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Liquid crystalline benzothiophene derivatives

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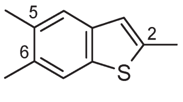
The role and position of the benzothiophene core in several series of calamitic liquid crystals was examined. Benzothiophene and its lateral 3-chloro- and 6-methoxy-substituted derivatives, where the benzothiophene unit is in the terminal position, support formation of broad nematic phases. On the other hand, introduction of a longer alkoxy chain in the 6-position or positioning the benzothiophene in the centre of the molecular structure led to appearance of smectic C and/or smectic A phases.

1. Introduction

The molecular structure of calamitic liquid crystals is very varied; consequently their mesomorphic properties differ significantly [1]. Among others, many types of five- and six-membered heterocyclic systems have been introduced to the molecular core. The presence of a thiophene ring in the core of liquid crystal molecules creates a bent molecular structure that substantially affects the transition temperatures, dielectric, optical and other properties of mesogens in comparison with the benzenoid analogues [2–10]. We showed recently that fused three- and four-ring thiophene-based heterocyclic systems can be successfully used for design of various mesogens with ferroelectric properties [11–15]. On the other hand, it seems to be surprising that only very few examples of liquid crystals possessing a very simple benzothiophene system in their molecule have been described in patents and in the literature. Thus, some materials based on fluorinated 6-alkoxybenzothiophene-2-carboxylic acid have been declared (without any data) as such or mixed for optical display elements [16]. It was also claimed [17] that fluorinated 2-aryl-6-alkoxybenzothiophenes have a favourable effect on the properties of liquid crystal mixtures, in particular chiral smectic mixtures. Finally, a 2,3-dihydro-4,5,6-trifluorobenzothiophene-based material was described as a component in liquid crystalline media [18]. In a study of nematogenic naphthalenes [19], two examples of 2,5-substitued benzothiophene mesogens have been prepared and it was shown that replacement of the naphthalene unit by benzothiophene leads to a depression of transition temperatures due to deformation from linearity of the benzothiophene core. Recently [20] a broad study of mesogens containing the benzofuran core showed that 2,5-disubstitution in benzofuran gives a bent core, which also to some extent adversely affects the mesogenicity. An example of analogous benzothiophene-based materials lacking mesogenicity was also shown and it was stated that change of benzofuran to benzothiophene leads to higher melting point, which may mask mesophase formation.

The above mentioned results inspired us to perform a broader study of benzothiophene-based calamitic mesogens and design materials exhibiting versatile mesomorphic properties to show the general utility of the benzothiophene core. When applying benzothiophene for design of liquid crystalline materials it is necessary to realize that the bond angles are quite different from those in 1,3-disubstituted benzene and 2,7-disubstituted naphthalene ring systems, which results in a bent molecular structure. We calculated the bond angles in benzothiophene from the X-ray data for 2-benzoylbenzothiophene [21]. The smallest deviation from linearity is for 2,6-disubstituted (~27°) and 2,5-disubstituted benzothiophenes (~34°), where for the former case the sulfur atom is placed inside whereas for the latter case the sulfur is outside the bend (see figure 1). In analogy with thiophene, the bend should lead to lowering of the transition temperatures; on the other hand, the presence



2,5-bonds = 146.8°
2,6-bonds = 153.3°

Figure 1. Bond angles in 2,5- and 2,6-substituted benzothiophenes.

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of the π-electron rich aromatic system and a strong permanent dipole of the sulfur atom cause an increase in polarizability and occurrence of the spontaneous polarization. In this paper, we report the synthesis and mesomorphic behaviour of several series of 2,6-disustituted benzothiophene-based liquid crystals to obtain structure–property relationships for these novel calamitic mesogens.

2. Experimental

2.1. *Characterization*

Structure confirmation for intermediates and products was obtained by ^{1}H NMR spectroscopy (Varian Gemini 300 HC instrument; $CDCl_3$ or DMSO-d_6 was used as solvent and signals of the solvents served as internal standards; *J* values are given in Hz). The numbering of aromatic protons in molecules of series **II**–**IV** compounds is shown in figure 2 and the signals were identified by COSY experiments. The numbering and assignment of protons in molecules of series **I** and **V** compounds were made analogously.

Elemental analyses were carried out on a Perkin-Elmer 2400 instrument. The purities of all final compounds were checked by HPLC analysis (Tessek C18 25 × 4,5 RP column) and were found >99.8%. Column chromatography was carried out using Merck Kieselgel 60 (60–100 µm). Procedures for the synthesis of representative intermediates and target compounds of series **I**–**V** are summarized in sections 2.2 and 2.3.

All materials were studied using differential scanning calorimetry (DSC, Perkin-Elmer Pyris Diamond). The mass of the samples was 2–4 mg. The samples were hermetically closed in aluminium pans and placed in nitrogen atmosphere. The cooling and heating rates of 5 K min^{-1} were applied.

The texture observations were carried out on planar samples 12 or 25 µm thick under polarizing optical microscope (POM, Nikon Eclipse). We prepared cells from glass plates provided with transparent ITO electrodes and polyimide layers unidirectional rubbed, which ensured a book-shelf (planar) geometry. The area of electrodes was 5 × 5 mm^2. The glasses were glued together with mylar sheets as a spacer. The cells were filled in the isotropic phase. Temperature was changed and stabilized with an accuracy of ±0.1°C in the hot stage (Linkam) placed on the table of the POM.

2.2. *Synthesis of intermediates*

Synthetic routes to the studied materials are shown in schemes 1–2. The initial benzothiophene derivatives were obtained by known or modified procedures (scheme 1). The acid chloride **1a** was obtained by condensation of *o*-nitrobenzaldehyde with methyl thioglycolate in basic medium [22], hydrolysis to benzothiophene-2-carboxylic acid and reaction with thionyl chloride. The 3-chloro substituted analogue **1b** was prepared by the Higa cyclization of cinnamic acid **2b** [23]. In this way, 3-chloro-6-methoxybenzothiophene-2-carbonyl chloride (**1c**) was also prepared. For design of materials with the benzothiophene unit in the centre of their molecule, 6-hydroxybenzothiophene-2-carboxylic acid represented the convenient difunctional intermediate. For this purpose, 4-acetoxycinnamic acid (**2d**) was newly cyclized under optimized reaction conditions and the formed chloride **1d** (62% yield) after methanolysis (ester **3a**) and subsequent hydrolysis afforded the required acid **4a**. Synthesis of the 6-alkoxysubstituted benzothiophene-2-carbonyl chlorides **1e$_n$** utilized the hydroxy ester **3a**. The 6-hydroxy group was alkylated with the corresponding alkyl bromide $C_nH_{2n+1}Br$ (n=6, 8, 10 and 12) and the alkylated products **3b$_n$** were hydrolyzed to the corresponding substituted acids **4b$_n$** and transformed to chlorides **1e$_n$**.

