d** and **9c**, respectively, with acid **5** and **4** had to be reversed (scheme 4). While the compounds **9b,d** were first reacted with acid **5** in the presence of DCC and a catalytic amount of DMAP in dry dichloromethane to give the monoesters **10b,d**, compound **9c** was acylated with acid **4** under the same conditions to afford **10c**. Deprotection of the silyl group with tetrabutylammonium fluoride in THF and subsequent esterifications of the formed **11b–d** with acid **4** and acid **5**, sequentially, led to the target materials **IIb–d**.

On the other hand, application of the same method of acylation of **9b,d** first with **4**, and second with **5** and acylation of **9c** first with **5** and second with **4**, led to the formation of isomeric materials **IIe–k**. Procedures for the synthesis of representative intermediates and target compounds of series **I** and **II** are summarized below.

<sup>1</sup>H NMR spectra were obtained on Varian-Gemini 300 HC spectrometers. Deuteriochloroform, and DMSO-d<sub>6</sub> served as solvents, and the signals of the solvent were used as internal standards. Chemical shifts are given in the  $\delta$ -scale (ppm), coupling constants  $J(\text{H,H})$  in Hz. IR spectra were recorded on a Nicolet FTIR 740 spectrometer in chloroform.

### 2.1. Methyl 4-(undec-10-enyloxy)benzoate (**1**)

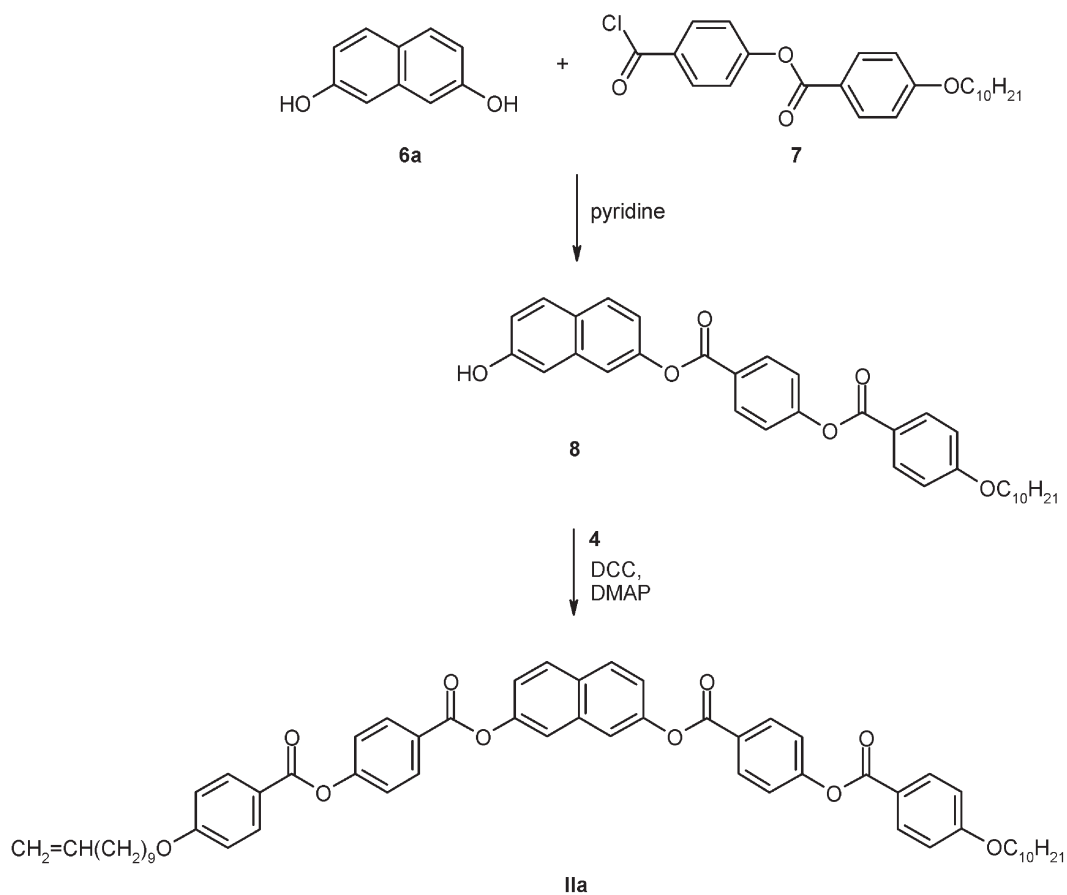
A mixture of methyl 4-hydroxybenzoate (11.6 g, 0.076 mol), 11-bromoundecene (15.1 g, 0.065 mol),



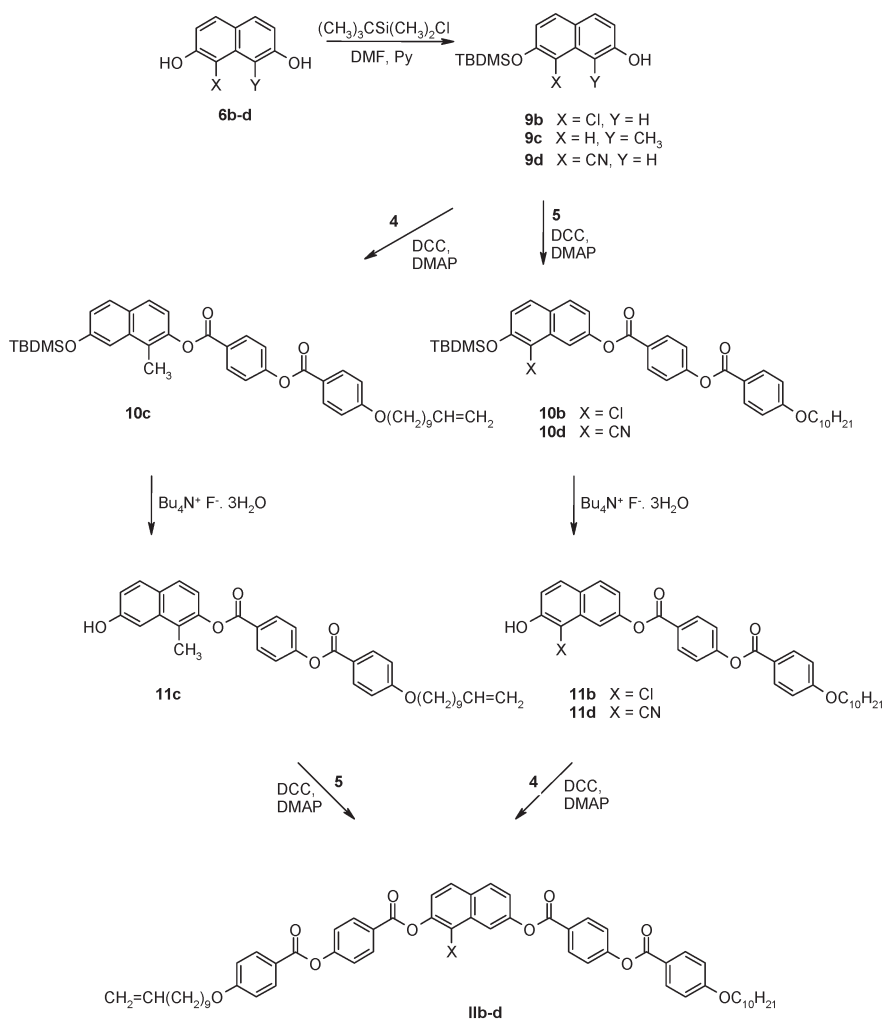
Scheme 2.

freshly fused potassium carbonate (12.4 g, 0.090 mol) and *N,N*-dimethylformamide (DMF) (80 ml) was stirred and heated at 65°C for 5 h. After cooling to room

temperature, the mixture was diluted with cold water (500 ml) and extracted with toluene (4 × 100 ml). The combined organic solution was washed with water



Scheme 3.



Scheme 4.

(50 ml) and dried over MgSO<sub>4</sub>. The crude product after evaporation was purified by column chromatography (silica gel, elution with toluene) and 18.7 g (95%) of ester **1** was isolated, m.p. 40.2–40.6°C, lit. [27] 40.0–41.0°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 1.20–1.56 (m, (CH<sub>2</sub>)<sub>6</sub>), 1.81 (m, CH<sub>2</sub>), 2.05 (m, CH<sub>2</sub>), 3.87 (s, OCH<sub>3</sub>), 4.02 (t, OCH<sub>2</sub>), 4.96 (m, CH<sub>2</sub>=CH), 5.81 (m, CH<sub>2</sub>=CH), 6.92 (d, *J*=7.7, arom. H), 8.03 (d, arom. H).

## 2.2. 4-(Undec-10-enyloxy)benzoic acid (**2**)

To a solution of ester **1** (18.7 g, 0.0614 mol) in methanol (120 ml), a solution of sodium hydroxide (6.14 g, 0.154 mol) in water (120 ml) was added and the mixture heated at 80°C for 5 h; it was then acidified with 5% aq. HCl (600 ml). The product was extracted with dichloromethane (4 × 200 ml), the organic solution was washed with water and dried over MgSO<sub>4</sub>. The solvent was evaporated and the crude product crystallized from ethyl acetate; 16.3 g (91%) of acid **2** was obtained, m.p.

84.7–146°C, lit. [26] 75–134°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 1.20–1.56 (m, (CH<sub>2</sub>)<sub>6</sub>), 1.81 (m, CH<sub>2</sub>), 2.05 (m, CH<sub>2</sub>), 4.02 (t, OCH<sub>2</sub>), 4.96 (m, CH<sub>2</sub>=CH), 5.81 (m, CH<sub>2</sub>=CH), 6.92 (d, *J*=7.7, arom. H), 8.03 (d, arom. H).

## 2.3. 4-Formylphenyl 4-(undec-10-enyloxy)benzoate (**3**)

A mixture of 4-hydroxybenzaldehyde (4.88 g, 0.040 mol), acid **2** (11.6 g, 0.040 mol), DCC (12.4 g, 60 mmol), DMAP (50 mg) and dichloromethane (150 ml) was stirred at room temperature under argon for 24 h. Water (0.5 ml) was added and after 30 min the mixture was filtered; the solid was washed with dichloromethane (2 × 10 ml) and the filtrate evaporated to dryness. The crude product was purified by crystallization from hexane to afford 14.51 g (92%) of ester **3**, m.p. 54–56°C, lit. [28] 58–60°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 1.20–1.56 (m, (CH<sub>2</sub>)<sub>6</sub>), 1.86 (m, CH<sub>2</sub>), 2.05 (m, CH<sub>2</sub>), 4.06 (t, OCH<sub>2</sub>), 4.96 (m, CH<sub>2</sub>=CH), 5.81 (m, CH<sub>2</sub>=CH), 6.98

(d,  $J=8.8$ , arom. H), 7.40 (d,  $J=8.8$ , arom. H), 7.96 (d, arom. H), 8.14 (d, arom. H), 10.02 (s, CHO).

