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Novel ferroelectric liquid crystals based on fused thieno[3,2-*b*]furan and thieno[3,2-*b*]thiophene cores

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Several series of new benzofused thieno[3,2-*b*]furan- and thieno[3,2-*b*]thiophene-based derivatives have been synthesized and their mesomorphic properties investigated. All the studied compounds exhibit a SmC* phase with very wide temperature interval. Additionally, some types of the compounds show the cholesteric, SmA or blue phase. In the ferroelectric SmC* phase we evaluated physical properties of relevance for possible applications.

1. Introduction

Ferro- and antiferro-electric liquid crystals are the focus of continuing interest due to their potential application in various electronic devices. Their rod-like molecules usually contain a convenient aromatic core, the structure and polarizability of which substantially affect the mesomorphic behaviour of the liquid crystalline materials [1–3]. Among various types of molecular cores, the bent-shaped thiophene ring system has been studied [4–8]. Recently, we have shown [9, 10] that the fused thiophene derivative benzothieno[3,2-*b*]benzothiophene (BTBT, see scheme 1) can be successfully applied to the design of novel antiferroelectric liquid crystals with a very simple molecular structure different from the common structure of ferroelectric materials. However, the presence of such a rigid, large and highly fused core led to relatively high transition temperatures for these materials [9]. At about the same time we introduced a related three-ring heterocyclic system, thienobenzofuran (formula **1** in scheme 1) to the core of novel liquid crystals [11, 12] and synthesised novel mesogenic compounds. Materials possessing a biphenyl unit with the heterocyclic core exhibited among other mesophases the SmC* phase in a very broad temperature range of about 100 K [11]. Further more we utilized other closely related thienobenzothiophene [13] and thienoindole [14] ring systems as new types of monomer for conductive polymers exhibiting luminescence properties. Based on these results we have extended the study and here we summarize the results of synthesis, mesomorphic behaviour and structure–property relationships of structurally related liquid crystals based on 2,6-disubstitued thieno[3,2-*b*]furan (**1**) and thieno[3,2-*b*]benzothiophene (**2**) (scheme 1).

While the linearity of the molecular structure of BTBT derivatives was preserved by the substitution of BTBT in positions 2 and 6 [9], 2,6-disubstitution in non-symmetric heterocyclic cores **1** and **2** leads to the formation of a slightly bent structure of the materials studied (see scheme 1). We calculated the bend angles of **1** and **2** using *ab initio* methods (Gammes program [15], method B3LYP//6-31G(d)) for energy and properties calculation. From the calculations it follows that the deviations from linearity are not sufficiently significant enough to break the rod-like molecular structure of these materials.

2. Chemistry

We previously studied extensively the chemistry of heterocyclic systems **1** and **2** and elaborated methods of synthesis of both the parent compounds and their 2,6-disubstitued derivatives [11, 13, 16]. Therefore, the design of the new materials is based on available methoxy esters **3*I*X** (*X*=O, S) (scheme 2), i.e. compounds possessing two different functionalities which can be selectively transformed to the target materials. The non-chiral chain is joined either by an ether or an ester group. These variations produce four modifications of the molecular structure, one of them (*X*=O and

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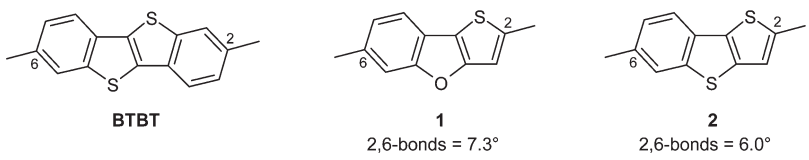
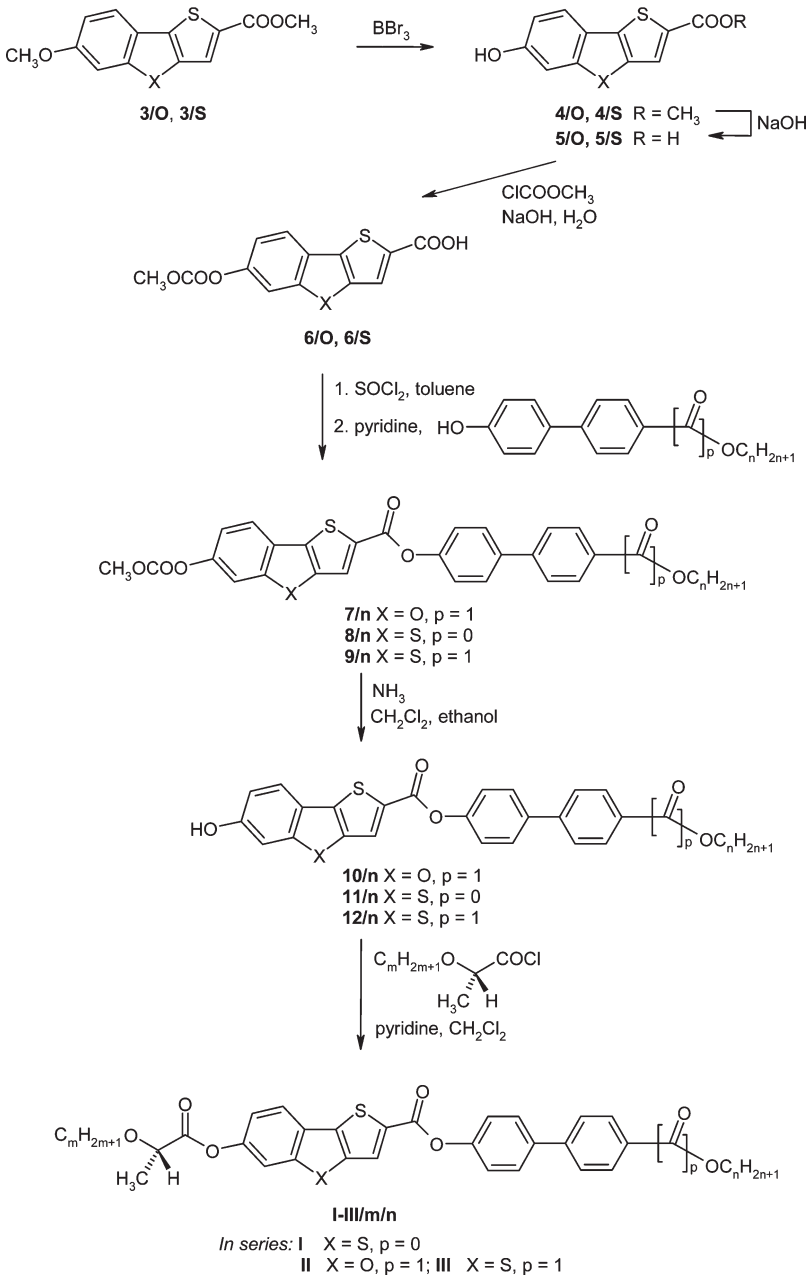