Octyl 4-hydroxybenzoate (**5**) (scheme 2) was prepared by azeotropic esterification of *p*-hydroxybenzoic acid according to a literature method [24], 4-hydroxy-4′-octyloxybiphenyl (**6**) was obtained by alkylation of 4, 4′-dihydroxybiphenyl [15], octyl 4′-hydroxy-1,1′-biphenyl-4-carboxylate (**7**) resulted from esterification of 4′-hydroxy-1,1′-biphenyl-4-carboxylic acid [15] and octyl 4-[(4′-hydroxybenzoyl)oxy]benzoate (**8**) was

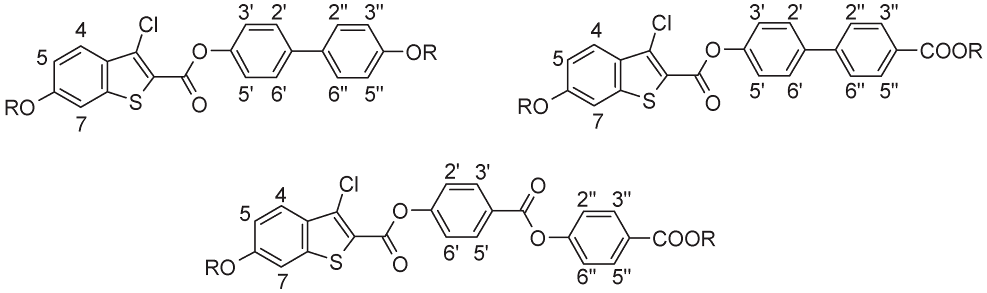
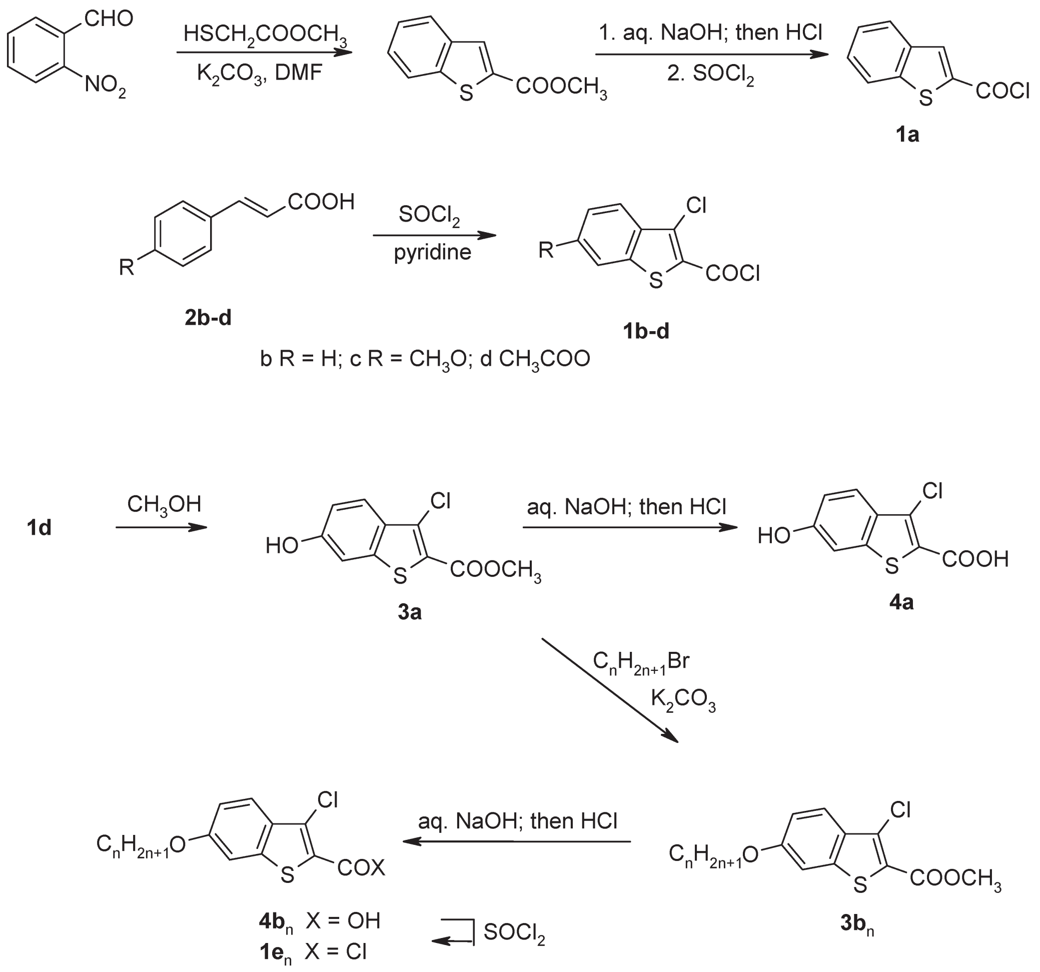
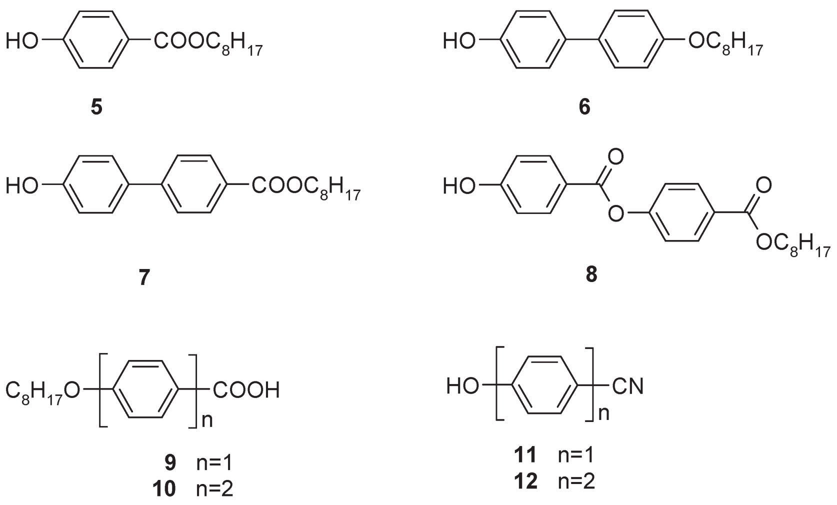


Figure 2. Numbering of aromatic protons in molecules of series **II**–**IV** compounds.



Scheme 1. Synthesis of the initial benzothiophene derivatives.