#### 2.4. 4-[4-(Undec-10-enyloxy)benzoyloxy]benzoic acid (4)

A solution of ester **3** (5.68 g, 14.4 mmol) in acetone (250 ml) was cooled to 0°C and during 15 min, 8.8 ml of Jones reagent was added dropwise. The mixture was stirred at room temperature for 24 h, diluted with cold water (1000 ml), and the precipitate was filtered off and washed with cold water. Crystallization from ethanol afforded 5.32 g (90%) of acid **4**, m.p. 113–194°C.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.20–1.56 (m,  $(\text{CH}_2)_6$ ), 1.86 (m,  $\text{CH}_2$ ), 2.05 (m,  $\text{CH}_2$ ), 4.06 (t,  $\text{OCH}_2$ ), 4.98 (m,  $\text{CH}_2=\text{CH}$ ), 5.82 (m,  $\text{CH}_2=\text{CH}$ ), 7.00 (d,  $J=8.8$ , arom. H), 7.35 (d,  $J=8.8$ , arom. H), 8.16 (d, arom. H), 8.21 (d, arom. H). Elemental analysis for  $\text{C}_{25}\text{H}_{30}\text{O}_5$  (410.51): calcd C 73.15, H 7.37; found C 73.06, H 7.11%.

#### 2.5. 1-Substituted naphthalene-2,7-diyl bis{4-[4-(undec-10-enyloxy)benzoyloxy]benzoate}-(IIX)

A mixture of naphthalene diol **6a–e** (10 mmol), acid **4** (25 mmol), DCC (6.30 g, 30 mmol) and DMAP (50 mg) in dry dichloromethane (100 ml) was stirred at room temperature under argon for 24 h. Water (0.5 ml) was added and after 30 min the mixture was filtered, the solid washed with dichloromethane ( $2 \times 10$  ml) and the filtrate evaporated to dryness. The product was purified by column chromatography (silica gel, elution with dichloromethane) and crystallization from toluene and acetone; yield 85–95%.

#### 2.6. Naphthalene-2,7-diyl bis{4-[4-(undec-10-enyloxy)benzoyloxy]benzoate} (IIH)

IR (v,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 2933, 2874, 1736 (COO), 1604, 1580, 1469, 1258, 1161.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.20–1.56 (m,  $(\text{CH}_2)_6$ ), 1.86 (m,  $\text{CH}_2$ ), 2.05 (m,  $\text{CH}_2$ ), 4.06 (t,  $\text{OCH}_2$ ), 4.96 (m,  $\text{CH}_2=\text{CH}$ ), 5.81 (m,  $\text{CH}_2=\text{CH}$ ), 6.98 (d,  $J=8.8$ , 2 H), 7.17 (d,  $J=2.2$ , H-1, H-8), 7.28 (d,  $J=8.8$ , 2 H), 7.39 (dd,  $J_1=8.8$ ,  $J_2=2.2$ , H-3, H-6), 7.41 (d,  $J=8.8$ , 2 H), 7.95 (d, H-4, H-5). 8.26 (d,  $J=8.8$ , 2 H). Elemental analysis for  $\text{C}_{60}\text{H}_{64}\text{O}_{10}$  (945.17): calcd C 76.25, H 6.83; found C 76.16, H 6.81%.

#### 2.7. 1-Chloronaphthalene-2,7-diyl bis{4-[4-(undec-10-enyloxy)benzoyloxy]benzoate} (IICl)

IR (v,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 2933, 1737 (COO), 1604, 1512, 1414, 1258, 1161.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.20–1.56 (m,  $(\text{CH}_2)_6$ ), 1.85 (m,  $\text{CH}_2$ ), 2.05 (m,  $\text{CH}_2$ ), 4.06 (t,  $\text{OCH}_2$ ), 4.96 (m,  $\text{CH}_2=\text{CH}$ ), 5.81 (m,

$\text{CH}_2=\text{CH}$ ), 7.00 (d, 4 H), 7.40 (dd,  $J_1=9.4$ ,  $J_2=2.0$ , H-6), 7.41 (d, 4 H), 7.42 (d,  $J=9.0$ , H-3), 7.44 (d,  $J=2.0$ , H-8), 7.44 (d,  $J=8.8$ , H-4), 7.98 (d,  $J=9.0$ , H-5), 8.17 (d, 4 H), 8.38 (m, 4 H). Elemental analysis for  $\text{C}_{60}\text{H}_{63}\text{ClO}_{10}$  (979.62): calcd C 73.57, H 6.48, Cl 3.62; found C 73.33, H 6.31, Cl 3.40%.

#### 2.8. 1-Methylnaphthalene-2,7-diyl bis{4-[4-(undec-10-enyloxy)benzoyloxy]benzoate} (II $\text{CH}_3$ )

IR (v,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 2933, 1735 (COO), 1604, 1512, 1258, 1160.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ), 1.20–1.56 (m,  $(\text{CH}_2)_6$ ), 1.85 (m,  $\text{CH}_2$ ), 2.05 (m,  $\text{CH}_2$ ), 2.54 (s,  $\text{CH}_3$ ), 4.06 (t,  $\text{OCH}_2$ ), 4.96 (m,  $\text{CH}_2=\text{CH}$ ), 5.82 (m,  $\text{CH}_2=\text{CH}$ ), 7.00 (d, 4 H), 7.32 (dd,  $J_1=9.4$ ,  $J_2=2.0$ , H-6), 7.33 (d,  $J=9.1$ , H-3), 7.41 (d, 4 H), 7.82 (d,  $J=9.4$ , H-5), 7.86 (d,  $J=2.0$ , H-8), 7.95 (d,  $J=9.1$ , H-4), 8.17 (d, 4 H), 8.36 (m, 4 H). Elemental analysis for  $\text{C}_{61}\text{H}_{66}\text{O}_{10}$  (959.20): calcd C 76.38, H 6.94; found C 76.14, H 6.86%.

#### 2.9. 1-Cyanonaphthalene-2,7-diyl bis{4-[4-undec-10-enyloxy)benzoyloxy]benzoate} (IICN)

IR (v,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 2933, 1735 (COO), 1604, 1512, 1258, 1160.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.20–1.56 (m,  $(\text{CH}_2)_6$ ), 1.86 (m,  $\text{CH}_2$ ), 2.05 (m,  $\text{CH}_2$ ), 4.06 (t,  $\text{OCH}_2$ ), 4.96 (m,  $\text{CH}_2=\text{CH}$ ), 5.82 (m,  $\text{CH}_2=\text{CH}$ ), 7.00 (d, 4 H), 7.41 (d, 4 H), 7.57 (dd,  $J_1=9.3$ ,  $J_2=2.1$ , H-6), 7.60 (d,  $J=9.1$ , H-3), 8.05 (d,  $J=9.1$ , H-3), 8.07 (d,  $J=2.1$ , H-8), 8.17 (d, 4 H), 8.19 (d,  $J=9.3$ , H-5), 8.36 (m, 4 H). Elemental analysis for  $\text{C}_{61}\text{H}_{63}\text{NO}_{10}$  (970.18): calcd C 75.52, H 6.55, N 1.44; found C 75.38, H 6.33, N 1.32%.

#### 2.10. 1-Nitronaphthalene-2,7-diyl bis{4-[4-(undec-10-enyloxy)benzoyloxy]benzoate} (IINO $_2$ )

IR (v,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 2929, 2858, 1739 (COO), 1603, 1512, 1255, 1159.  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.20–1.56 (m,  $(\text{CH}_2)_6$ ), 1.86 (m,  $\text{CH}_2$ ), 2.05 (m,  $\text{CH}_2$ ), 4.06 (t,  $\text{OCH}_2$ ), 4.96 (m,  $\text{CH}_2=\text{CH}$ ), 5.81 (m,  $\text{CH}_2=\text{CH}$ ), 7.00 (d, 4 H), 7.41 (d, 4 H), 7.55 (d,  $J=9.5$ , H-5), 7.56 (dd,  $J_1=9.5$ ,  $J_2=2.0$ , H-6), 7.82 (d,  $J=9.5$ , H-5), 7.88 (d,  $J=2.0$ , H-8), 8.05 (d,  $J=9.1$ , H-4), 8.17 (d, 4 H), 8.36 (m, 4 H). Elemental analysis for  $\text{C}_{60}\text{H}_{63}\text{NO}_{12}$  (990.17): calcd C 72.78, H 6.41, N 1.41; found C 72.53, H 6.35, N 1.26%.

#### 2.11. 7-Hydroxynaphthalen-2-yl 4-(4-decyloxybenzoyloxy)benzoate (8, n=10)

To a mixture of **6a** (0.325 g, 2.01 mmol) and pyridine (1 ml) in dry dichloromethane (10 ml), a solution of chloride **7** (0.209 g, 0.501 mmol) in dichloromethane (5 ml) was added dropwise at 0°C. The solution was

stirred at 0°C for 1 h, diluted with water (60 ml) and extracted with dichloromethane (3 × 40 ml). The combined organic solution was washed with water (50 ml), dried over MgSO<sub>4</sub> and evaporated. Chromatographic purification (silica gel, elution with hexane/ethyl acetate 4/1 mixture) afforded 235 mg (87%) of **8**, m.p. 146–147°C. IR (ν, CHCl<sub>3</sub>, cm<sup>-1</sup>): 2930, 2857, 1730 (COO), 1607, 1265, 1251, 1164. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 0.89 (t, *J*=7.4, CH<sub>3</sub>), 1.15–1.60 (m, (CH<sub>2</sub>)<sub>9</sub>), 1.83 (m, CH<sub>2</sub>), 4.06 (t, CH<sub>2</sub>O), 5.05 (s, OH), 6.99 (d, 2 H), 7.09 (dd, *J*<sub>1</sub>=8.8, *J*<sub>2</sub>=2.3, H-6), 7.12 (d, *J*=8.8, H-8), 7.21 (dd, *J*<sub>1</sub>=8.8, *J*<sub>2</sub>=2.3, H-3), 7.40 (d, *J*=8.8, 2 H), 7.52 (d, H-1), 7.77 (d, *J*=8.8, H-5), 7.82 (d, H-4), 8.16 (d, 2 H), 8.31 (d, 2 H). Elemental analysis for C<sub>34</sub>H<sub>36</sub>O<sub>6</sub> (540.66): calcd C 75.53, H 6.71; found C 75.43, H 6.65%.