Scheme 1

ether joint group) we studied previously [11]. The other three, series **I**–**III**, are the subject of this study. The general concept for the synthesis of materials of series **I**–**III** is summarized in scheme 2. In all the materials, chirality was introduced through the easily accessible (*S*)-2-alkoxypropionic acids.



Scheme 2

First, the methoxy group in **3/O** and **3/S** was deprotected with BBr_3 to release the hydroxylic group of esters **4/O** and **4/S**, which were next hydrolysed to acids **5/O** and **5/S**. The hydroxylic group of **5/O** and **5/S** was protected with methyl chloroformate to afford the protected acids **6/O** and **6/S**. Acylation of 4-(4-alkoxyphenyl)phenols (series **I**), and alkyl 4′-hydroxy-1,1′-biphenyl-4-carboxylates (series **II** and **III**) with the chlorides of acids **6/O** and **6/S** afforded esters **7/*n*–9/*n*** in good yields. The carbonate protecting group was then removed by means of ammonia and the hydroxylic group of the intermediate hydroxy esters **10/*n*–12/*n*** was acylated with the corresponding (*S*)-2-alkoxypropionyl chloride in the presence of pyridine. The obtained materials of series **I–III/*m*/*n*** were purified by column chromatography and multiple crystallization.

3. Synthesis

Melting points of all intermediates were determined on a Leica VM TG block. Elemental analyses were carried out on a Perkin-Elmer 2400 instrument. IR spectra were recorded on a Nicolet 740 FTIR spectrometer in chloroform sdution or as KBr pellets. NMR spectra were recorded on a Varian Gemini 300 HC (300 MHz) instrument; deuteriochloroform or DMSO-d_6 was used as solvent and signals of the solvents served as internal standards. Because of close structural similarity, only representative procedures and spectral data for a selection of the new compounds are presented.

4-Alkoxy-4′-hydroxybiphenyls were obtained [17] by alkylation of 4,4′-biphenol with the corresponding alkyl iodides (alkyl, yield, m.p. °C: octyl, 31%, 111–130; nonyl, 25%, 114–129; decyl, 22%, 110–130; dodecyl, 25%, 112–129). Intermediate alkyl 4′-hydroxy-1,1′-biphenyl-4-ylcarboxylates were prepared by a TsOH-catalysed azeotropic esterification of 4′-hydroxy-1,1′-biphenyl-4-ylcarboxylic acid [18] (alkyl, yield, m.p. °C: octyl, 94%, 99–101; nonyl, 94%, 99–100; decyl, 95%, 110–111; dodecyl, 94%, 104–105).

(*S*)-2-Alkoxypropionic acids were synthesized by alkylation of (*S*)-ethyl lactate with the corresponding alkyl iodide and subsequent saponification of the intermediate (*S*)-2-alkoxypropionate ester according to [19]: (*S*)-2-(hexyloxy)propionic acid: oil, $[\alpha]_D^{20}$ –13.6° (*c* 1.36, $CHCl_3$); (*S*)-2-(octyloxy)propionic acid: oil, $[\alpha]_D^{20}$ −10.7° (*c* 1.36, $CHCl_3$); (*S*)-2-(decyloxy)propionic acid, oil: $[\alpha]_D^{20}$ −8.35° (*c* 1.44, $CHCl_3$); (*S*)-2-(dodecyloxy)propionic acid: m.p. 37–38 °C, $[\alpha]_D^{20}$ −16.5° (*c* 4.14, $CHCl_3$). The optical purity of these acids, established by HPLC analysis of the corresponding diastereoisomeric *N*-[(*S*)-1-methylbenzyl]amides, was higher than 99% e.e.

3.1. *Methyl 6-hydroxythieno[3,2-b]benzofuran-2-carboxylate (4/O)*

A solution of ester **3/O** [11] (1.5 g, 5.72 mmol) in dry dichloromethane (70 ml) was cooled to −20°C. Boron tribromide was added (12.5 ml of a 1 M solution in dichloromethane, 12.5 mmol) and the mixture was held at −10°C for 8 days, decomposed with cold water and washed with ethyl acetate (2 × 300 ml). The combined organic solutions were washed with brine, dried with anhydrous magnesium sulphate and evaporated. Column chromatography of the residue (silica gel, eluant chloroform and then toluene/methanol/acetic acid 16/1/1 v/v/v) afforded 0.95 g (67%) of **4/O**, m.p. 240–243°C, and 0.32 g (24%) of acid **5/O**. For $C_{12}H_8O_4S$ (248.3) % calculated: 58.06 C, 3.25 H, 12.92 S; % found: 57.85 C, 2.95 H, 12.56 S. IR: 3420 (OH), 3164, 1667 (C=O), 1496, 1136. ^{1}H NMR (DMSO-d_6): 3.85 s, 3 H (OCH_3); 6.88 dd, 1 H, J_1=8.8, J_2=2.2 (H-7); 7.07 d, 1 H, J=2.2 (H-5); 7.79 d, 1 H, J=8.8 (H-8); 8.01 s, 1 H (H-3); 10.10 s, 1 H (OH).