Scheme 2. Structures of other intermediates.

obtained by the known procedure [25], i.e. acylation of **5** with 4-(methoxycarbonyloxy)benzoic acid and subsequent deprotection of the protecting carbonate group with aqueous NH_3. 4-Octyloxybenzoic acid (**9**) and 4′-octyloxy-1,1′-biphenyl-4-carboxylic acid (**10**) were prepared by alkylation of the corresponding hydroxybenzoic acids [26, 27]. 4-Hydroxybenzonitrile (**11**) was prepared starting with *p*-anisaldehyde [28, 29] and 4′-hydroxy-1,1′-biphenyl-4-carbonitrile (**12**) was obtained from 4-methoxy-1,1′-biphenyl-4-carboxylic acid [29, 30] *via* the corresponding chloride, amide, nitrile, and final deprotection of the methoxy group.

2.2.1. 6-Acetoxy-3-chlorobenzo[*b*]thiophen-2-carbonyl chorlide (1d). Thionyl chloride (18 ml, 250 mmol) was added dropwise to a mixture of 4-acetoxycinnamic acid (10.0 g, 48 mmol), pyridine (1.5 ml) and chlorobenzene (250 ml) during 30 min and then refluxed at 130°C for 72 h. After cooling, the solution was decanted from the oily tar and evaporated to dryness. Crystallization of the residue from heptane afforded 8.60 g (62%) of chloride **1d**, m.p. 127°C. ^{1}H NMR ($CDCl_3$): 8.01 (d, 1 H, $J_{4,5}$=8.8, H-4), 7.65 (d, 1 H, $J_{5,7}$=2.1, H-7), 7.14 (dd, 1 H, H-5), 2.37 (s, 3 H, CH_3). Elemental analysis: for $C_{11}H_6Cl_2O_3S$ (289.14), calculated C 45.70, H 2.09, Cl 24.52; found C 45.55, H 2.10, Cl 24.05%.

2.2.2. Methyl 3-chloro-6-hydroxybenzo[*b*]thiophen-2-carboxylate (3a). Chloride **1d** (5.0 g, 17.3 mmol) was dissolved in dry methanol (150 ml) and heated to reflux for 2 h. After cooling the deposited crystals were filtered off and washed with cold methanol. 3.72 g (90%) of ester **3** was obtained, m.p. 212°C. ^{1}H NMR (DMSO-*d₆*): 7.97 (d, 1 H, $J_{4,5}$=8.8, H-4), 7.28 (d, 1 H, $J_{5,7}$=2.2, H-7), 7.19 (dd, 1 H, H-5), 3.93 (s, 3 H, OCH_3). Elemental analysis: for $C_{10}H_7ClO_3S$ (242.68), calculated C 49.49, H 2.91, Cl 14.61; found C 49.50, H 2.89, Cl 14.50%.

2.2.3. 3-Chloro-6-hydroxybenzo[*b*]thiophen-2-carboxylic acid (4a). Ester **3a** (3.72 g, 15.3 mmol) was added to a solution of sodium hydroxide (3.19 g, 80 mmol) in 50% aq. methanol (60 ml) and the mixture was heated to boiling for 2 h and after cooling poured on cold 4% aqueous hydrochloric acid (120 ml). The solid was filtered and washed thoroughly with water. Crystallization from THF afforded 3.44 g (98%) of acid **4**, m.p. >360°C. ^{1}H NMR (DMSO-*d₆*): 7.98 (d, 1 H, $J_{6,7}$=8.8, H-7), 7.14 (d, 1 H, $J_{4,6}$=2.2, H-4), 6.97 (dd, 1 H, H-6). Elemental analysis: for $C_9H_5ClO_3S$ (228.66), calculated C 47.28, H 2.20, Cl 15.50; found C 47.36, H 2.18, Cl 15.48%.

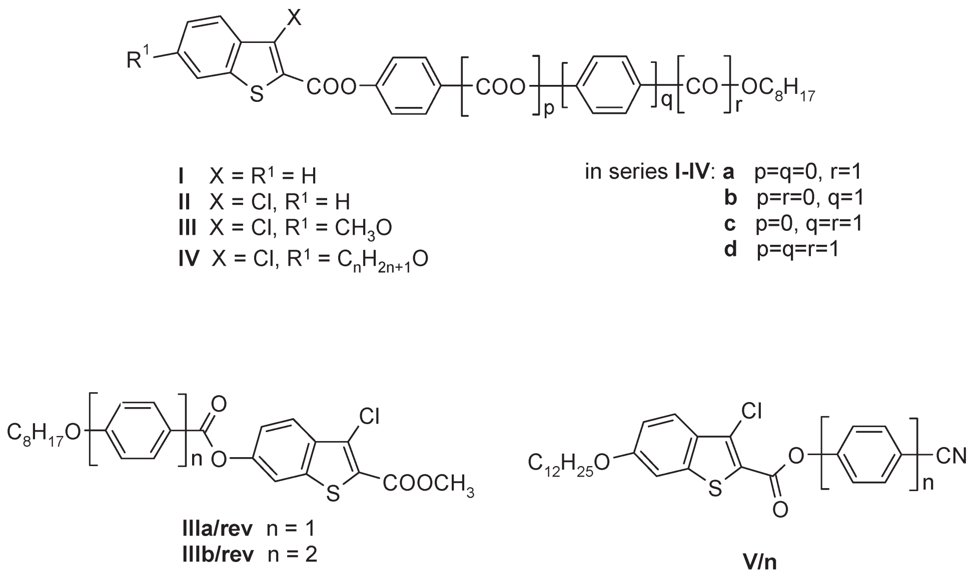
2.2.4. Methyl 3-chloro-6-hexyloxybenzothiophene-2-carboxylate (3b₆). A mixture of hydroxy ester **3a** (1.0 g, 4.2 mmol), 1-bromohexane (2.1 g, 12.7 mmol), potassium carbonate (2.0 g, 14.5 mmol), sodium iodide (0.5 g) and acetone (50 ml) was stirred and heated to boiling for 20 h. After cooling, the mixture was filtered and the filtrate was evaporated to dryness. Column chromatography (elution with chloroform) afforded 1.23 g (90%) of ester **3b**, m.p. 78°C (methanol). ^{1}H NMR: 7.81 (d, 1 H, *J*=8.8, H-4), 7.19 (s, 1 H, H-7), 7.08 (d, 1 H, H-5), 4.03 (t, 2 H, *J*=6.4, CH_2O), 3.93 (s, 3 H, OCH_3), 1.82 (m, 2 H, CH_2), 1.43–1.28 (m, 6 H, $(CH_2)_3$), 0.88 (t, 3 H, CH_3). Elemental analysis: for $C_{16}H_{19}ClO_3S$ (326.85), calculated C 58.80, H 5.85, Cl 10.85; found C 58.78, H 5.71, Cl 10.58%. In the same way, esters $\mathbf{3b_8}$ (*n*=8), m.p. 83°C, $\mathbf{3b_{10}}$ (*n*=10), m.p. 85°C, and $\mathbf{3b_{12}}$ (*n*=12), m.p. 91°C, were obtained.