In the same way, benzoate **8** (*n*=12) was obtained in 64% yield, m.p. 147–178°C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 0.88 (t, *J*=7.4, CH<sub>3</sub>), 1.20–1.60 (m, (CH<sub>2</sub>)<sub>9</sub>), 1.83 (m, CH<sub>2</sub>), 4.06 (t, CH<sub>2</sub>O), 5.05 (s, OH), 6.99 (d, 2 H), 7.08 (dd, *J*<sub>1</sub>=8.8, *J*<sub>2</sub>=2.3, H-6), 7.12 (d, *J*=8.8, H-8), 7.20 (dd, *J*<sub>1</sub>=8.8, *J*<sub>2</sub>=2.3, H-3), 7.39 (d, *J*=8.8, 2 H), 7.52 (d, H-1), 7.77 (d, *J*=8.8, H-5), 7.82 (d, H-4), 8.16 (d, 2 H), 8.31 (d, 2 H). Elemental analysis for C<sub>36</sub>H<sub>40</sub>O<sub>6</sub> (568.72): calcd C 76.03, H 7.09; found C 75.83, H 6.98%.

## 2.12. Silylation of 6b–d

Naphthalenediol **6b–d** (1 mmol) was dissolved in a mixture of dry pyridine (2 ml) and DMF (4 ml). A solution of *tert*-butyl(dimethyl)silyl chloride (0.150 g, 1.1 mmol) in dry DMF (6 ml) was added dropwise over 20 min. The mixture was stirred at room temperature for 24 h, diluted with water (20 ml) and extracted with ethyl acetate (3 × 30 ml). The combined organic solution was dried over MgSO<sub>4</sub>, evaporated, and the crude product purified by column chromatography (silica gel, elution with hexane/ethyl acetate 4/1 mixture) to afford the protected derivatives **9b–d**.

**2.12.1. 7-[*tert*-Butyl(dimethyl)silyloxy]-8-chloronaphthalen-2-ol (9b).** Yield 49%, m.p. 119–121°C. IR (ν, CHCl<sub>3</sub>, cm<sup>-1</sup>): 3605 (OH), 3031, 2959, 2933, 2888, 2860, 1512, 1470, 1263. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 0.30 (s, 2 × CH<sub>3</sub>), 1.10 (s, C(CH<sub>3</sub>)<sub>3</sub>), 5.33 (s, OH), 7.01 (d, *J*=8.8, H-3), 7.05 (dd, *J*<sub>1</sub>=8.8, *J*<sub>2</sub>=2.1, H-6), 7.53 (d, H-8), 7.60 (d, H-4), 7.71 (d, H-5). Elemental analysis for C<sub>16</sub>H<sub>21</sub>ClO<sub>2</sub>Si (308.88): calcd C 62.22, H 6.85, Cl 11.48; found C 62.06, H 6.75, Cl 11.27%.

**2.12.2. 7-[*tert*-Butyl(dimethyl)silyloxy]-1-methylnaphthalen-2-ol (9c).** Yield 51%, m.p. 128–130°C. IR (ν, CHCl<sub>3</sub>, cm<sup>-1</sup>): 3593 (OH), 2960, 2932, 2888, 2861, 1518, 1469, 1369, 1246. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>),

δ: 0.30 (s, 2 × CH<sub>3</sub>), 1.09 (s, C(CH<sub>3</sub>)<sub>3</sub>), 2.49 (s, CH<sub>3</sub>), 4.92 (s, OH), 6.91 (d, *J*=8.8, H-3), 6.93 (dd, *J*<sub>1</sub>=8.8, *J*<sub>2</sub>=2.1, H-6), 7.24 (d, H-8), 7.54 (d, H-4), 7.63 (d, H-5). Elemental analysis for C<sub>17</sub>H<sub>24</sub>O<sub>2</sub>Si (288.47): calcd C 70.78, H 8.39; found C 70.56, H 8.34%.

**2.12.3. 7-[*tert*-Butyl(dimethyl)silyloxy]-8-cyanonaphthalen-2-ol (9d).** Yield 47%, m.p. 165°C. IR (ν, CHCl<sub>3</sub>, cm<sup>-1</sup>): 3323 (OH), 3024, 2960, 2933, 2888, 2862, 2225 (CN), 1528, 1473, 1444, 1257. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 0.36 (s, 2 × CH<sub>3</sub>), 1.12 (s, C(CH<sub>3</sub>)<sub>3</sub>), 6.91 (d, *J*=8.8, H-3), 7.14 (dd, *J*<sub>1</sub>=8.8, *J*<sub>2</sub>=2.1, H-6), 7.61 (d, H-8), 7.64 (s, OH), 7.74 (d, H-4), 7.87 (d, H-5). Elemental analysis for C<sub>17</sub>H<sub>21</sub>NO<sub>2</sub>Si (299.45): calcd C 68.19, H 7.07, N 4.68; found C 68.14, H 7.01, N 4.44%.

## 2.13. Acylation of silyl derivatives 9b–d

Acid **5** (resp. **4**) was coupled with the protected naphthols **9b–d** by the same method as for preparation of materials **I**. The crude product was purified by column chromatography (silica gel, elution with hexane/ethyl acetate 4/1 mixture).

**2.13.1. 7-*tert*-Butyl(dimethyl)silyloxy-8-chloronaphthalen-2-yl 4-(4-decyloxybenzoyloxy)benzoate (10b).** Yield 42%, m.p. 137°C. IR (ν, CHCl<sub>3</sub>, cm<sup>-1</sup>): 2959, 2931, 2859, 1735 (COO), 1604, 1255, 1160. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 0.27 (s, 2 × CH<sub>3</sub>), 0.88 (t, CH<sub>3</sub>), 1.07 (m, C(CH<sub>3</sub>)<sub>3</sub>), 1.10–1.45 (m, (CH<sub>2</sub>)<sub>7</sub>), 1.84 (m, CH<sub>2</sub>), 4.06 (t, CH<sub>2</sub>O), 6.99 (d, 2 H), 7.13 (d, *J*=8.8, H-3), 7.29 (dd, *J*<sub>1</sub>=8.5, *J*<sub>2</sub>=2.2, H-6), 7.39 (d, 2 H), 7.68 (d, *J*=8.8, H-4), 8.01 (d, H-8), 7.84 (d, H-5), 8.16 (d, 2 H), 8.33 (d, 2 H). Elemental analysis for C<sub>40</sub>H<sub>49</sub>ClO<sub>6</sub>Si (689.37): calcd C 69.69, H 7.16, Cl 5.14; found C 69.44, H 7.07, Cl 4.98%.

**2.13.2. 7-*tert*-Butyl(dimethyl)silyloxy-1-methylnaphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyl]oxy]benzoate (10c).** Yield 67%, m.p. 97–99°C. IR (ν, CHCl<sub>3</sub>, cm<sup>-1</sup>): 2931, 2857, 1735 (COO), 1604, 1255, 1160. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>), δ: 0.29 (s, 2 × CH<sub>3</sub>), 1.06 (m, C(CH<sub>3</sub>)<sub>3</sub>), 1.15–1.53 (m, (CH<sub>2</sub>)<sub>6</sub>), 1.86 (m, CH<sub>2</sub>), 2.05 (m, CH<sub>2</sub>), 2.54 (s, CH<sub>3</sub>), 4.06 (t, OCH<sub>2</sub>), 4.96 (m, CH<sub>2</sub>=CH), 5.82 (m, CH<sub>2</sub>=CH), 7.01 (d, 2 H), 7.05 (d, *J*=8.8, H-3), 7.11 (dd, *J*<sub>1</sub>=8.5, *J*<sub>2</sub>=2.2, H-6), 7.38 (d, H-8), 7.41 (d, 2 H), 7.71 (d, *J*=8.8, H-4), 7.76 (d, H-5), 8.18 (d, 2 H), 8.37 (d, 2 H). Elemental analysis for C<sub>41</sub>H<sub>52</sub>O<sub>6</sub>Si (668.95): calcd C 73.62, H 7.84; found C 73.35, H 7.74%.

**2.13.3. 7-*tert*-Butyl(dimethyl)silyloxy-8-cyanonaphthalen-2-yl 4-(4-decyloxybenzoyloxy)benzoate (10d).** Yield 62%, m.p. 171°C. IR (ν, CHCl<sub>3</sub>, cm<sup>-1</sup>): 2932, 2859, 2225

(CN), 1736 (COO), 1604, 1512, 1256, 1160.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.34 (s,  $2 \times \text{CH}_3$ ), 0.88 (t,  $\text{CH}_3$ ), 1.09 (m,  $\text{C}(\text{CH}_3)_3$ ), 1.20–1.50 (m,  $(\text{CH}_2)_7$ ), 1.82 (m,  $\text{CH}_2$ ), 4.06 (t,  $\text{CH}_2\text{O}$ ), 6.99 (d, 2 H), 7.08 (d,  $J=8.8$ , H-3), 7.40 (dd,  $J_1=8.5$ ,  $J_2=2.2$ , H-6), 7.40 (d, 2 H), 7.89 (d,  $J=8.8$ , H-4), 7.91 (d, H-8), 7.95 (d, H-5), 8.17 (d, 2 H), 8.32 (d, 2 H). Elemental analysis for  $\text{C}_{41}\text{H}_{49}\text{NO}_6\text{Si}$  (679.94): calcd C 72.43, H 7.26, N 2.06; found C 72.29, H 7.09, N 1.99%.

## 2.14. Deprotection of benzoates 10b–d

A mixture of **10b–d** (1 mmol), tetrabutylammonium fluoride trihydrate (3 mmol) and THF (90 ml) was stirred at room temperature for 24 h. The solution was diluted with water (250 ml) and extracted with ethyl acetate ( $3 \times 150$  ml). The combined organic solution was dried over  $\text{MgSO}_4$ . The residue after evaporation was crystallized from a hexane/toluene mixture to afford the product **11b–d**. The isomers **11e–k** were obtained in an analogous way.

**2.14.1. 8-Chloro-7-hydroxynaphthalen-2-yl 4-(4-decyloxybenzoyloxy)benzoate (11b).** Yield 96%, m.p. 139.5–148.5°C. IR ( $\nu$ ,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 3480 (OH), 2933, 2858, 1731 (COO), 1606, 1250, 1166.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.89 (t,  $\text{CH}_3$ ), 1.10–1.60 (m,  $(\text{CH}_2)_7$ ), 1.83 (m,  $\text{CH}_2$ ), 4.06 (t,  $\text{CH}_2\text{O}$ ), 5.92 (s, OH), 6.99 (d,  $J=8.8$ , 2 H), 7.26 (d,  $J=8.8$ , H-3), 7.29 (dd,  $J_1=8.8$ ,  $J_2=2.1$ , H-6), 7.40 (d, 2 H), 7.74 (d,  $J=8.8$ , H-4), 7.86 (d,  $J=9.0$ , H-5), 7.90 (d, H-8), 8.17 (d, 2 H), 8.33 (d, 2 H). Elemental analysis for  $\text{C}_{34}\text{H}_{35}\text{ClO}_6$  (575.11): calcd C 71.01, H 6.13, Cl 6.16; found C 70.88, H 6.11, Cl 6.00%.