3.2. *Methyl 6-hydroxythieno[3,2-b]benzothiophene-2-carboxylate (4/S)*

Deprotection of **3/S** [13] (1.5 g; 5.39 mmol) with boron tribromide was performed as for **3/O**. 0.95 g (67%) of ester **4/S**, m.p. 265–267°C, and 0.36 g (27%) of acid **5/S** were isolated. For $C_{12}H_8O_3S_2$ (264.3) % calculated: 54.53 C, 3.05 H, 24.26 S; % found 54.88 C, 3.23 H, 23.96 S. IR: 3588 (OH), 3025, 1695 (C=O), 1630, 1384, 1258, 1160, 1125. ^{1}H NMR (DMSO-d_6): 3.95 s, 3 H (OCH_3); 7.03 d, 1 H, J=8.8 (H-7); 7.38 s, 1 H (H-5); 7.78 d, 1 H, J=8.8 (H-8); 8.03 s, 1 H (H-3); 10.03 s, 1 H (OH).

3.3. *6-Hydroxythieno[3,2-b]benzofuran-2-carboxylic acid (5/O)*

Ester **4/O** (3.5 g, 14.1 mmol) was added to a solution of potassium hydroxide (3.7 g, 66.1 mmol) in 50% aqueous ethanol (300 ml) and heated under stirring at reflux for 3 h, cooled and neutralized with diluted hydrochloric acid to pH 3. The precipitate was filtered off, washed with water (50 ml) and dried under reduced pressure. 3.1 g (94%) of **5/O** was obtained, m.p. >360°C. For $C_{11}H_6O_4S$ (234.2) % calculated: 56.41 C, 2.58 H, 13.69 S; % found: 56.36 C, 2.46 H, 13.25 S. IR (KBr): 3416 (OH), 3106, 1660 (C=O), 1438, 1415, 1381, 1120. ^{1}H NMR (DMSO-d_6): 6.85 d, 1 H, J=8.8 (H-7); 7.07 s, 1 H (H-5); 7.69 d, 1 H, J=8.8 (H-8); 7.75 s, 1 H (H-3).

3.4. *6-Hydroxythieno[3,2-b]benzothiophene-2-carboxylic acid (5/S)*

Saponification of ester **4/S** (5.0 g, 18.9 mmol) under the above conditions afforded 4.5 g (95%) of **5/S**, m.p.

>360°C. For $C_{11}H_6O_3S_2$ (250.3) % calculated: 52.79 C, 2.42 H, 25.62 S; % found: 52.54 C, 2.36 H, 25.33 S. IR (KBr): 3395 (OH), 3152, 1690 (C=O), 1625, 1590, 1440, 1415, 1340, 1290, 1180. ^{1}H NMR (DMSO-d_6): 7.08 d, 1 H, J=8.8 (H-7); 7.25 s, 1 H (H-5); 7.78 d, 1 H, J=8.8 (H-8); 8.05 s, 1 H (H-3).

3.5. *6-[(Methoxycarbonyl)oxy]thieno[3,2-b]benzofuran-2-carboxylic acid (6/O)*

To a solution of sodium hydroxide (2.3 g; 57.5 mmol) in water (30 ml), acid **5/O** (4.5 g, 19.2 mmol) was added and the mixture was cooled to 0°C with stirring. Methyl chloroformate (3.0 g; 31.7 mmol) was added dropwise at 0–5°C, stirring was continued for 0.5 h, and the mixture was then acidified with diluted hydrochloric acid to pH 3. The solid was filtered, washed with water (30 ml) and dried. Crystallization from ethyl acetate afforded 4.9 g (87%) of **6/O**, m.p. 259–261°C. For $C_{13}H_8O_6S$ (292.3) % calculated: 53.43 C, 2.76 H, 10.97 S; % found: 52.89 C, 2.74 H, 11.21 S. IR (KBr): 3105, 3000–2400 (COOH), 1763 (C=O), 1250, 1121. ^{1}H NMR (DMSO-d_6): 3.83 s, 3 H (OCH_3); 7.31 d, 1 H, J=8.2 (H-7); 7.80 s, 1 H (H-5); 8.02 s, 1 H (H-3); 8.08 d, 1 H, J=8.2 (H-8).

3.6. *6-[(Methoxycarbonyl)oxy]thieno[3,2-b]benzothiophene-2-carboxylic acid (6/S)*

In the same way as for **6/O**, acid **5/S** (4.80 g, 19.2 mmol) was protected with methyl chloroformate (3.01 g, 31.7 mmol). After crystallization from ethyl acetate, 5.01 g (85%) of **6/S** was obtained, m.p. 264–265°C. For $C_{13}H_8O_5S_2$ (308.3) % calculated: 50.64 C, 2.62 H, 20.80 S; % found: 50.45 C, 2.52 H, 20.44 S. IR: 3426 (OH), 1761 (C=O), 1665, 1442, 1307, 1285, 1209. ^{1}H NMR (DMSO-d_6): 4.35 s, 3 H (OCH_3); 7.38 d, 1 H, J=8.5 (H-7); 8.00 s, 1 H (H-5); 8.03 s, 1 H (H-3); 8.10 d, 1 H, J=8.5 (H-8).

3.7. *4′-Octyloxy-1,1′-biphenyl-4-yl 6-[(methoxycarbonyl)oxy]thieno[3,2-b]benzothiophene-2-carboxylate (8/8)*