2.2.5. 3-Chloro-6-hexyloxybenzothiophene-2-carboxylic acid (4b₆). Ester $\mathbf{3b_6}$ (1.24 g, 3.8 mmol) was added to a solution of sodium hydroxide (0.6 g, 15 mmol) in a mixture of ethanol (20 ml) and water (10 ml) and heated to reflux for 2 h, diluted with water (5.0 ml) and acidified with hydrochloric acid (10 ml). The solid was filtered and washed with water. Crystallization from toluene afforded 1.18 g (99%) of acid $\mathbf{4b_6}$, m.p. 157°C. ^{1}H NMR (DMSO-*d₆*): 7.78 (d, 1 H, *J*=8.8, H-4), 7.16 (s, 1 H, H-7), 7.08 (d, 1 H, H-5), 4.02 (t, 2 H, *J*=6.4, CH_2O), 1.82 (m, 2 H, CH_2), 1.42–1.24 (m, 6 H, $(CH_2)_3$), 0.88 (t, 3 H, CH_3). Elemental analysis: for $C_{15}H_{17}ClO_3S$ (312.82), calculated C 57.59, H 5.48, Cl 11.33; found C 57.44, H 5.29, Cl 11.19%. Acids $\mathbf{4b_8}$ (*n*=8), m.p. 160°C, $\mathbf{4b_{10}}$ (n=10), m.p. 180°C, and $\mathbf{4b_{12}}$ (*n*=12), m.p. 188°C, were prepared in the same manner.

2.3. *Synthesis of the target series I–V compounds*

Synthesis of the target substances involved reaction of acid chlorides **1a**–**1d**, $\mathbf{1e_n}$ with the corresponding hydroxy derivatives **5**–**8** (materials denoted **a**, **b**, **c** and **d**, were obtained by acylation of **5**, **6**, **7** and **8**, respectively), and nitriles **11** and **12**, respectively (series **I**–**V**) (scheme 3). Materials **III/rev**, which possess the reversed sequence of cores in comparison with series **I**–**III**, were obtained by acylation of ester **3a** with acids **9** and **10**.

Hydroxy derivative, **5**–**8**, **11**, **12** and **3a** (1.3 mmol), respectively, was added to a solution of the corresponding acid chloride, **1a**–**1c**, $\mathbf{1e_n}$, and acid chlorides of **9**, **10** (1 mmol), respectively, in toluene (30 ml). After dissolution, DMAP (1.05 mmol) was added and the mixture was stirred at room temperature. When the starting hydroxy derivative disappeared (tlc), the mixture was diluted with chloroform (30 ml) and washed with water (2 × 30 ml) and dried with anhydrous magnesium sulfate. The residue after evaporation was



Scheme 3. Structures of the target compounds.

chromatographed and crystallized to afford the target compounds of the series **I**–**V**.

2.3.1. Octyl (4-benzothiophen-2-carbonyloxy)benzoate (Ia). Crystal (Cr) 45°C isotropic (I). ^{1}H NMR: 8.29 (s, 1 H, H-3), 8.13 (d, 2 H, $J_{2',3'}=8.8$, H-2′,6′); 7,95 (d, 1 H, $J_{4,5}=7.3$, H-4), 7.92 (d, 1 H, $J_{6,7}=8.2$, H-7), 7.53 (t, 1 H, H-5), 7.51 (t, 1 H, H-6), 7.36 (d, 2 H, H-3′,5′); 4.33 (t, 2 H, $J=6.8$, OCH$_2$), 1.78 (m, 2 H, CH$_2$), 1.45–1.35 (m, 6 H, (CH$_2$)$_5$), 0.91 (t, 3 H, $J=7.04$, CH$_3$). Elemental analysis: for $C_{24}H_{26}O_4S$ (410.54), calculated C 70.22, H 6.38; found C 70.06, H 6.29%.

2.2.5. 3-Chloro-6-hexyloxybenzothiophene-2-carboxylic acid (4b$_6$). Cr 114°C nematic (N) 195°C I. ^{1}H NMR: 8.03 (d, 1 H, $J_{4,5}=7.6$, H-4), 7.87 (d, 1 H, $J_{6,7}=7.9$, H-7), 7.60 (d, 2 H, $J_{2'',3''}=8.0$, H-3″,5″), 7.58 (t, 1 H, H-5), 7.54 (t, 1 H, H-6), 7.59 (d, 2 H, $J_{2',3'}=8.5$, H-2′,6′), 7.32 (d, 2 H, H-2″,6″), 6.98 (d, 2 H, H-3′,5′), 4.00 (t, 2 H, $J=6.4$, CH$_2$O), 1.81 (m, 2 H, CH$_2$), 1.47–1.30 (m, 10 H, (CH$_2$)$_5$), 0.89 (t, 3 H, $J=6.8$, CH$_3$). Elemental analysis: for $C_{29}H_{29}ClO_3S$ (493.07), calculated C 70.64, H 5.93, Cl 7.19; found C 70.36, H 5.89, Cl 7.03%.

2.3.3. Octyl 4′-(3-chloro-6-methoxybenzothiophen-2-carbonyloxy)-1,1′-biphenyl-4-carboxylate (IIIc). Cr 67°C N 192°C I. ^{1}H NMR: 8.12 (d, 2 H, $J_{2',3'}=8.2$, H-3′,5′), 7.90 (d, 1 H, $J_{4,5}=9.0$, H-4), 7.69 (d, 2 H, $J_{2'',3''}=8.8$, H-3″,5″), 7.65 (d, 2 H, H-2′,6′), 7.37 (d, 2 H, H-2″,6″); 7.27 (d, 1 H, $J_{5,7}=2.25$, H-7), 7.14 (dd, 1 H, H-5), 4.34 (t, 2 H, $J=6.5$, CH$_2$O), 3.93 (s, 3 H, CH$_3$O), 1.81 (m, 2 H, CH$_2$), 1.47–1.30 (m, 10 H, (CH$_2$)$_5$), 0.89 (t, 3 H, $J=6.8$, CH$_3$). Elemental analysis: for $C_{31}H_{31}ClO_5S$ (551.11), calculated C 67.56, H 5.67, Cl 6.43; found C 67.48, H 5.55, Cl 6.31%.