**2.14.2. 7-Hydroxy-1-methylnaphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (11c).** Yield 98%, m.p. 132–171°C. IR ( $\nu$ ,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 3480 (OH), 2930, 2857, 1731 (COO), 1605, 1251, 1160.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.10–1.55 (m,  $(\text{CH}_2)_6$ ), 1.83 (m,  $\text{CH}_2$ ), 2.05 (q,  $\text{CH}_2$ ), 2.45 (s,  $\text{CH}_3$ ), 4.05 (t,  $\text{OCH}_2$ ), 4.97 (m,  $\text{CH}_2=\text{CH}$ ), 5.33 (s, OH), 5.82 (m,  $\text{CH}_2=\text{CH}$ ), 6.99 (d,  $J=8.8$ , 2 H), 7.09 (dd,  $J_1=8.8$ ,  $J_2=2.0$ , H-6), 7.14 (d,  $J=8.8$ , H-3), 7.31 (s, H-8), 7.39 (d, 2 H), 7.69 (d, H-5), 7.77 (d,  $J=9.1$ , H-4), 8.16 (d, 2 H), 8.34 (d, 2 H). Elemental analysis for  $\text{C}_{36}\text{H}_{38}\text{O}_6$  (566.70): calcd C 76.30, H 6.76; found C 75.98, H 6.47%.

**2.14.3. 8-Cyano-7-hydroxynaphthalen-2-yl 4-(4-decyloxybenzoyloxy)benzoate (11d).** Yield 90%, m.p. 171–178°C. IR ( $\nu$ ,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 3480 (OH), 2931, 2857, 2190 (CN), 1734 (COO), 1604, 1256, 1163.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.88 (t,  $\text{CH}_3$ ), 1.20–1.41 (m,  $(\text{CH}_2)_7$ ), 1.83 (m,  $\text{CH}_2$ ), 4.06 (t,  $\text{CH}_2\text{O}$ ), 5.91 (s, OH),

7.00 (d, 2 H), 7.11 (d,  $J=9.0$ , H-3), 7.34 (dd,  $J_1=8.8$ ,  $J_2=2.3$ , H-6), 7.43 (d,  $J=8.8$ , 2 H), 7.80 (s, H-8), 7.92 (d,  $J=8.8$ , H-5), 7.93 (d,  $J=9.1$ , H-4), 8.17 (d,  $J=9.1$ , 2 H), 8.34 (d, 2 H). Elemental analysis for  $\text{C}_{35}\text{H}_{35}\text{NO}_6$  (565.67): calcd C 74.32, H 6.24, N 2.48; found C 74.21, H 6.17, N 2.23%.

**2.14.4. 8-Chloro-7-hydroxynaphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (11e).** Yield 98%, m.p. 132–139°C. IR ( $\nu$ ,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 3475 (OH), 2932, 2858, 1731 (COO), 1605, 1250, 1165.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.00–1.50 (m,  $(\text{CH}_2)_6$ ), 1.83 (m,  $\text{CH}_2$ ), 4.06 (t,  $\text{CH}_2\text{O}$ ), 4.97 (m,  $\text{CH}_2=\text{CH}$ ), 5.82 (m,  $\text{CH}_2=\text{CH}$ ), 5.90 (s, OH), 7.00 (d,  $J=9.0$ , 2 H), 7.27 (d,  $J=8.8$ , H-3), 7.29 (dd,  $J=8.8$ , H-6), 7.40 (d, 2 H), 7.74 (d,  $J=8.8$ , H-4), 7.86 (d,  $J=9.0$ , H-5), 7.90 (s, H-8), 8.17 (d, 2 H), 8.34 (d, 2 H). Elemental analysis for  $\text{C}_{35}\text{H}_{35}\text{ClO}_6$  (587.12): calcd C 71.60, H 6.01, Cl 6.04; found C 71.44, H 5.98, Cl 5.89%.

**2.14.5. 7-Hydroxy-1-methylnaphthalen-2-yl 4-(4-decyloxybenzoyloxy)benzoate (11f).** Yield 70% m.p. 137.5–190°C. IR ( $\nu$ ,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 3480 (OH), 2931, 2857, 1732 (COO), 1604, 1252, 1160.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.89 (t,  $\text{CH}_3$ ), 1.20–1.58 (m,  $(\text{CH}_2)_7$ ), 1.83 (m,  $\text{CH}_2$ ), 2.46 (s,  $\text{CH}_3$ ), 4.06 (t,  $\text{OCH}_2$ ), 4.98 (s, OH), 6.99 (d,  $J=8.8$ , 2 H), 7.09 (dd,  $J_1=8.8$ ,  $J_2=2.0$ , H-6), 7.14 (d,  $J=8.8$ , H-3), 7.31 (d,  $J=2.1$ , H-8), 7.39 (d, 2 H), 7.70 (d, H-5), 7.77 (d,  $J=8.8$ , H-4), 8.17 (d, 2 H), 8.35 (d, 2 H). Elemental analysis for  $\text{C}_{35}\text{H}_{38}\text{O}_6$  (554.69): calcd C 75.79, H 6.81; found C 75.38, H 6.77%.

**2.14.6. 8-Cyano-7-hydroxynaphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (11g).** Yield 90%, m.p. 188–193°C. IR ( $\nu$ ,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 3482 (OH), 2932, 2860, 2190 (CN), 1733 (COO), 1605, 1255, 1164.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 1.20–1.55 (m,  $(\text{CH}_2)_6$ ), 1.83 (m,  $\text{CH}_2$ ), 2.05 (q,  $\text{CH}_2$ ), 4.06 (t,  $\text{CH}_2\text{O}$ ), 4.97 (m,  $\text{CH}_2=\text{CH}$ ), 5.82 (m,  $\text{CH}_2=\text{CH}$ ), 6.43 (s, OH), 7.00 (d, 2 H), 7.11 (d,  $J=9.0$ , H-3), 7.35 (dd,  $J_1=8.8$ ,  $J_2=2.3$ , H-6), 7.42 (d,  $J=8.8$ , 2 H), 7.80 (s, H-8), 7.92 (d,  $J=8.8$ , H-5), 7.93 (d,  $J=9.1$ , H-4), 8.17 (d,  $J=9.1$ , 2 H), 8.34 (d, 2 H). Elemental analysis for  $\text{C}_{36}\text{H}_{35}\text{NO}_6$  (577.68): calcd C 74.85, H 6.11, N 2.42; found C 74.52, H 6.01, N 2.33%.

**2.14.7. 7-Hydroxy-1-methylnaphthalen-2-yl 4-(4-dodecyloxybenzoyloxy)benzoate (11j).** Yield 74%, m.p. 125.5–152°C. IR ( $\nu$ ,  $\text{CHCl}_3$ ,  $\text{cm}^{-1}$ ): 3480 (OH), 2931, 2860, 1731 (COO), 1604, 1252, 1160.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ),  $\delta$ : 0.88 (t,  $\text{CH}_3$ ), 1.15–1.60 (m,  $(\text{CH}_2)_9$ ), 1.83 (m,  $\text{CH}_2$ ), 2.46 (s,  $\text{CH}_3$ ), 4.06 (t,  $\text{OCH}_2$ ), 4.99 (s, OH), 6.99 (d,  $J=8.8$ , 2 H), 7.10 (dd,  $J_1=8.8$ ,  $J_2=2.3$ , H-6), 7.14 (d,  $J=8.8$ , H-3), 7.32 (d,  $J=2.3$ , H-8), 7.40 (d, 2 H),



7.70 (d, H-5), 7.78 (d,  $J=8.8$ , H-4), 8.17 (d, 2 H), 8.35 (d, 2 H). Elemental analysis for  $C_{37}H_{42}O_6$  (582.74): calcd C 76.26, H 7.26; found C 76.23, H 7.18%.

**2.15. 7-[4-(4-Decyloxybenzoyloxy)benzoyloxy]naphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (IIa)**

A mixture of benzoate **11a** (50 mg, 0.093 mmol), acid **4** (46 mg, 0.111 mmol), DCC (31 mg, 0.15 mmol) and DMAP (5 mg) in dry dichloromethane (20 ml) was stirred at room temperature for 24 h, the precipitate was filtered off and washed with dichloromethane ( $2 \times 10$  ml). The residue after evaporation of the solvent was purified by column chromatography (silica gel, elution with toluene/*tert*-butyl methyl ether 20/1) and crystallization from acetone; 78 mg (90%) of **IIa** was obtained. IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2930, 2857, 1736 (COO), 1604, 1258, 1234, 1161, 1143.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.89 (t,  $CH_3$ ), 1.20–1.62 (m,  $13 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.04 (q,  $CH_2$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.95 (m,  $\underline{CH_2=CH}$ ), 5.83 (m,  $CH_2=CH$ ), 7.00 (d,  $J=9.0$ , 4 H), 7.39 (m, H-3, H-6), 7.41 (d,  $J=8.8$ , 4 H), 7.70 (s, H-1, H-8), 7.95 (d,  $J=8.8$ , H-4, H-5), 8.17 (d, 4 H), 8.33 (d, 4 H). Elemental analysis for  $C_{59}H_{64}O_{10}$  (933.16): calcd C 75.94, H 6.91; found C 75.71, H 6.88%.

Compounds **IIb–k** were prepared by acylation of **11b–j** with acid **4** and **5**, respectively, in an analogous manner.

**2.16. 1-Chloro-7-[4-(4-decyloxybenzoyloxy)-benzoyloxy]naphthalen-2-yl 4-[4-(undec-10-enyloxy)-benzoyloxy]benzoate (IIb)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2928, 2857, 1738 (COO), 1605, 1259, 1159, 1056.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.89 (t,  $CH_3$ ), 1.20–1.60 (m,  $13 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.05 (q,  $CH_2$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.98 (m,  $\underline{CH_2=CH}$ ), 5.82 (m,  $CH_2=CH$ ), 6.99 (d,  $J=8.8$ , 4 H), 7.40 (m, 4 H), 7.44 (m, H-6), 7.44 (m, H-3), 7.89 (d,  $J=8.8$ , H-4), 7.98 (d,  $J=8.8$ , H-5), 8.15 (s, H-8), 8.17 (d, 4 H), 8.36 (d, 4 H). Elemental analysis for  $C_{59}H_{63}ClO_{10}$  (967.61): calcd C 73.24, H 6.56, Cl 3.66; found C 73.10, H 6.29, Cl 3.47%.