Acid **6/S** (1.40 g, 4.55 mmol), thionyl chloride (5.0 g, 42.1 mmol) and toluene (20 ml) were heated at 70–75°C for 2 h under stirring under nitrogen and evaporated to dryness to afford the crude acyl chloride. It was dissolved in toluene (50 ml) and added to a mixture of 4-hydroxy-4′-octyloxybiphenyl (1.79 g, 6.00 mmol), pyridine (0.5 g, 6.3 mmol), and (4-dimethylamino)pyridine (20 mg, 0.16 mmol), then heated at 60°C for 50 h. The mixture was subsequently washed with 5% aqueous hydrochloric acid (10 ml) and chloroform (2 × 250 ml). The combined organic layers were washed with water (300 ml), brine (100 ml) and dried with anhydrous magnesium sulphate. After evaporation, the product was purified by column chromatography (silica gel, eluant chloroform) and crystallized from an ethanol/chloroform mixture (5/1 v/v) to afford 1.58 g (59%) of **8/8**, m.p. 168–170°C. For $C_{33}H_{32}O_6S_2$ (588.75) % calculated: 67.32 C, 5.48 H, 10.89 S; % found: 67.21 C, 5.72 H, 10.58 S. IR: 3026, 2958, 2930, 1765 (C=O), 1708 (C=O), 1389, 1248, 1168. ^{1}H NMR: 0.89 t, 3 H (CH_3); 1.27 m, 8 H, [$(CH_2)_4$]; 1.47 m, 2 H (CH_2); 1.70 m, 2 H (CH_2); 3.97 t, 2 H (OCH_2); 4.01 s, 3 H (OCH_3); 6.98 d, 2 H, J=8.8; 7.23 dd, 1 H, J_1=8.8, J_2=2.2 (H-7); 7.30 d, 2 H, J=8.8; 7.52 d, 1 H (H-5); 7.52 d, 2 H, J=8.8; 7.61 d, 2 H; 7.78 d, 1 H, J=8.8 (H-8); 7.61 d, 2 H; 8.04 s, 1 H (H-3).

The related esters were obtained analogously: **8/9**, yield 56%, m.p. 149–151°C; **8/10**, yield 60%, m.p. 155–157°C; **8/12**, yield 57%, m.p. 162–164°C.

3.8. *4′-(Dodecyloxycarbonyl)-1,1′-biphenyl-4-yl 6-[(methoxycarbonyl)oxy]thieno[3,2-b]benzofuran-2-carboxylate (7/12)*

Acid **6/O** (0.50 g; 1.71 mmol) was transformed to the corresponding acid chloride as above. The crude chloride was dissolved in THF (10 ml) and added to a mixture of dodecyl 4′-hydroxy-1,1′-biphenyl-4-carboxylate (0.57 g, 1.5 mmol), THF (30 ml), pyridine (0.5 g, 6.3 mmol) and (4-dimethylamino)pyridine (20 mg, 0.16 mmol). The mixture was stirred at room temperature for 72 h, washed with 5% aqueous hydrochloric acid (10 ml) and chloroform (2 × 250 ml). The combined organic layers were washed with water (300 ml), brine (100 ml) and dried with anhydrous magnesium sulphate. After evaporation, the product was purified by column chromatography (silica gel, eluant toluene). Yield 0.64 g (65%) of **7/12**, m.p. 255–257°C. For $C_{38}H_{40}O_8S$ (656.8) % calculated: 69.49 C, 6.14 H, 4.88 S; % found: 69.91 C, 6.05 H, 4.82 S. IR: 3022, 2959, 2928, 1765 (C=O), 1716, 1393, 1248, 1166. ^{1} H NMR: 0.95 t, 3 H (CH_3); 1.20–1.90 m, 20 H (CH2); 3.97 s, 3 H (OCH_3); 4.38 t, 2 H (OCH_2); 7.22 d, 1 H, J=8.8 (H-7); 7.38 d, 2 H, J=8.2; 7.52 s, 1 H (H-5); 7.65 d, 2 H, J=8.2; 7.69 d, 2 H; 7.78 d, 1 H, J=8.8 (H-8); 8.05 s, 1 H (H-3); 8.15 d, 2 H.

In the same way, the following esters were obtained: **7/8**, yield 61%, m.p. 230–232°C; **7/9**, yield 62%, m.p. 226–228°C; **7/10**, yield 64%, m.p. 238–240°C. The related compounds **9/*n*** were obtained analogously starting with acid **6/S**: **9/8**, yield 55%, m.p. 238–240°C; **9/9**, yield 52%, m.p. 244–245°C; **9/10**, yield 56%, m.p. 249–251°C; **9/12**, yield 61%, m.p. 257–259°C.

3.9. *Deprotection of esters 7/n-9/n*

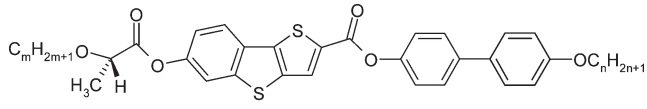
To the solution of ester **7/*n*–9/*n*** (0.4 mmol) in a mixture of ethanol (300 ml) and dichloromethane (50 ml), 23% aq. solution of ammonia (4 ml) was added dropwise and

the mixture was stirred at room temperature until the starting ester disappeared (monitored by thin layer chromatography). The reaction mixture was acidified with diluted hydrochloric acid to pH 3, diluted with water (300 ml) and washed with chloroform (2 × 300 ml). The combined organic layers were washed with brine, dried with anhydrous magnesium sulphate and evaporated. Crystallization form ethanol afforded esters **10/*n*–12/*n***.

3.9.1. 4′-Octyloxy-1,1′-biphenyl-4-yl 6-hydroxythieno [3,2-*b*]benzothiophene-2-carboxylate (11/8). Yield 82%, m.p. 248-259°C. For $C_{31}H_{30}O_4S_2$ (530.7) % calculated: 70.16 C, 5.70 H, 12.08 S; % found: 70.00 C, 5.49 H, 11.95 S. IR (KBr): 3363 (OH), 3010, 2953, 2920, 1726 (C=O), 1704, 1623, 1499, 1396, 1249, 1179. ^{1}H NMR (DMSO-d_6): 0.87 t, 3 H (CH_3); 1.27 m, 8 H, $(CH_2)_4$; 1.41 m, 2 H (CH_2); 1.72 m, 2 H (CH_2); 4.00 t, 2 H (CH_2O); 6.92 d, 1 H, $J_{7,8}$=8.8 (H-7); 7.01 d, 2 H, J=6.0; 7.12 s, 1 H (H-5); 7.35 d, 2 H, J=6.0; 7.61 d, 2 H, J=6.0; 7.69 d, 2 H; 7.85 d, 1 H (H-8); 8.23 s, 1 H (H-3); 10.15 s, 1 H (OH). The homologous compounds **11/*n*** were obtained in the same way: **11/9**, yield 84%, m.p. 241–253°C; **11/10**, yield 86%, m.p. 232–239°C; **11/12**, yield 83%, m.p. 227–236°C.