2.3.4. Methyl 3-chloro-6-(4′-octyloxy-1,1′-biphenyl-4-carbonyloxy)benzothiophene-2-carboxylate (IIIb/rev). Cr 78°C smectic A (SmA) 250°C I. ^{1}H NMR: 8.25 (d, 2 H, $J_{2',3'}=8.5$, H-2′,6′), 8.02 (d, 1 H, $J_{4,5}=8.8$, H-4), 7.75 (d, 1 H, $J_{5,7}=2.2$, H-7), 7.71 (d, 2 H, H-3′,5′), 7.60 (d, 2 H, $J_{2'',3''}=8.5$, H-2″,6″), 7.39 (d, 1 H, H-5), 7.01 (d, 2 H, H-3″,5″), 4.04 (t, 2 H, $J=6.5$, CH$_2$O), 3.96 (s, 3 H, OCH$_3$), 1.82 (m, 2 H, CH$_2$), 1.47–1.35 (m, 10 H, (CH$_2$)$_5$), 0.92 (t, 3 H, CH$_3$). Elemental analysis: for $C_{31}H_{31}ClO_5S$ (551.11), calculated C 67.56, H 5.67, Cl 6.43; found C 67.43, H 5.45, Cl 6.30%.

2.3.5. (4′-Octyloxy-1,1′-biphenyl-4-yl) 3-chloro-6-octyloxybenzothiophene-2-carboxylate (IVb/8). Cr 88°C smectic C (SmC) 113°C N 189°C I. ^{1}H NMR: 7.89 (d, 1 H, $J=8.8$, H-4), 7.59 (d, 2 H, $J=8.5$, H-3″,5″), 7.51 (d, 2 H, $J=8.5$, H-2′,6′); 7.31 (d, 2 H, H-2″,6″), 7.27 (d, 1 H, $J=2.1$, H-7), 7.14 (dd, 1 H, H-5), 6.97 (d, 2 H, H-3′,5′), 4.03 (t, 2 H, $J=6.4$, CH$_2$O), 4.00 (t, 2 H, $J=6.4$, OCH$_2$), 1.85 (m, 2 H, CH$_2$), 1.81 (m, 2 H, CH$_2$), 1.47–1.30 (m, 20 H, CH$_2$), 0.92 (t, 3 H, CH$_3$), 0.89 (t, 3 H, CH$_3$). Elemental analysis: for $C_{37}H_{45}ClO_4S$ (621.29), calculated C 71.53, H 7.30, Cl 5.71; found C 71.44, H 7.18, Cl 5.66%.

2.3.6. Octyl 4′-(3-chloro-6-octyloxybenzothiophen-2-carbonyloxy)-1,1′-biphenyl-4-carboxylate (IVc/8). Cr 60°C SmA 167°C I. ^{1}H NMR: 8.12 (d, 2 H, $J_{2',3'}=8.2$, H-3′,5′), 7.90 (d, 1 H, $J_{4,5}=8.8$, H-4), 7.69 (d, 2 H, $J_{2'',3''}=8.8$, H-3″,5″), 7.65 (d, 2 H, H-2′,6′), 7.37 (d, 2 H, H-2″,6″); 7.27 (d, 1 H, $J_{5,7}$=2.3, H-7), 7.14 (dd, 1 H, H-5), 4.05 (t, 2 H, *J*=6.4, CH_2O), 4.00 (t, 2 H, *J*=6.4, OCH_2), 1.81 (m, 2 H, CH_2), 1.47–1.30 (m, 20 H, CH_2), 0.92 (t, 3 H, CH_3), 0.89 (t, 3 H, CH_3). Elemental analysis: for $C_{38}H_{45}ClO_5S$ (649.30), calculated C 70.30, H 6.99, Cl 5.46; found C 70.21, H 6.88, Cl 5.29%.

2.3.7. Octyl 4-[4-(3-chloro-6-octyloxybenzothiophen-2-carbonyloxy)benzoyloxy]benzoate (IVd/8). Cr 48°C SmA 183°C I. ^{1}H NMR: 8.30 (d, 2 H, $J_{2'',3''}$=8.8, H-2″,6″), 8.14 (d, 2 H, $J_{2',3'}$=8.8, H-2′,6′), 7.89 (d, 1 H, H-4), 7.47 (d, 2 H, H-3″,5″), 7.32 (d, 2 H, H-3′,5′), 7.27 (d, 1 H, $J_{5,7}$=2.2, H-7), 7,14 (dd, 1 H, H-5), 4.33 (t, 2 H, *J*=6.7, CH_2O), 4.05 (t, 2 H, *J*=6.4, CH_2O), 1.85 (m, 2 H, CH_2), 1.78 (m, 2 H, CH_2), 1.45–1.35 (m, 10 H, $(CH_2)_{10}$), 0.92 (t, 3 H, CH_3), 0.89 (t, 3 H, CH_3). Elemental analysis: for $C_{39}H_{45}ClO_7S$ (693.31), calculated C 67.56, H 6.69, Cl 5.11; found C 67.45, H 6.57, Cl 5.01%.

2.3.8. (4′-Cyano-1,1′-biphenyl-4-yl) 3-chloro-6-octyloxy-benzothiophene-2-carboxylate (V/2). Cr 81°C SmA 224°C I. ^{1}H NMR: 7.67 (d, 2 H, $J_{2',3'}$=8.8, H-2′,6′), 7.73 (d, 2 H, $J_{2'',3''}$=8.8, H-2″,6″), 7.88 (d, 1 H, $J_{4,5}$=8.70, H-4), 7.45 (d, 1 H, $J_{5,7}$=2.2, H-7), 7.36 (d, 2 H, H-3′,5′), 7.36 (d, 2 H, H-3″,5″), 7.13 (d, 1 H, H-5), 4.05 (t, 2 H, *J*=6.4, CH_2O), 1.85 (m, 2 H, CH_2), 1.45–1.35 (m, 10 H, $(CH_2)_5$), 0.92 (t, 3H, CH_3). Elemental analysis: for $C_{34}H_{36}ClNO_3S$ (574.19), calculated C 71.12, H 6.32, Cl 6.17, N 2.44; found C 71.03, H 6.11, Cl 5.98, N 2.35%.

3. Results and discussion

A benzothiophene unit was introduced into the core of a new type of mesogens and its effect on mesomorphic properties was studied in several series. To induce mesogenicity, their molecular structure was extended by one or two benzene units (see scheme 2) connected by a bond or an ester functionality, and possessing a terminal alkyl ether, ester or cyano group, i.e. structural motifs that usually appear in calamitic liquid crystals for which their influence on mesogenicity has been well documented [1]. Most often we have used octyl as a terminal alkyl chain. In series **I**, materials with benzothiophene in a terminal position were prepared. In series **II**, lateral chloro atom in position 3 of benzothiophene was appended. To study the influence of the bend, small methoxy group (series **III**) and longer alkyloxy moieties (series **IV**) were connected at the position 6 of the benzothiophene. Change of the benzene/benzothiophene sequence in the molecular structure of the mesogens led to synthesis of materials **IV/rev**. Finally, the influence of the terminal cyano group on the mesomorphic behaviour is shown in series **V**.