**2.17. 7-[4-(4-Decyloxybenzoyloxy)benzoyloxy]-1-methylnaphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (IIc)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2930, 2857, 1736 (COO), 1605, 1257, 1159.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.89 (t,  $CH_3$ ), 1.06–1.55 (m,  $13 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.05 (q,  $CH_2$ ), 2.54 (s,  $CH_3$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.98 (m,  $\underline{CH_2=CH}$ ), 5.82 (m,  $CH_2=CH$ ), 6.99 (d,  $J=8.5$ , 4 H), 7.31 (d,  $J=8.8$ , H-3), 7.40 (d, 4 H), 7.40 (d, H-6), 7.82 (d,  $J=9.1$ , H-4), 7.87 (s, H-8), 7.94 (d, H-5), 8.17 (d, 4 H), 8.35 (d, 4 H). Elemental analysis for  $C_{60}H_{66}O_{10}$  (947.19): calcd C 76.09, H 7.02; found C 75.88, H 6.90%.

**2.18. 1-Cyano-7-[4-(4-decyloxybenzoyloxy)benzoyloxy]naphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (II d)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2929, 2858, 2220 (CN), 1739 (COO), 1604, 1255, 1159, 1054.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.89 (t,  $CH_3$ ), 1.15–1.45 (m,  $13 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.06 (q,  $CH_2$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.96 (m,  $\underline{CH_2=CH}$ ), 5.82 (m,  $CH_2=CH$ ), 7.00 (d, 4 H), 7.40 (m, H-3), 7.40 (m, 4 H), 7.57 (dd,  $J(5,6)=9.4$ ,  $J(6,8)=2.1$ , H-6), 8.05 (d,  $J(3,4)=9.1$ , H-4), 8.07 (d,  $J(6,8)=2.1$ , H-8), 8.17 (d, 4 H), 8.19 (d, H-5), 8.32 (m, 4 H). Elemental analysis for  $C_{60}H_{63}NO_{10}$  (958.17): calcd C 75.21, H 6.63, N 1.46; found C 75.09, H 6.35, N 1.29%.

**2.19. 8-Chloro-7-[4-(4-decyloxybenzoyloxy)-benzoyloxy]naphthalen-2-yl 4-[4-(undec-10-enyloxy)-benzoyloxy]benzoate (II e)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2930, 2857, 1735 (COO), 1605, 1255, 1160.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.89 (t,  $CH_3$ ), 1.20–1.56 (m,  $13 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.05 (q,  $CH_2$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.98 (m,  $\underline{CH_2=CH}$ ), 5.83 (m,  $CH_2=CH$ ), 7.00 (d,  $J=8.5$ , 4 H), 7.41 (d,  $J=8.0$ , 4 H), 7.44 (d,  $J=8.8$ , H-6), 7.47 (dd,  $J_1=9.0$ ,  $J_2=2.1$ , H-3), 7.89 (d,  $J=9.1$ , H-5), 7.98 (d,  $J=8.8$ , H-4), 8.15 (s, H-1), 8.17 (d, 4 H), 8.36 (d, 4 H). Elemental analysis for  $C_{59}H_{63}ClO_{10}$  (967.61): calcd C 73.24, H 6.56, Cl 3.66; found C 73.12, H 6.40, Cl 3.51%.

**2.20. 7-[4-(4-Decyloxybenzoyloxy)benzoyloxy]-8-methylnaphthalen-2-yl 4-[4-(undec-10-enyloxy)-benzoyloxy]benzoate (II f)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2931, 2857, 1735 (COO), 1605, 1253, 1161.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.89 (t,  $CH_3$ ), 1.10–1.60 (m,  $13 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.05 (q,  $CH_2$ ), 2.54 (s,  $CH_3$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.97 (m,  $\underline{CH_2=CH}$ ), 5.82 (m,  $CH_2=CH$ ), 6.99 (d,  $J=8.8$ , 4 H), 7.31 (d,  $J=8.8$ , H-6), 7.40 (d, 4 H), 7.40 (m, H-3), 7.81 (d,  $J=8.8$ , H-5), 7.86 (s, H-1), 7.95 (d,  $J=9.1$ , H-4), 8.17 (d, 4 H), 8.36 (d, 4 H). Elemental analysis for  $C_{60}H_{66}O_{10}$  (947.19): calcd C 76.09, H 7.02; found C 75.88, H 6.92%.

**2.21. 8-Cyano-7-[4-(4-decyloxybenzoyloxy)-benzoyloxy]naphthalen-2-yl 4-[4-(undec-10-enyloxy)-benzoyloxy]benzoate (II g)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2930, 2856, 2218 (CN), 1738 (COO), 1606, 1253, 1161.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.89 (t,  $CH_3$ ), 1.10–1.60 (m,  $13 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.05 (q,  $CH_2$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.97 (m,  $\underline{CH_2=CH}$ ), 5.82 (m,  $CH_2=CH$ ), 6.99 (d,  $J=9.1$ , 4 H), 7.42 (d,  $J=9.0$ , 4 H), 7.56 (dd,  $J_1=8.8$ ,  $J_2=2.3$ , H-3), 7.60 (d,  $J=9.1$ , H-6), 8.05 (d,  $J=9.1$ , H-4), 8.08 (s, H-1), 8.17

(d, 4 H), 8.19 (d, H-5), 8.36 (m, 4 H). Elemental analysis for  $C_{60}H_{63}NO_{10}$  (958.17): calcd C 75.21, H 6.63, N 1.46; found C 75.15, H 6.48, N 1.33%.

**2.22. 7-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-naphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (IIh)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2930, 2855, 1735 (COO), 1604, 1255, 1234, 1160.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.89 (t,  $CH_3$ ), 1.20–1.54 (m,  $15 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.04 (q,  $CH_2$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.97 (m,  $\underline{CH_2=CH}$ ), 5.82 (m,  $CH_2=\underline{CH}$ ), 6.99 (d,  $J=9.0$ , 4 H), 7.38 (m, H-3, H-6), 7.40 (d,  $J=8.8$ , 4 H), 7.70 (s, H-1, H-8), 7.95 (d,  $J=8.8$ , H-4, H-5), 8.16 (d, 4 H), 8.33 (d, 4 H). Elemental analysis for  $C_{61}H_{68}O_{10}$  (961.22): calcd C 76.22, H 7.13; found C 76.01, H 6.98%.

**2.23. 8-Chloro-7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (IIi)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2930, 2855, 1735 (COO), 1605, 1253, 1160.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.88 (t,  $CH_3$ ), 1.15–1.60 (m,  $15 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.05 (q,  $CH_2$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.97 (m,  $\underline{CH_2=CH}$ ), 5.82 (m,  $CH_2=CH$ ), 6.99 (d,  $J=9.0$ , 4 H), 7.41 (d,  $J=8.4$ , 4 H), 7.44 (d,  $J=8.8$ , H-6), 7.46 (dd,  $J_1=8.8$ ,  $J_2=2.3$ , H-3), 7.89 (d,  $J=8.8$ , H-5), 7.97 (d,  $J=8.8$ , H-4), 8.15 (s, H-1), 8.17 (d, 4 H), 8.36 (d, 4 H). Elemental analysis for  $C_{61}H_{67}ClO_{10}$  (995.66): calcd C 73.59, H 6.78, Cl 3.56; found C 73.41, H 6.59, Cl 3.29%.

**2.24. 7-[4-(4-Dodecyloxybenzoyloxy)benzoyloxy]-8-methylnaphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (IIj)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2931, 2855, 1736 (COO), 1602, 1251, 1159.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.88 (t,  $CH_3$ ), 1.15–1.60 (m,  $15 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.05 (q,  $CH_2$ ), 2.54 (s,  $CH_3$ ), 4.06 (t,  $2 \times CH_2O$ ), 4.97 (m,  $\underline{CH_2=CH}$ ), 5.82 (m,  $CH_2=CH$ ), 6.99 (d,  $J=8.8$ , 4 H), 7.31 (d,  $J=8.8$ , H-6), 7.40 (d, 4 H), 7.40 (m, H-3), 7.82 (d,  $J=8.8$ , H-5), 7.86 (s, H-1), 7.95 (d,  $J=9.1$ , H-4), 8.17 (d, 4 H), 8.36 (d, 4 H). Elemental analysis for  $C_{62}H_{70}O_{10}$  (975.24): calcd C 76.36, H 7.23; found C 76.25, H 7.20%.

**2.25. 8-Cyano-7-[4-(4-dodecyloxybenzoyloxy)benzoyloxy]naphthalen-2-yl 4-[4-(undec-10-enyloxy)benzoyloxy]benzoate (IIk)**

IR ( $\nu$ ,  $CHCl_3$ ,  $cm^{-1}$ ): 2930, 2857, 2220 (CN), 1738 (COO), 1605, 1253, 1160.  $^1H$  NMR (300 MHz,  $CDCl_3$ ),  $\delta$ : 0.88 (t,  $CH_3$ ), 1.16–1.56 (m,  $15 \times CH_2$ ), 1.83 (m,  $2 \times CH_2$ ), 2.05 (q,  $CH_2$ ), 4.06 (t,  $2 \times CH_2O$ ),

4.98 (m,  $\underline{CH_2=CH}$ ), 5.82 (m,  $CH_2=CH$ ), 6.99 (d,  $J=8.8$ , 4 H), 7.42 (d,  $J=8.8$ , 4 H), 7.56 (dd,  $J=2.1$ , H-3), 7.60 (d,  $J=9.1$ , H-6), 8.05 (d,  $J=8.8$ , H-4), 8.08 (s, H-1), 8.17 (d, 4 H), 8.19 (d, H-5), 8.36 (m, 4 H). Elemental analysis for  $C_{62}H_{67}NO_{10}$  (986.23): calcd C 75.51, H 6.85, N 1.42; found C 75.35, H 6.74, N 1.28%.

### 3. Characterization

Phase transition temperatures and enthalpies were determined by differential scanning calorimetry (DSC) (Pyris Diamond Perkin-Elmer 7) under cooling and heating runs at a rate of  $5 K min^{-1}$ . The samples of 2–5 mg were placed in a nitrogen atmosphere and hermetically sealed in aluminium pans.

The planar samples for texture and electric field studies were composed of glass slides with ITO transparent electrodes ( $5 \times 5 mm^2$ ) and filled by capillary action in the isotropic phase. The sample thickness was defined by mylar sheets, usually of  $6 \mu m$  thickness. For dielectric spectroscopy several cells with non-transparent gold electrodes were prepared.

The mesophase identification was based on microscopic examination of textures in both planar and free-standing films, switching and dielectric properties and X-ray studies. A Nikon polarizing microscope equipped with a Linkam hot stage was used. The memory oscilloscope leCroy 9304 provided the switching characteristics. The measurement of the frequency dispersion of permittivity was performed on cooling using a Schlumberger 1260 impedance analyser in the frequency range 1 Hz–1 MHz, keeping the temperature of the sample stable within  $\pm 0.1 K$  during sweeps.