3.9.2. 4′-(Nonyloxycarbonyl)-1,1′-biphenyl-4-yl 6-hydroxythieno[3,2-*b*]benzofuran-2-carboxylate (10/9). Yield 79%, m.p. 216–218°C. For $C_{32}H_{30}O_6S$ (542.7) % calculated: 70.83 C, 5.57 H, 5.91 S; % found: 70.48 C, 5.42 H, 5.76 S. IR: 3397 (OH), 2956, 2920, 1707 (C=O), 1620, 1470, 1436, 1397, 1327, 1188. ^{1}H NMR:

Table 1. Transition temperatures (°C) detected on cooling at a rate of 5 K min^{-1}, T_{tr}, crystallization temperature, T_{cr}, and corresponding transition enthalpies, ΔH (kJ mol^{-1}), for series **I**. M.p. is melting point.



I/m/n

I/*m*/*n*	M.p. Δ*H*	Cr	T_{cr} Δ*H*	SmC*	T_{tr} Δ*H*	N*	BP	T_{tr} Δ*H*	I
I/6/8	119	•	112	•	203	•	—	210	•
	+23.9		−17.2		−4.9			−4.9	
I/6/9	116	•	111	•	207	•	—	208	•
	+28.4		−27.7		−3.8			−0.9	
I/6/10	120	•	112	•	215	•	—	217	•
	+29.5		−24.5		−4.6			−2.1	
I/6/12	119	•	114	•	210	•	—	211	•
	+31.1		−29.1		−6.1			−1.4	
I/8/8	120	•	114	•	219	•	•	225	•
	+24.6		−23.9		−3.8			−1.5	
I/8/9	114	•	106	•	205	•	•	211	•
	+22.0		−25.4		−0.7			−1.6	
I/8/10	117	•	111	•	208	•	—	210	•
	+21.0		−24.3		−2.7			−2.1	
I/8/12	114	•	110	•	205	—	—	—	•
	+32.5		−30.9		−4.9				
I/10/8	115	•	110	•	217	•	—	218	•
	+30.0		−29.2		−5.3			−0.2	
I/10/9	113	•	106	•	215	—	—		•
	+26.0		−26.1		−1.4				
I/10/10	118	•	115	•	215	—	—		•
	+29.4		−23.3		−4.9				
I/12/8	116	•	111	•	203	—	—		•
	+39.6		−34.2		−3.4				
I/12/9	113	•	106	•	224	•	•	225	•
	+23.2		−27.2		−0.1			−5.5	
I/12/10	126	•	112	•	218	•	•	224	•
	+25.5		−26.9		−0.2			−4.1	
I/12/12	122	•	113	•	211	—	—		•
	+33.0		−29.1		−4.2				
	117	•	114	•	204	—	—		•
	+42.3		−42.8		−6.0				

0.95–1.90 m, 15 H; 4.38 t, 2 H (CH_2O); 6.91 d, 1 H, J=8.8 (H-7); 7.08 s, 1 H (H-5); 7.30 d, 2 H, J=8.8; 7.60 d, 2 H, J=8.2; 7.66 d, 2 H, J=8.2; 7.78 d, 1 H, J=8.8 (H-8), 8.00 s, 1 H (H-3); 8.18 d, 2 H, J=8.2.

In the same way the homologous derivatives **10/*n*** and the related **12/*n*** were obtained: **10/8**, yield 86%, m.p. 205–207°C; **10/10**, yield 92%, m.p. 219–221°C; **10/12**, yield 91%, m.p. 231–233°C; **12/8**, yield 85%, m.p. 218–221°C; **12/9**, yield 88%, m.p. 225–227°C; **12/10**, yield 85%, m.p. 233–235°C; **12/12**, yield 85%, m.p. 238–240°C.

3.10. *General procedure for synthesis of series I–III*

To a solution of the corresponding (*S*)-2-alkoxypropionic acid (2.5 mmol) in toluene (5 ml), oxalyl chloride (0.65 g, 5.1 mmol) was added with stirring under nitrogen. The mixture was heated to 50°C for 1 h and evaporated to dryness. The crude acyl chloride was dissolved in dry dichloromethane (2 ml) and added dropwise to a solution of ester **10/*n*–12/*n*** (1 mmol) and pyridine (0.5 g, 6.33 mmol) in dry dichloromethane (5 ml). The mixture was stirred at room temperature for 3 h, poured into 1% aqueous hydrochloric acid (70 ml) and washed with dichloromethane (2 × 50 ml). The organic solution was washed with water (50 ml) and dried with anhydrous magnesium sulphate. The crude product after evaporation was purified by column chromatography (silica gel, elution with chloroform) and crystallized to afford the corresponding target compounds **I/*m*/*n*–III/*m*/*n*** (yield 80–97%).

3.10.1. 4′-Octyloxy-1,1′-biphenyl-4-yl 6-{[(S)-2-(hexyloxy) propionyl]oxy}thieno[3,2-*b*]benzothiophene-2-carboxylate (I/6/8). Yield 94%. For $C_{40}H_{46}O_6S_2$ (686.94) % calculated: 69.94 C, 6.75 H, 9.34 S; % found: 69.81 C, 6.58 H, 9.19 S. IR: 3027, 3013, 2957, 2931, 2859, 1769 (C=O), 1721 (C=O), 1384, 1167, 1137, 1120. ^{1}H NMR: 0.90 t, 6 H (CH_3); 1.32 m, 20 H (CH_2); 1.60 d, 3 H (CH_3); 1.66 m, 2 H (CH_2); 1.81 m, 2 H (CH_2); 3.52 and 3.72 dq, 2 H (CH_2O); 4.01 t, 2 H (CH_2O); 4.24 q, 1 H (CH); 6.98 d, 2 H, J=8.8; 7.15 dd, 1 H, $J_{7,8}$=8.8, $J_{5,7}$=2.2 (H-7); 7.31 d, 2 H; 7.45 d, 1 H (H-5); 7.52 d, 2 H; 7.61 d, 2 H; 7.78 d, 1 H (H-8); 8.03 s, 1 H (H-3).