The molecular structure of materials in series **I**–**III** with a terminal aromatic system or with a small polar substituent (methoxy group) represents a system that usually appears in nematogenic materials. The terminal position of the benzothiophene unit should ensure that the molecular geometry remains nearly linear and the mesomorphic properties depend on the shape, size and electronic properties. The results of DSC studies and texture observation are summarized in table 1 for series **I**, **II** and **III**.

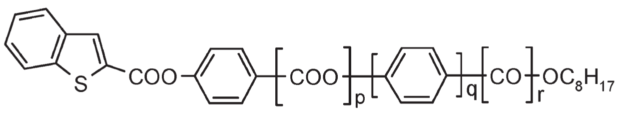
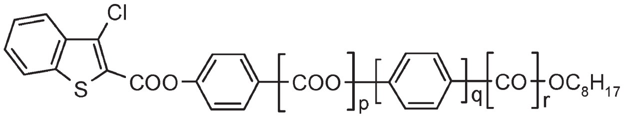
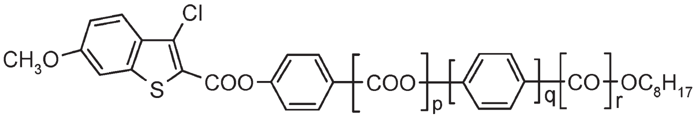
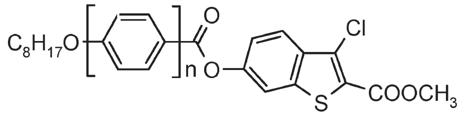
The two-ring compounds **Ia**, **IIa** and **IIIa** did not exhibit mesomorphic behaviour, obviously due to insufficient molecular anisotropy (length-to-breadth ratio). For this reason we did not investigate two-ring systems further. With the exception of **Id**, where the smectic A (SmA) phase was also formed below the nematic one on cooling, all other materials from series **I**–**III** are nematogenic. In figure 3, the phase transition from the nematic to SmA phase is shown for compound **Id**. When comparing two related mesogens found in the literature [31], which have terminal phenyl ring or thiophene ring (see structures in figure 4), with **Ib** compound it is evident that presence of the terminal benzothiophene unit increases the transition temperatures. On the other hand, terminal benzothiophene unit in **Ib** stabilizes the nematic phase in broad temperature interval of 57 K.

Generally, introduction of lateral chloro substituent generates a dipole, which supports intermolecular packing. On the other hand, the greater size of the chlorine atom lowers the liquid crystal phase stability. The results for series **II** show a substantial decrease in transition temperatures; however, the interval of nematic phase is preserved or increased. The little polar methoxy group in the position 6 of the benzothiophene (series **III**) exerts a pronounced effect on the decrease of transition temperatures and further supports the nematogenic behaviour of materials **III**, where the nematic phase appears in temperature interval of almost 120 K. Comparison of materials **IIIb** and **IIId** with the only known benzene analogues [32, 33] (figure 5, the two upper structures) shows that mesomorphic properties of the benzothiophene based materials are identical and comparable.

Figure 6 shows the structure–property relationships for series **I**–**III** in the form of the columnar phase diagram. The decrease of transition temperatures after introduction of lateral chloro atom and methoxy group and significant broadening of the nematic phase are apparent.

In addition, we investigated the effect of the position of the benzothiophene ring and orientation of the ester groups in the molecular structure of the mesogen. For this purpose we also studied two materials, **IIIa/rev** and

Table 1. Phase transition temperatures (°C) and corresponding enthalpies (kJ mol^{-1}, in parentheses) of series **I**, **II** and **III** compounds measured on cooling from the isotropic (I) phase. M.p. is the melting point (in °C), with corresponding enthalpy (kJ mol^{-1}, in parentheses).

Compound	*p*	*q*	*r*	M.p.	Cr		SmA		N		I
											
Ia	0	0	1	92 (+38.1)	•	45 (−34.4)	–		–		•
Ib	0	1	0	165 (+37.6)	•	156 (−37.3)	–		•	213 (−0.95)	•
Ic	0	1	1	132 (+40.6)	•	105 (−37.4)	–		•	190 (−0.40)	•
Id	1	1	1	136 (+34.9)	•	115 (−34.9)	•	157 (−0.78)	•	172 (−0.53)	•
											
IIa	0	0	1	59 (+39.1)	•	36 (−30.8)	–		–		•
IIb	0	1	0	123 (+32.8)	•	114 (−24.0)	–		•	195 (−0.89)	•
IIc	0	1	1	108 (+18.2)	•	86 (−18.1)	–		•	173 (−0.18)	•
IId	1	1	1	89 (+24.3)	•	84 (−21.7)	–		•	145 (−0.26)	•
											
IIIa	0	0	1	80 (+26.7)	•	73 (−22.6)	–		–		•
IIIb	0	1	0	118 (+32.0)	•	93 (−24.8)	–		•	203 (−0.28)	•
IIIc	0	1	1	79 (+29.2)	•	67 (−13.1)	–		•	192 (−0.64)	•
IIId	1	1	1	104 (+28.9)	•	75 (−12.7)	–		•	192 (−0.52)	•
											
IIIa/rev *n*=**1**				104 (+38.3)	•	50 (−25.4)	•		–	108 (−3.6)	•
IIIb/rev *n*=**2**				98 (+41.4)	•	78 (−11.5)	•		–	250 (−6.8)	•

IIIb/rev, where the location of benzothiophene and phenyl rings was reversed (see table 1). Such a change caused preferential formation of the SmA phases: unlike of compound **IIIa**, the two ring system **IIIa/rev** exhibited formation of the SmA phase in the interval of 58 K and the three ring material **IIIb/rev** exhibits a broad temperature interval of the SmA phase instead the N phase appearing in **IIIb**.