The experimental set-up for the investigation of second harmonic generation (SHG) used a Q-switched Nd-YAG laser as the light source. The sample was placed in a  $45^\circ$  position, the fundamental wave having p-polarization. The SHG light at 532 nm was detected by a photomultiplier and boxcar averager. To avoid possible sample damage very weak pulses were employed ( $<0.1 mJ$ , 6 ns, repetition rate 20 Hz) with no focusing. The spot size was 1 mm, allowing investigation of the 'mean' signal from the observed complicated texture. It was not possible to obtain larger single domains, which of course would be very desirable for quantitative measurements. Hysteresis loops were measured quasistatically using low frequency (0.01–0.003 Hz) triangular voltage.

## 4. Results

### 4.1. Calorimetric studies

DSC studies were performed for all the compounds; phase transition temperatures and associated enthalpy

changes are collected in tables 1 and 2 for series **I** and **II**, respectively. In all the studied compounds one mesophase was detected. DSC thermograms are shown in figures 1 (a) and 1 (b) for selected compounds from series **I** and **II**, respectively. The mesophases are overcooled typically by 3 up to 43 K. By analogy to the related materials studied earlier [24, 25], the type of lateral substituent governs the type the mesophase formed. The identification of phases and their properties are described below more in detail.

#### 4.2. Texture observation and application of electric field

All unsubstituted compounds presented here, **I/H**, **IIa** and **IIh**, exhibit a phase with typical low-birefringence domains with opposite sense of rotation of transmitted light (see figure 2 for **I/H**). In free-standing films this phase shows specific texture consisting of very small and slightly birefringent domains with diffuse boundaries (see, for example, figure 3 for compound **IIh**). The contrast between these domains grows and is interchanged on rotating the polarizer clockwise or anticlockwise by an angle of about  $3^\circ$ – $5^\circ$  from the crossed position. The texture in the planar samples is reminiscent of a relatively rare type of the  $B_2$  phase texture [22, 29–31], but the texture in the free-standing films, showing in-layer order, is inconsistent with this phase. Moreover, this phase shows no switching or any response in an electric field up to  $50 \text{ V } \mu\text{m}^{-1}$ , so we denote it as a  $B_X$  phase.

Substituted compounds from series **I**, 1-chloro (**I/Cl**) and 1-methyl (**I/CH<sub>3</sub>**), exhibit a phase with mosaic non-switchable domains, which is typical for the rectangular columnar  $B_1$  phase; see figure 4(a) for **I/CH<sub>3</sub>**. The cyano lateral substituent in **I/CN** induces the  $B_7$  phase below the isotropic phase on cooling. In the vicinity of the phase transition from the isotropic to the  $B_7$  phase typical spiral nuclei were observed. Free-standing films form a specific texture, (see figure 5 (a) for **I/CN**) similar to that observed in the  $B_7$  phase for compounds reported in [32, 33].

1-Nitroderivative **I/NO<sub>2</sub>** exhibits the  $B_2$  phase. Unfortunately this compound is insufficiently stable under the electric field, so that precise texture and switching studies could not be performed. For these reasons, the nitro-substituted core was not used in the design of compounds of series **II**.

The non-symmetrical monomeric materials of series **II** are laterally substituted on the core of the bent-shaped molecule; they have a saturated alkyl chain in one molecular arm and an unsaturated alkyl chain in the second arm. Two isomeric subseries of related materials have been synthesized. Materials **IIb–d** possess the lateral substituent closer to the unsaturated chain, while the isomeric compounds **IIe–k** are laterally substituted closer to the saturated alkyl chain, **IIa** being non-substituted (see schemes 3 and 4).

The texture study showed that mesomorphic properties of the decyl-substituted compounds **IIa–d** are identical to these of analogous symmetrical compounds

Table 1. Phase transition temperatures ( $^\circ\text{C}$ ) and associated enthalpy changes ( $\text{KJ mol}^{-1}$ ) for compounds of series **I**.

Compound	M.p.	$\Delta H$	$T_{\text{cr}}$	$\Delta H$	$M_1$	$T_{\text{tr}}$	$\Delta H$	I
<b>I/H</b>	128	+12.8	123	−28.9	$B_X$	152	−11.3	•
<b>I/Cl</b>	124	+35.2	110	−16.9	$B_1$	122	−13.5	•
<b>I/CH<sub>3</sub></b>	127	+14.9	106	−8.4	$B_1$	136	−17.9	•
<b>I/CN</b>	94	+39.7	67	−5.7	$B_7$	157	−22.6	•
<b>I/NO<sub>2</sub></b>	99	+17.1	58	−10.3	$B_2$	120	−14.6	•

Table 2. Phase transition temperatures ( $^\circ\text{C}$ ) and associated enthalpy changes ( $\text{KJ mol}^{-1}$ ) for compounds of series **II**.

Compound	$X$	$n$	M.p.	$\Delta H$	$T_{\text{cr}}$	$\Delta H$	$M$	$T_{\text{tr}}$	$\Delta H$	I
<b>IIa</b>	H	10	135	8.2	121	−8.0	$B_X$	157	−14.4	•
<b>IIb</b>	Cl	10	121	16.1	108	−16.9	$B_1$	131	−35.8	•
<b>IIc</b>	CH <sub>3</sub>	10	129	11.3	108	−6.0	$B_1$	146	−14.5	•
<b>IId</b>	CN	10	127	12.2	122	−11.7	$B_7$	156	−3.9	•
<b>IIe</b>	Cl	10	122	15.7	105	−14.1	$B_1$	129	−12.6	•
<b>IIf</b>	CH <sub>3</sub>	10	121	9.9	99	−5.2	$B_1$	143	−12.4	•
<b>IIf</b>	CN	10	111	39.4	68	−4.5	$B_7$	161	−19.1	•
<b>IIh</b>	H	12	119	9.4	116	−9.5	$B_X$	162	−16.1	•
<b>IIi</b>	Cl	12	124	11.7	101	−8.2	$B_2$	133	−14.1	•
<b>IIj</b>	CH <sub>3</sub>	12	131	16.8	114	−7.9	$B_2$	143	−16.3	•
<b>IIk</b>	CN	12	90	35.9	79	−15.3	$B_7$	164	−20.4	•

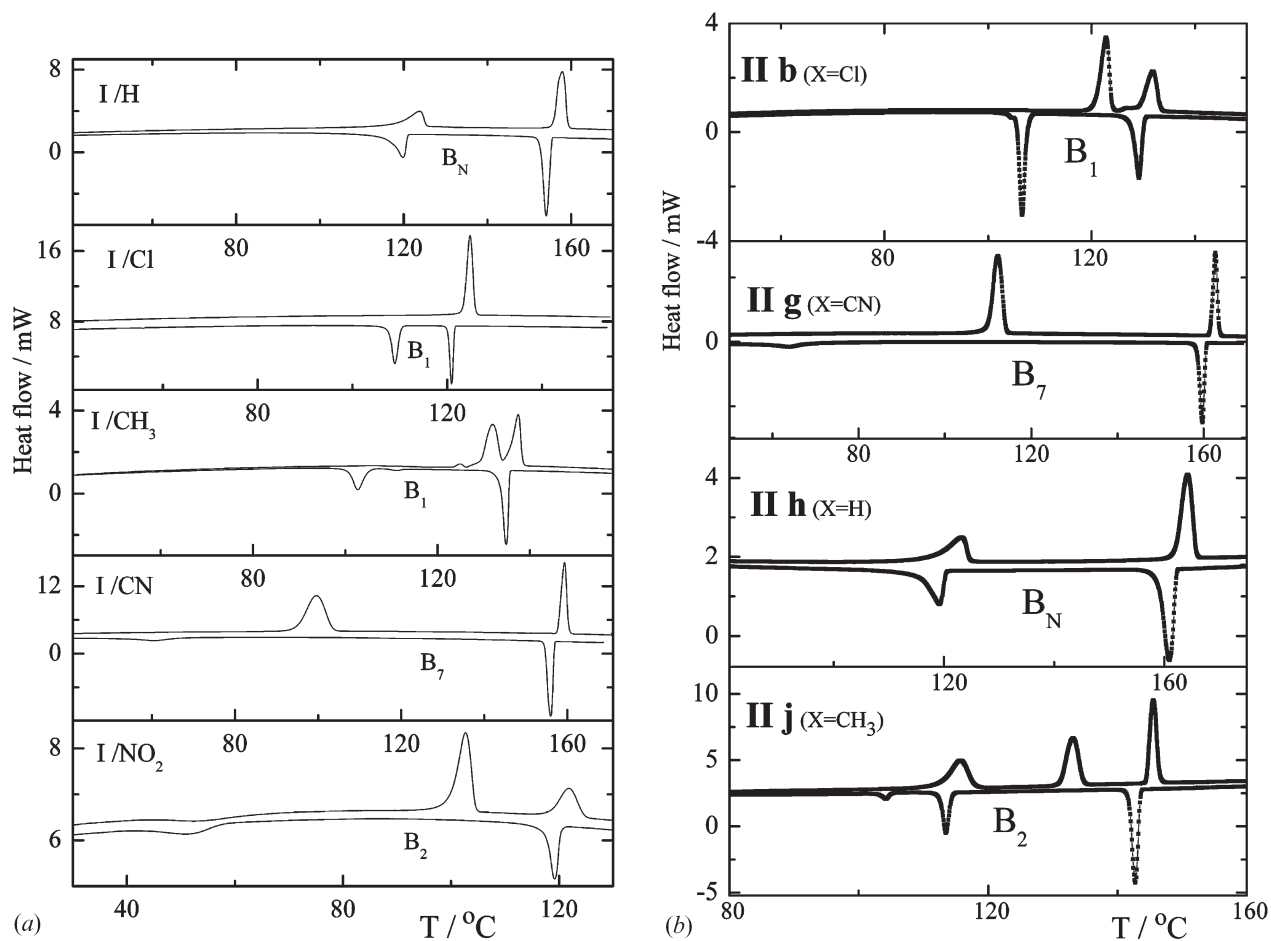


Figure 1. Typical DSC plots for compounds from series (a) **I** and (b) **II**. The upper and lower curves show second heating and cooling runs, resp. The slopes are adjusted for convenience, phases are indicated.