3.10.2. 4′-(Octyloxycarbonyl)-1,1′-biphenyl-4-yl 6-{[(*S*)-2-(dodecyloxy)propionyl]oxy}thieno[3,2-*b*]benzofuran-2-carboxylate (II/12/8). Yield 87%. For $C_{47}H_{58}O_8S$ (783.05) % calculated: 72.09 C, 7.47 H, 4.09 S; % found 71.89 C, 7.26 H, 3.86 S. IR: 2957, 2928, 1769 (C=O), 1716 (C=O), 1465, 1392, 1262, 1156, 1116. ^{1}H NMR: 0.95–1.90 m, 41 H; 4.22 t, 2 H (CH_2O); 4.38 t, 2 H (CH_2O); 7.18 d, 1 H, J=8.8 (H-7); 7.38 d, 2 H, J=8.2; 7.45 s, 1 H (H-5); 7.64 d, 2 H, J=8.2; 7.69 d, 2 H, J=8.2; 7.80 d, 1 H, J=8.8 (H-8); 8.03 s, 1 H (H-3); 8.18 d, 2 H, J=8.2.

3.10.3. 4′-(Octyloxycarbonyl)-1,1′-biphenyl-4-yl 6-{[(*S*)-2-(dodecyloxy)propionyl]oxy}thieno[3,2-*b*]benzothiophene-2-carboxylate (III/12/8). Yield 85%. For $C_{47}H_{58}O_7S_2$ (799.11) % calculated: 70.64 C, 7.32 H, 8.02 S; % found 70.49 C, 7.26 H, 7.89 S. IR: 2958, 2928, 1768 (C=O), 1715 (C=O), 1465, 1392, 1262, 1156, 1116. ^{1}H NMR: 0.95–1.90 m, 41 H; 4.22 t, 2 H (CH_2O); 4.38 t, 2 H (CH_2O); 7.18 d, 1 H, J=8.8 (H-7); 7.38 d, 2 H, J=8.2; 7.48 d, 1 H (H-5); 7.64 d, 2 H, J=8.2; 7.69 d, 2 H, J=8.2; 7.83 d, 1 H, J=8.8 (H-8); 8.11 s, 1 H (H-3); 8.18 d, 2 H, J=8.2.

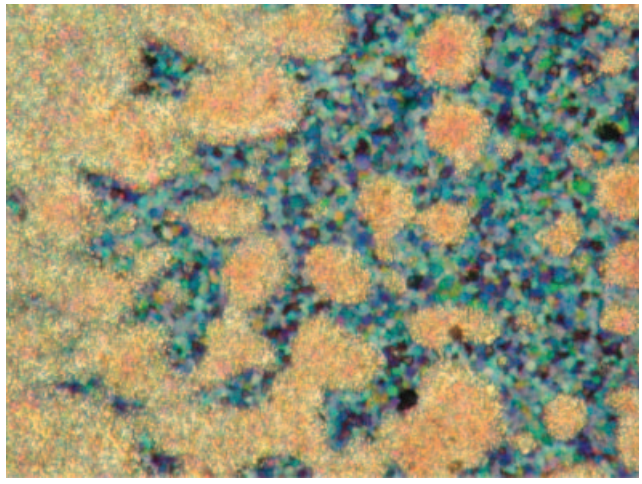


Figure 1. Planar sample textures of **I8/8** at the transition from the blue phase to the cholesteric phase at T=225°C. The width of microphotographs is about 250 μm.

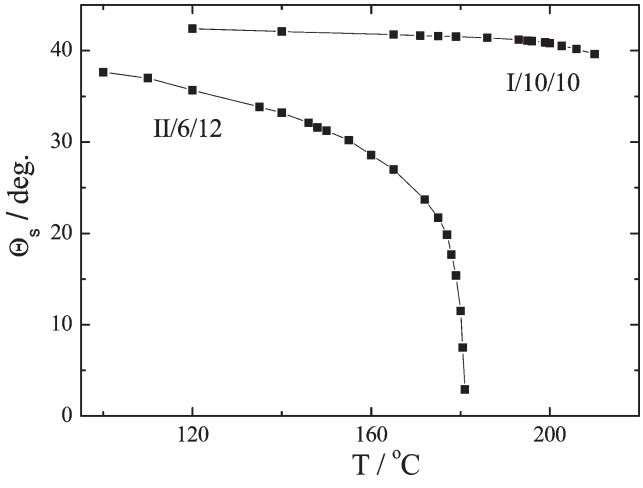


Figure 2. Temperature dependence of the spontaneous tilt angle, Θ_s, for two selected compounds: (*a*) **I/10/10**, (*b*) **II/6/12**.

4. Characterization

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

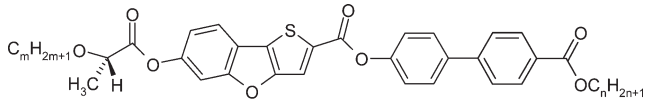
The texture observation, dielectric measurements and measurements of spontaneous polarization were carried out on planar samples 6 or 25 μm thick, the area $5 \times 5\,mm^2$. The glasses were provided with transparent ITO electrodes and polyimide layers unidirectionally rubbed, which ensured the bookshelf (planar) geometry. The cells were filled in the isotropic phase. The temperature was varied and stabilized with an accuracy of $\pm 0.1^{\circ}C$ in the hot stage (Linkam) placed on the table of the polarizing microscope.

Spontaneous polarisation, $\mathbf{P}_S$, was determined from hysteresis loops detected during switching at a frequency of 60 Hz and an electric field of about $40\,kV\,cm^{-1}$. Spontaneous tilt angle, Θ_S, was determined on unwinding the helicoidal structure in a d.c. electric field of $10\,V\,cm^{-1}$, by measuring the angular difference between extinction positions of opposite unwound structures.