To facilitate formation and stabilization of the lamellar arrangement we introduced a longer alkoxy chain in position 6 of the benzothiophene instead of the methoxy group (series **IV**). As a consequence, the bent shaped structure of the benzothiophene unit is more pronounced, which should lead to broadening the molecular structure and decrease in transition temperatures. Mesomorphic properties of series **IV** are

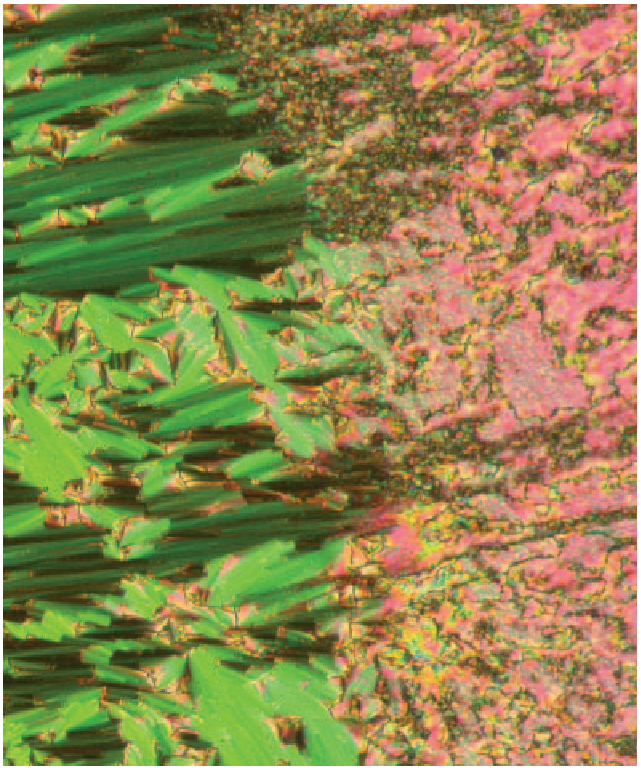


Figure 3. Microphotographs of the planar texture of the phase transition from the nematic phase (right) to the SmA phase (left) for **Id**. The width of the photo is about 300 µm.

summarized in table 2. In materials **IVb** with the biphenylether moiety, the compound with the shortest alkyl substituent (**IVb/6**) exhibits only the nematic phase, materials substituted by longer aliphatic chain C_8H_{17}–$C_{12}H_{21}$ posses broad temperature interval of the nematic and SmC phases.

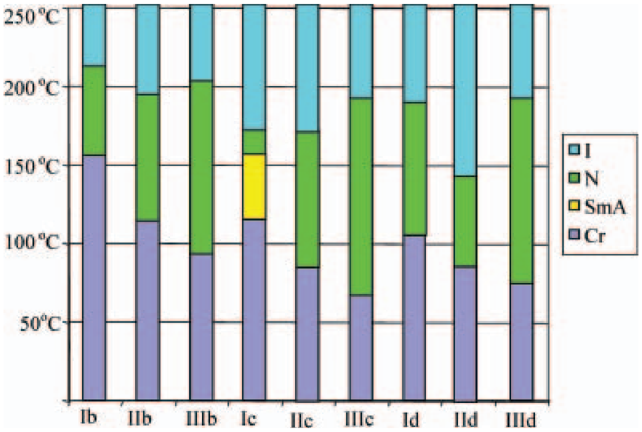
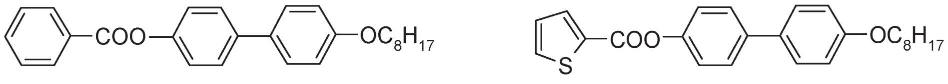


Figure 6. Columnar phase diagram for series **I–III**. The structures of compounds **b–d** are described in scheme 3.

In figure 7 the effect of the alkyl chain length for **IVb** series is demonstrated in a columnar phase diagram. It can be seen that the lengthening of the alkyl chain causes a slight decrease in transition temperatures and substantial broadening of the SmC phase temperature interval at the expense of the nematic phase.

The texture of compound **IVb/8** in the nematic phase under a d.c. electric field of about 5 V µm^{-1} is shown in figure 8. Parallel, electrically stimulated domains aligned along initial orientation of nematic liquid crystal are observed for **IVb** compounds. Similar domains and their behaviour in dependence on field and sample thickness were described in literature (see Hinov and Vistin [34] and references therein). Such a type of domain (Williams' domain) could be ascribed to a strong molecular anisotropy and/or flexoelectric effect.

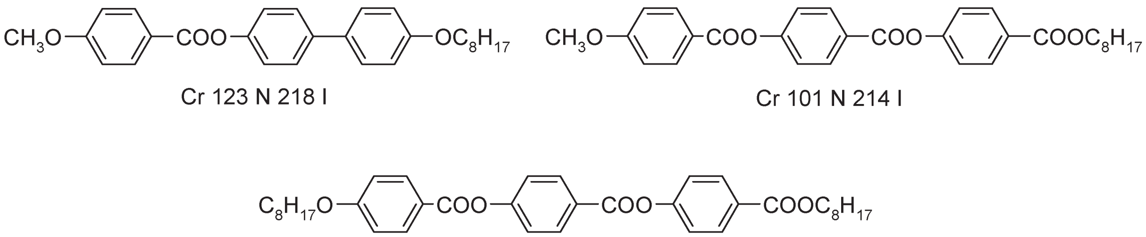
Change of the biphenyl ether for biphenyl ester (materials **IVc**) caused a change of mesomorphic



Cr 113 N 134 Iso

Cr 93 N 117 Iso

Figure 4. Structures and transition temperatures (°C) of related mesogens with terminal phenyl ring or thiophene ring.



Cr 123 N 218 I

Cr 101 N 214 I

Cr 84 N 188 I

Figure 5. Benzene analogues of materials **IIIb** and **IIId**.

Table 2. Phase transition temperatures (°C) and corresponding enthalpies (kJ mol^{-1}, in parentheses) for compounds **IV/n** measured on cooling from the isotropic (I) phase/M.p. is the melting point (in °C), with corresponding enthalpy (kJ mol^{-1}, in parentheses).

Compound/*n*	*p*	*q*	*r*	M.p.	Cr		SmC		SmA		N		I
IVb/6	0	1	0	106 (+32.4)	•	78 (−30.1)	–		–		•	197 (−1.30)	•
IVb/8	0	1	0	99 (+19.6)	•	66 (−27.2)	•	113 (−0.66)	–		•	189 (−1.29)	•
IVb/10	0	1	0	104 (+32.6)	•	65 (−29.5)	•	135 (−0.71)	–		•	184 (−1.04)	•
IVb/12	0	1	0	101 (+34.9)	•	66 (−33.1)	•	147 (−1.0)	–		•	177 (−1.5)	•
IVc/6	0	1	1	103 (+29.5)	•	36 (−24.7)	–		•	165 (−0.19)	•	176 (−0.06)	•
IVc/8	0	1	1	72 (+26.3)	•	60 (−16.5)	–		•	167 (−0.35)	–		•
IVc/10	0	1	1	71 (+58.9)	•	34 (−36.9)	–		•	164 (−5.4)	–		•
IVc/12	0	1	1	78 (+66.8)	•	36 (−48.4)	–		•	162 (−6.0)	–		•
IVd/6	1	1	1	98 (+28.3)	•	52 (−22.2)	–		•	183 (−4.7)	–		•
IVd/8	1	1	1	99 (+32.5)	•	48 (−33.5)	–		•	183 (−5.7)	–		•
IVd/10	1	1	1	76 (+31.8)	•	44 (−26.6)	–		•	178 (−6.7)	–		•
IVd/12	1	1	1	77 (+35.4)	•	43 (−29.3)	–		•	174 (−7.2)	–		•