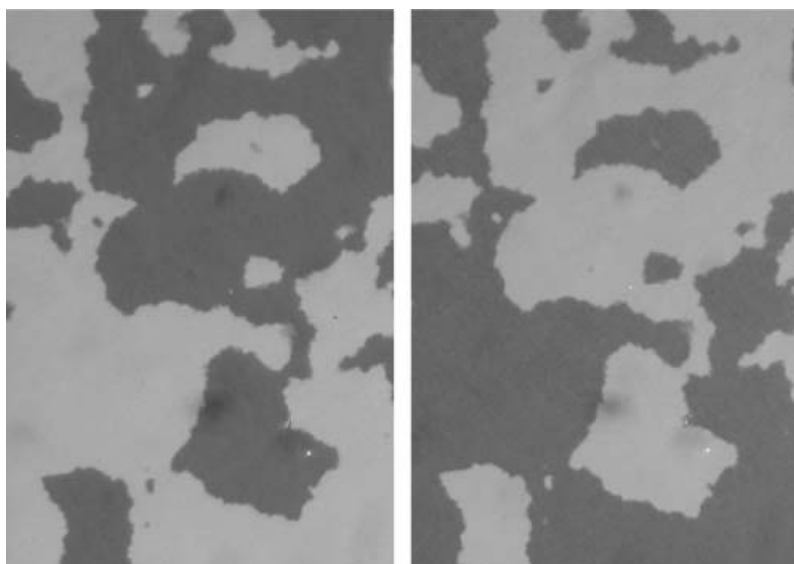


Figure 2. Planar texture of compound **I/H** in the  $B_x$  phase at  $T=142^\circ\text{C}$ . The frames differ in the sense of rotation of the analyser from the crossed position (clockwise or anticlockwise) by an angle of about  $6^\circ$ . Width of frames corresponds to  $200\ \mu\text{m}$ .

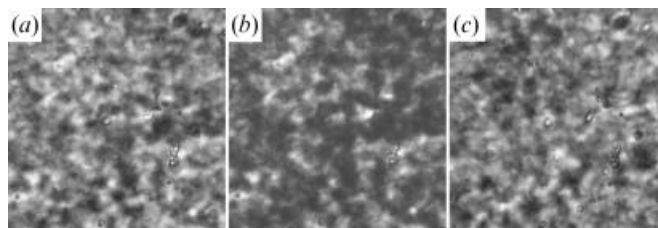


Figure 3. Texture of a free-standing film of compound **IIIh** in the  $B_X$  phase: (b) under crossed polarizers, (a) and (c) with the analyser rotated by an angle of about  $5^\circ$  from the crossed position, clockwise and anticlockwise, respectively. The width of each photomicrographs is about  $150\ \mu\text{m}$ .

of series **I**: the chloro- and methyl-substituted materials **IIb,c** form the columnar  $B_1$  phase, the cyano-substituted **IIId** exhibits the  $B_7$  phase and non-substituted **IIa** the  $B_X$  phase.

Compounds **IIe–g** are the structural isomers of **IIb–d**, differing in the site of the lateral substituent. Texture observations showed that compounds **IIe–g** exhibit the same phases—see figure 4(b)—and DSC studies confirmed that the phase transition temperatures are similar to those values for structural isomers **IIb–d** with the same substituent. Thus, 1-chloro (**IIb** and **IIe**) and 1-methyl (**IIc** and **IIf**) substituted compounds exhibit the  $B_1$  phase, the transition temperatures from the isotropic phase to the mesophase differing only by about 3 K. The cyano-substituted **IIg** shows the  $B_7$  phase as does compound **IIId**. From this comparison, and taking into account results from series **I**, we can conclude that the relative positions of the lateral substituent and the saturated and/or unsaturated alkyl chain have not influenced the mesomorphic properties.

From compounds **IIIh–k** with the dodecyl alkyl chain, the unsubstituted **IIIh** and the cyano-substituted **IIIk**

exhibit the same mesomorphic properties as their shorter analogues ( $B_X$  and  $B_7$  phase, respectively). For compound **IIIk** the  $B_7$ -family phase is observed. Irregular spiral nuclei and straight lancet-like germs arise on cooling from the isotropic phase (see figure 6). Free-standing films form a texture revealing specific features of layers; see figure 5(b) for **IIIk**. The exact character of undulation or modulation should be indicated by synchrotron measurements. For chloro- (**IIIi**) and methyl- (**IIIj**) substituted materials with a dodecyl terminal chain, the  $B_2$  phase was found with a relatively wide temperature range of  $\sim 30\ \text{K}$ .

#### 4.3. Properties of the $B_2$ phase

In compound **IIIi**, the planar texture of the  $B_2$  phase is a very fine. The intensity of the light transmitted through a sample is proportional to the applied d.c. field up to a value of about  $20\ \text{V}\ \mu\text{m}$ . The methyl-substituted **IIIj** exhibits a fan-shaped texture with fine stripes in planar geometry, which is typical for the  $B_2$  phase, see figure 7(a). The overall extinction position is parallel

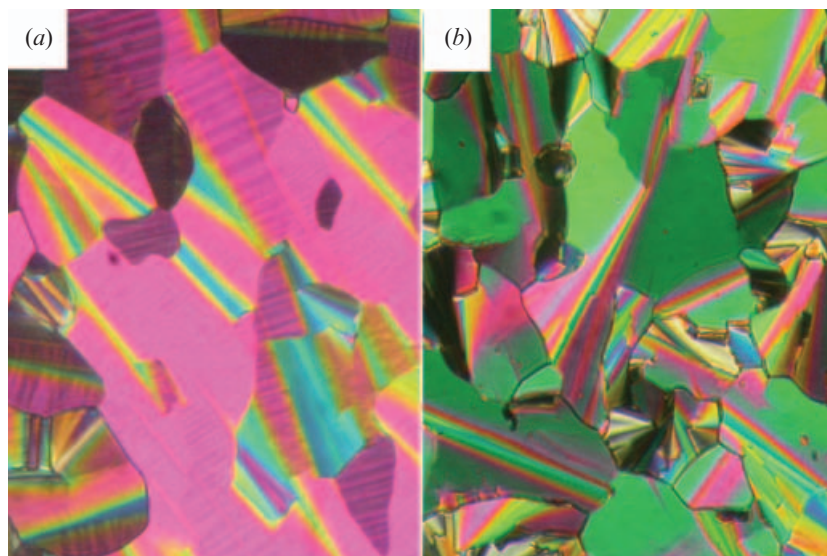


Figure 4. Photomicrographs of the planar texture of (a) **I/CH<sub>3</sub>** and (b) **IIe** in the  $B_1$  phase. The width of a frame is  $250\ \mu\text{m}$ .

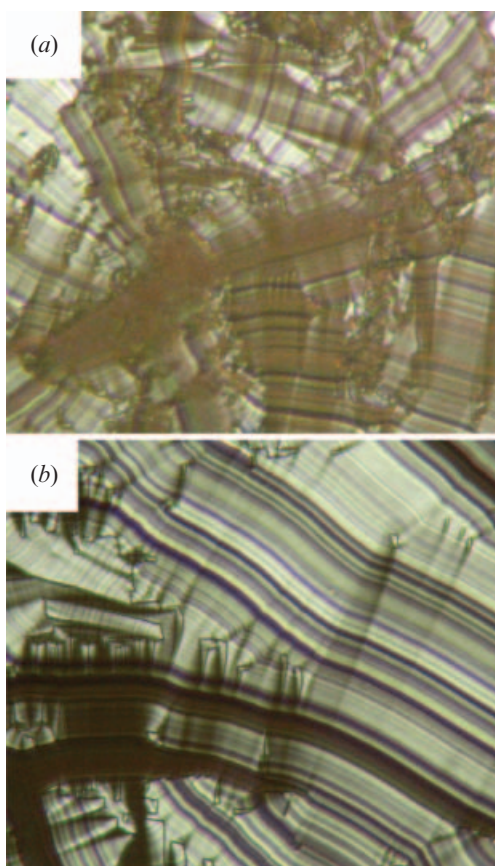


Figure 5. Free-standing film in the  $B_7$  phase of (a) **I/CN** and (b) **IIk**. The width of each frame is about  $200\ \mu\text{m}$ .

to the smectic layer normal. Under the electric field the birefringence increases, fine stripes gradually disappearing. As the remains of stripes, linear defects emerge parallel to the smectic layers, figure 7(b). In a few cases the lines separate stripe domains with the opposite sense of rotation of extinction brushes from the layer

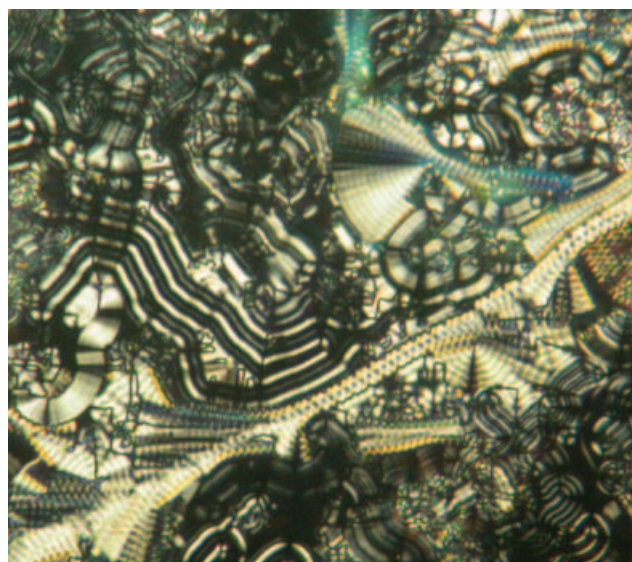


Figure 6. Planar texture of **IIk** in the  $B_7$  phase at  $T=138^\circ\text{C}$ . Width of figure corresponds to  $350\ \mu\text{m}$ .

normal—see, for example, stripes with dark–bright contrast in the bottom right corner in figure 7(b). At a threshold value of about  $20\ \text{V}\ \mu\text{m}$  the birefringence abruptly increases to a value of about 0.2 and extinction brushes become inclined about  $45^\circ$  from the layer normal within the whole sample, see figure 7(c). The linear defects are present even in the high field texture. The properties of this texture do not change up to the highest applied field,  $30\ \text{V}\ \mu\text{m}^{-1}$ .