5. Results and discussion

The phase transition temperatures and enthalpies were determined from DSC studies. The mesophases were identified from texture observation using polarizing microscopy. Results obtained for series **I**, with heterocyclic core **2** substituted by a sulphur atom (see scheme 1), are presented in table 1. All the compounds

Table 2. Transition temperatures, T_{tr} (°C), and corresponding transition enthalpies, ΔH ($kJ\,mol^{-1}$) evaluated from DSC on cooling at a rate of $5\,K\,min^{-1}$ for series **II**. M.p. is melting point.



II/m/n

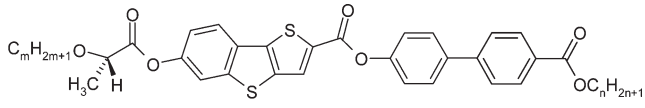
II/*m*/*n*	M.p. Δ*H*	Cr	T_{cr} Δ*H*	SmC*	T_{tr} Δ*H*	SmA	T_{tr} Δ*H*	I
II/6/8	96	•	91	•	197	—		•
	+23.9		−20.5		−0.1			
II/6/9	97	•	89	•	194	—		•
	+22.9		−21.5		−0.2			
II/6/10	92	•	84	•	187	—		•
	+26.1		−27.1		−0.3			
II/6/12	77	•	66	•	180	•	186	•
	+37.9		−42.2		−0.1		−0.1	
II/8/8	94	•	87	•	198	—		•
	+26.0		−25.6		−0.4			
II/8/9	101	•	93	•	196	—		•
	+23.9		−26.0		−0.2			
II/8/10	96	•	83	•	195	—		•
	+24.3		−23.0		−0.2			
II/8/12	111	•	106	•	182	•	197	•
	+28.8		−31.1		−0.2		−0.2	
II/10/8	122	•	112	•	210			•
	+30.4		−26.7		−1.6			
II/10/9	119	•	111	•	208	—		•
	+36.5		−30.1		−0.9			
II/10/10	119	•	113	•	208	—		•
	+38.4		−31.9		−1.1			
II/10/12	112	•	111	•	204	•	206	•
	+32.5		−28.6		−0.5		−0.1	
II/12/8	118	•	110	•	215	—		•
	+33.0		−31.5		−0.6			
II/12/9	121	•	114	•	210	•	213	•
	+33.0		−31.3		−0.3		−4.2	
II/12/10	121	•	116	•	211	•	212	•
	+33.0		−31.6		−0.2		−3.8	
II/12/12	122	•	113	•	209	•	210	•
	+35.3		−32.2		−0.2		−5.4	

show a broad temperature interval for the ferroelectric phase. Materials with one shorter alkyl chain **I/6/8**–**I/8/10** and **I/10/8**, **I/12/8** and **I/12/9** exhibited also a narrow cholesteric phase (1–7 K). Moreover, the blue phase (temperature interval up to 1 K) between the isotropic and cholesteric phase was observed for **I/8/8**, **I/8/9**, **I/12/8** and **I/12/9**. Sometimes the coexistence of BP and the N* phase has been observed in temperature interval of 0.2 K (see figure 1). In thin samples (less than 2 μm) of **I/6/8**, **I/6/10**, **I/6/12**, **I/8/9** and **I/8/10** the N* phase is preserved until crystallization. In these cases the SmC* phase could be induced by the application of an electric field. For such a compound in several cases after switching off the field the SmC* phase vanished and the N* phase reappeared. This effect could be connected with low stability of the ferroelectric phase.

The spontaneous tilt angle, Θ_s, and spontaneous polarization, $\mathbf{P}_s$, were measured in the ferroelectric SmC* phase. The temperature dependence of Θ_s for compound **I/10/10** is shown in figure 2. The Θ_s value remains almost constant over the whole temperature interval of the SmC* phase, which is a typical feature of the first order phase transition from the cholesteric to the SmC* phase. For all compounds from series **I**, Θ_s ranges between 40° and 42°. $\mathbf{P}_s$ exhibits a slight increase on cooling, reaching 50–80 nC cm^{-2} at T_c-50 K, where T_c is the phase transition temperature to the ferroelectric phase.

The mesomorphic behaviour of the thienobenzothiophene series **I** shows no substantial differences when compared with that of the structurally related thienobenzofuran-based materials [11]. The phase sequences

Table 3. Transition temperatures, T_{tr} (°C), and corresponding transition enthalpies, ΔH (kJ mol^{-1}), evaluated from DSC on cooling at a rate of 5 K min^{-1} for the series **III**. M.p. is melting point.



III/m/n

III/*m*/*n*	M.p. Δ*H*	Cr	T_{cr} Δ*H*	SmC*	T_{tr} Δ*H*	SmA	T_{tr} Δ*H*	I
III/6/6	90	•	87	•	205	—		•
	+20.7		−23.6		−2.7			
III/6/8	118	•	110	•	202	—		•
	+20.7		−22.1		−0.2			
III/6/10	95	•	82	•	192	•	204	•
	+28.2		−29.6		−0.1		−0.8	
III/6/12	121	•	115	•	210	•	212	•
	+29.3		−35.4		−0.1		−0.7	
III/8/6	122	•	116	•	211	—		•
	+25.0		−27.9		−1.0			
III/8/8	117	•	112	•	209	—		•
	+10.9		−11.5		−0.4			
III/8/10	123	•	115	•	204	•	207	•
	+24.1		−28.2		−0.2		−0.5	
III/8/12	114	•	107	•	204	•	206	•
	+20.5		−25.0		−0.2		−2.2	
III/10/6	91	•	86	•	209	—		•
	+26.9		−25.7		−2.9			
III/10/8	123	•	119	•	208	—		•
	+22.4		−37.7		−0.2			
III/10/10	96	•	90	•	200	•	203	•
	+17.3		−25.3		−0.3		−4.0	
III/10/12	91	•	84	•	190	•	201	•
	+29.9		−28.2		−0.3		−1.2	
III/12/6	93	•	87	•	172	•	199	•
	+37.7		−36.7		−0.7		−1.5	
III/12/8	90	•	83	•	173	•	189	•
	+29.1		−27.9		−0.2		−1.2	
III/12/10	99	•	84	•	184	•	200	•
	+24.7		−30.1		−0.3		−1.5	
III/12/12	88	•	86	•	175	•	199	•
	+33.5		−38.1		−0.1		−0.8	

of the studied compounds from series **I** are similar to the mesomorphic properties already reported [11]. In both cases a very wide SmC* phase occurs for all the studied homologues, and the cholesteric phase (which may be accompanied by the blue phase) appears for compounds with shorter aliphatic chains. On the other hand in series **I** the transition temperatures do not correlate with the length of the terminal alkyl chains, while in the thienobenzofuran-based materials the temperatures slightly decrease with elongation of terminal chains.