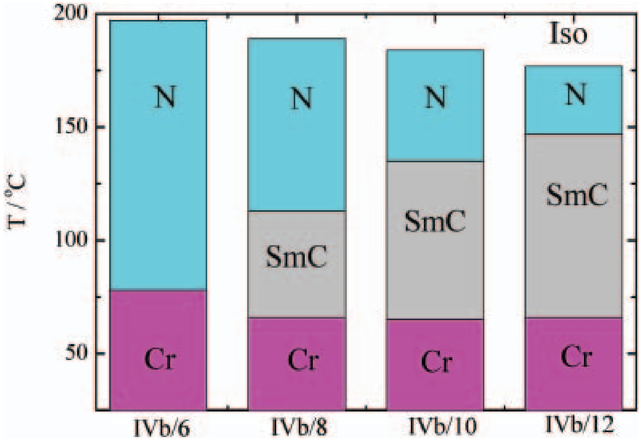


Figure 7. Phase diagram for compounds from series **IVb/n**.

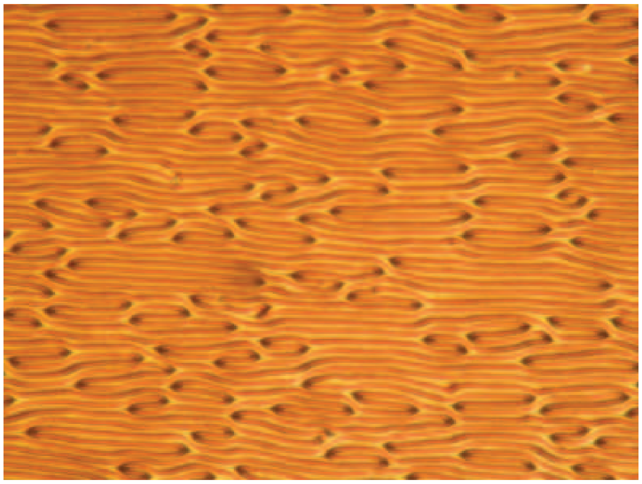


Figure 8. Microphotographs of the planar texture in the nematic phase of compound **IVb/8** under d.c. electric field of about 5 V µm^{-1}. The width of the photo is about 150 µm.

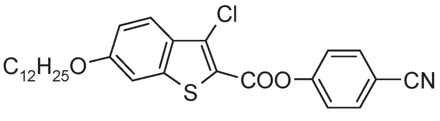
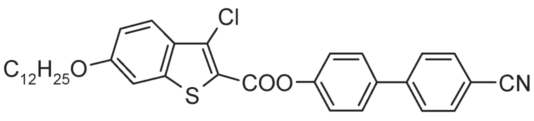
behaviour only the SmA phase appearing in a broad temperature interval over 100 K. Introduction of another ester moiety (materials **IVd**) has no significant effect on the type of the formed mesophase; all the compounds exhibit the SmA phase only. Unlike materials **IVb** the length of the alkyl chain in materials **IVc** and **IVd** has almost no influence on transition temperatures and the width of temperature interval of the formed SmA phase. The mesomorphic behaviour of materials **IVb–IVd** differs from the known benzene substituted related material (figure 5, the bottom structure), which exhibited the nematic phase only [35]. For all the materials of series **IV**, lengthening of the terminal alkyl chain in benzothiophene leads in comparison with the methoxy substituted materials of series **III** to a drop of transition temperatures which may be due to the bend molecular structure.

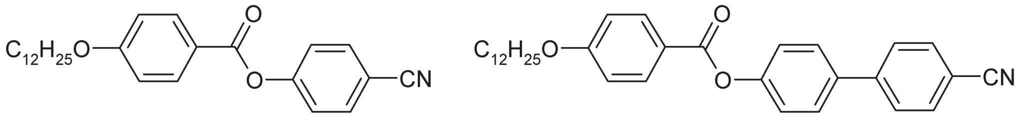
For the terminal cyano-substituted compounds, the most known biphenyl-based materials are nematogenic; lengthening the alkyl chain and the presence of three-ring systems support additional formation of smectic phases [1]. Two model compounds were synthesized possessing the nitrile group connected to the benzene ring and long alkoxy chain ($C_{12}H_{25}$) at the benzothiophene moiety (table 3). Whereas the two-ring material **V/1** exhibited formation of a narrow SmA phase, introduction of the biphenyl unit in **V/2** leads to substantial broadening and stabilization of the SmA phase. Analogous compounds found in the literature [36, 37], which have the phenyl ring instead of the 2,6-disubstituted benzothiophene (see figure 9), exhibit similar mesomorphic properties in comparison with **V/n**, i.e. the occurrence of the SmA phase and comparable transition temperatures.

4. Conclusion

The role of the benzothiophene unit in the molecular core of new liquid crystalline compounds and its effect

Table 3. Phase transition temperatures (°C) and corresponding enthalpies (kJ mol^{-1}, in parentheses) for compounds **V/1** and **V/2** measured on cooling from the isotropic (I) phase. M.p. is the melting point (in °C), with corresponding enthalpy (kJ mol^{-1}, in parentheses).

Compound	M.p.	Cr		SmA		I
 **V/1**	99 (+51.8)	•	82 (−41.3)	•	89 (−1.7)	•
 **V/2**	105 (+46.9)	•	81 (−67.0)	•	224 (−4.0)	•



Cr 72 SmA 90 Iso

Cr 102 SmA 224 Iso

Figure 9. Analogues of 2,6-disubstituted benzothiophenes with phenyl ring.

on mesomorphic properties has been established. Substances with benzothiophene in the terminal position (series **I**–**III**) exhibit almost exclusively nematic phases. Introduction of lateral chloro atom in position 3 leads to a substantial decrease of transition temperatures and subsequent introduction of the 6-methoxy group broadens the interval of mesomorphic behaviour. Exchange of the benzene and benzothiophene sequence leads to appearance of SmA phases. Introduction of a long terminal alkyl chain (series **IV**) causes stabilization of smectic behaviour, decrease of transition temperatures and further extension of the phase temperature range. The increasing number of ester groups markedly supports formation of the SmA phase. Compounds possessing a terminal nitrile unit (**V/n**) form the SmA phase, for **V/2** compound with biphenyl unit in extremely wide temperature range. The study of novel benzothiophene-based mesogens has shown that the 2,6-disubstituted benzothiophene can be successfully applied to design various mesogens.

Acknowledgements

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