The switching current profile for both the chloro-substituted (**IIi**) and methyl-substituted (**IIj**) compounds exhibits two peaks in the  $B_2$  phase for a low frequency a.c. field, which provides evidence of the antiferroelectric character of this phase (see figure 8). In dielectric spectroscopy studies, a single weak mode is

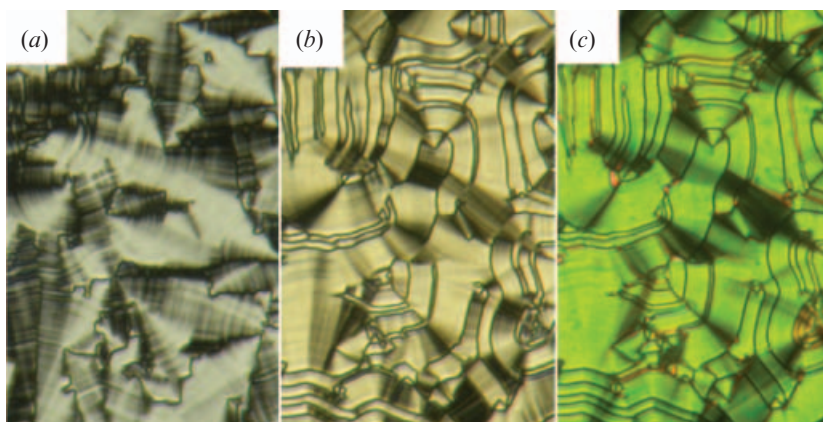


Figure 7. Planar texture of **IIj** in the  $B_2$  phase (a) with no electric field, (b) in a d.c. field of  $15\ \text{V}\ \mu\text{m}^{-1}$  and (c)  $25\ \text{V}\ \mu\text{m}^{-1}$ . The width of each frame corresponds to  $200\ \mu\text{m}$ .

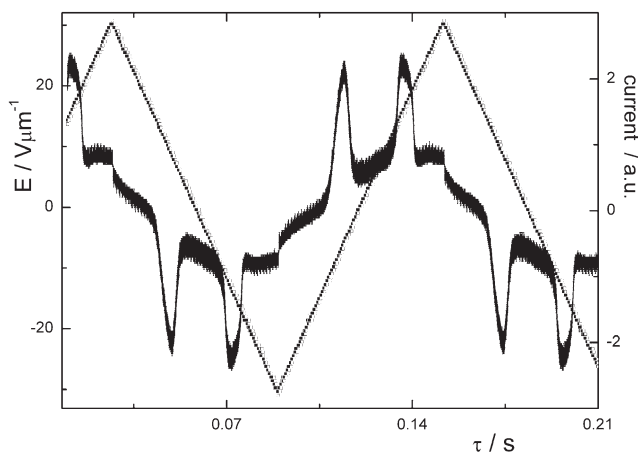


Figure 8. Switching current profile for **IIj** at  $T=175^{\circ}\text{C}$  taken at a frequency of 8 Hz.

observed in the  $B_2$  phase with a relaxation frequency of some hundreds kHz, which decreases with decreasing temperature (see figure 9). Using gold electrodes, the cut-off frequency was shifted to the megahertz region and thus the high frequency mode could be detected. The studied mode completely disappears in the isotropic as well as in the crystalline phases (figure 9). Temperature dependence of the fitted relaxation frequency and dielectric strength for **IIj** compound is shown in figure 10.

SHG measurements were performed in the  $B_2$  phase for compounds **IIIi** and **IIj** (figure 11). The SHG signal

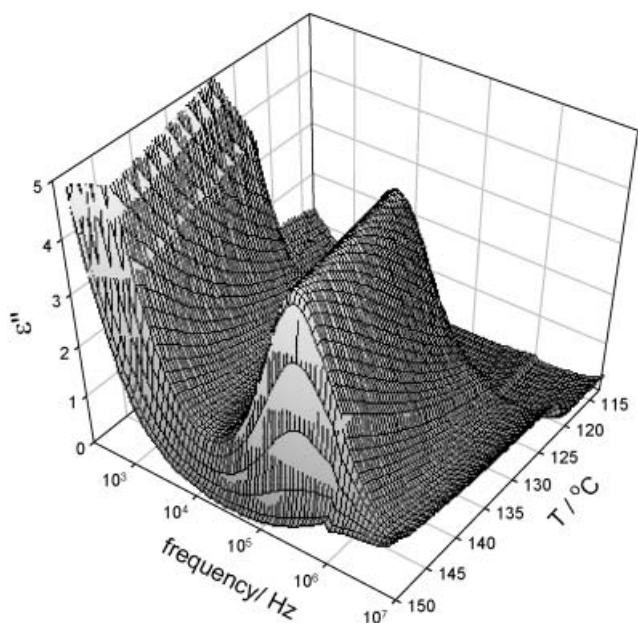


Figure 9. Temperature–frequency plots of the imaginary part of the dielectric permittivity taken on cooling from the isotropic phase for compound **IIj**.

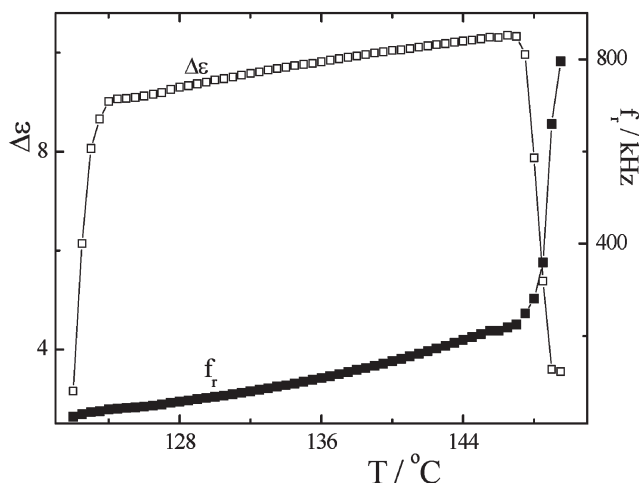


Figure 10. Fitted value of relaxation frequency,  $f_r$ , and dielectric strength,  $\Delta\epsilon$ , for **IIj**.

for a quasistatic electric field was measured at a temperatures about 10 K below the isotropic– $B_2$  phase transition. Detected signals decrease gradually, depending the applied electric field, up to values of about 35 and 25  $\text{kV}\mu\text{m}^{-1}$  for **IIIi** and **IIj**, respectively. At higher fields the SHG signals reveal saturation.

## 5. Discussion and conclusions

Two new series of naphthalene-2,7-diol-based mesogens have been synthesized with a polymerizable (non-saturated) site at the ends of one (series **II**), or both

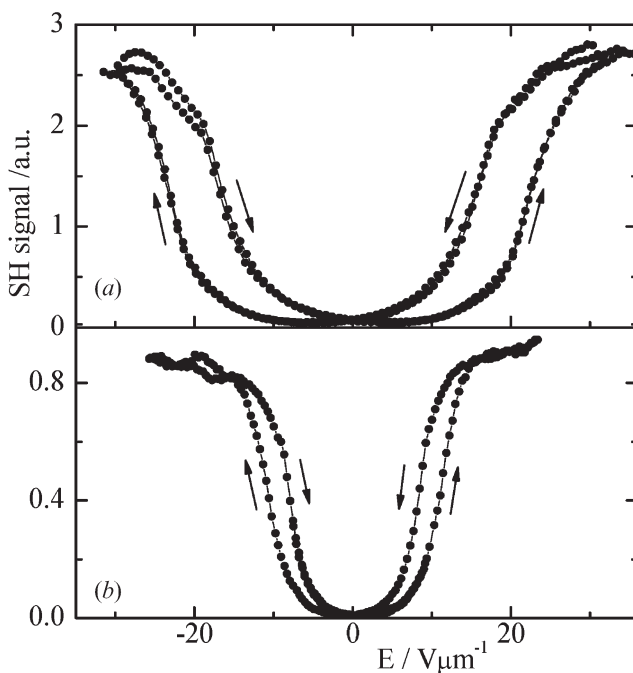


Figure 11. SHG signal versus applied electric field for compounds (a) **IIIi** and (b) **IIj**.

(series **I**) lateral alkyl chains. The naphthalene central core was substituted by Cl, CH<sub>3</sub>, CN and NO<sub>2</sub> in the series with symmetrical molecules (series **I**). In the non-symmetrical molecules (series **II**) the Cl, CH<sub>3</sub> and CN substituents were attached to one of each central rings. Except for the nitro-substituted compound, these materials proved to be more stable under an electric field than to those with the same central core but possessing the Schiff's base linkage group in the branches [24].

In both series **I** and **II** the mesomorphic behaviour is the same and uninfluenced by the position of substituents on the central core. On the other hand, we have found a strong effect by the type of lateral substituent on the occurrence of phases of the materials studied. For non-substituted compounds an unidentified B<sub>X</sub> mesophase occurs, which cannot be unambiguously assigned to any phase so far described in the literature [29–31, 34]. Free-standing films of the B<sub>X</sub> phase have shown features not yet reported. Identification of the B<sub>X</sub> phase structure will require further investigation.

In compounds with the CN substituent the B<sub>7</sub> phase occurs over a relatively wide temperature interval, from 40 to 90 K. When Cl and CH<sub>3</sub> substituents are used, the phases are determined by the length of the lateral alkyl chain: for  $n=10$  or  $12$  the B<sub>1</sub> or B<sub>2</sub> phase occurs. NO<sub>2</sub> substitution was used only in the symmetrical series **I**, and brought about the B<sub>2</sub> phase. As this material exhibited poor stability under the electric field nitro substitution was not applied in series **II**.

Mesomorphic properties of the compounds described here agree with those of saturated analogues with the same substituents, which were studied previously for several lengths of the alkyl chain [25]. The only difference is that for saturated Cl- and CH<sub>3</sub>-substituted compounds the B<sub>2</sub> phase appeared also for  $n=10$ . We note that NO<sub>2</sub> substitution led to B<sub>7</sub> phase in the analogous saturated compound [25] instead of the B<sub>2</sub> phase observed in series **I**.

Properties of the B<sub>2</sub> phase were studied in detail. The optical properties, namely the position of the optical extinction, indicate an anticlinic structure, which is transformed to the synclinic under a sufficiently high (critical) electric field. The high field structure has strong birefringence with the optical axis inclined by 45° from the smectic layer normal (orthoconic structure). In intermediate fields, there is another distinct structure, which has lower birefringence and the optical axis inclined by an angle less than 45°.

The profile of the switching current with two peaks, as well as the existence of a very weak high frequency mode, provide evidence of the antiferroelectric

character of the B<sub>2</sub> phase. The SHG signal measured during switching also gives evidence for the transition from the antiferroelectric to the ferroelectric state. A gradual increase of the SHG signal with field indicates gradual transformation into the ferroelectric state, which is consistent with relatively wide peak profile in the plot of transient current versus applied electric field. The analysis of the behaviour of the B<sub>2</sub> phase in the compounds studied allows us to conclude that this phase has the SmC<sub>A</sub>P<sub>A</sub> structure, which is transformed into the SmC<sub>S</sub>P<sub>F</sub> phase under an electric field.

The present study has shown that the introduction of double bonds at the end of the alkyl chains do not influence significantly the mesogenic properties of this class of compounds. The non-saturated molecules can be used for the preparation of main or side chain polymeric liquid crystals. A polymerization study of selected compounds is under way.

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