Although in all materials from series **I** the required broad ferroelectric phase was found, the clearing temperatures are relatively high. With the aim of lowering the transition temperatures we decided to introduce the ester group instead of the ether group to the biphenyl moiety. Application of the esters of 4-hydroxy-1,1′-biphenyl-4-ylcarboxylic acids (scheme 2) then led to the synthesis of two new series: **II** (X=O, see scheme 2) and **III** (X=S).

Results obtained for series **II** and **III** are summarized in tables 2 and 3 respectively. In series **II** and **III**, a broad temperature interval for the ferroelectric SmC* phase also occurs for all the studied materials. No cholesteric phase is seen, even for the shortest chain homologues. In addition, materials of series **II** and **III** with sufficiently long non-chiral alkyl chains (n=10, and n=12 respectively) exhibit also the SmA phase regardless of the length of the chiral chain. For shorter non-chiral alkyl chains the SmA phase exists only for the chiral chain with m=12.

The temperature dependences of the spontaneous polarization was measured for all the compounds studied and the results are shown in figures 3 (*a*) and 3 (*b*) for selected compounds of series **II** and **III**, respectively. The results show that lengthening both terminal chains produces an increase in the $\mathbf{P}_S$ values. This effect is more pronounced for the non-chiral alkyl chain C_nH_{2n+1} up to n=10 (for n=12 sometimes saturation takes place). While in series **II** (X=O) the **P**s values change from 50 to 95 nC cm^{-2}, in series **III** (X=S) they increase from 100 to 190 nC cm^{-2} (measured at temperatures approximately 100 degrees below the SmA (I)–SmC* phase transition). For compound **II/6/12** the temperature dependence of the tilt angle is presented in figure 2. Its profile corresponds to typical second order phase transition. The saturated values of Θ_s are typically 30°–40°.

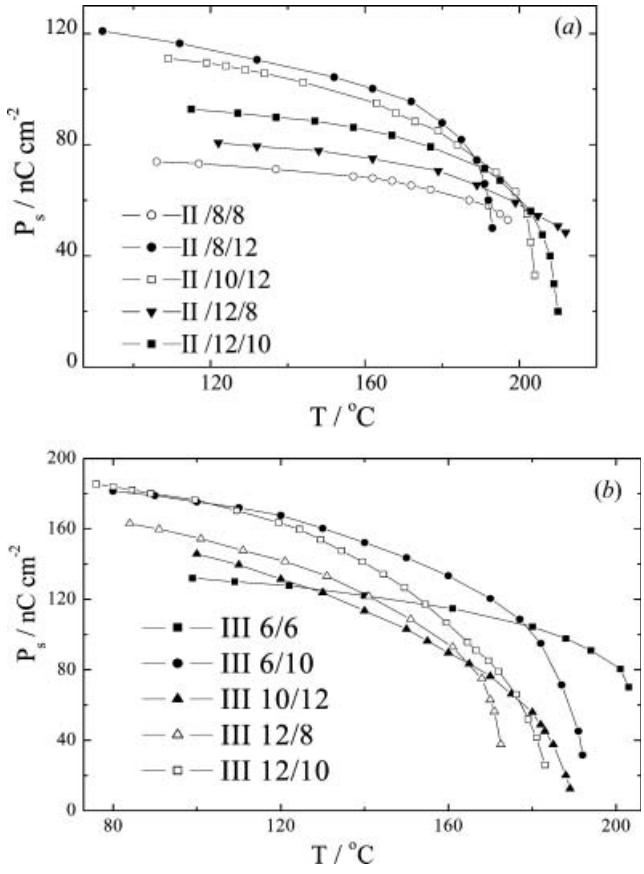


Figure 3. Temperature dependence of spontaneous polarization, $\mathbf{P}_S$, for selected compounds from (*a*) series **II**, (*b*) series **III**.

6. Conclusions

Three series of substances containing new types of fused heterocyclic cores were synthesized and their mesomorphic properties studied. In series with the ether linkage at the non-chiral chain, the replacement of the oxygen heteroatom by sulur in the core does not significantly influence the phase transition temperatures or the temperature interval of the ferroelectric phase (cf. table 1 for series **I** and related data in [11]). The same result is obtained when comparing series **II** and **III** having the ester linkage. On the other hand, the exchange of the ether and ester linkage has a strong effect. The cholesteric phase, which occurs in some homologues of series **I**, disappears with the ester linkage in series **II** and **III**, in which, by contrast, the SmA phase may appear. However, due to the higher polarizability of sulphur in comparison with oxygen we found substantially higher spontaneous polarization values for series **III**. The introduction of the ester moiety leads to a drop of transition temperatures by around. 10 K (cf. compounds in [11] with series **II**, and **I** with **III**).

If we compare the results obtained for series **II** and **III** with the very few known examples of related compounds [20–22] with similar molecular structure, where the heterocyclic system (see **1** and **2** in scheme 1) is replaced by a benzene ring, it is clear that the fused

heterocycles substantially enhance the width of the SmC* phase and stabilizes the mesomorphic behaviour of these materials. Thus, in conclusion, both thienobenzofuran and thienobenzothiophene heterocyclic systems may be successfully utilized in the design of novel ferroelectric liquid crystals.

Acknowledgements

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