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Novel liquid crystals based on [1]benzothieno[3,2-*b*][1]benzothiophene

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Four series of new [1]benzothieno[3,2-*b*][1]benzothiophene derivatives have been synthesized. In the non-chiral series a SmA phase occurs, while the chiral series exhibits a rather wide antiferroelectric SmC$^*_A$ phase just below the SmA phase. The SmA–SmC$^*_A$ phase transition has been studied using DSC and dielectric spectroscopy. In the SmC$^*_A$ phase the spontaneous quantities have been measured. The tilt angle shows a typical temperature dependence and the values of spontaneous polarization are rather moderate. The length of the helical pitch increases on increasing the length of the non-chiral alkyl chain.

1. Introduction

The majority of liquid crystals contain a rigid 1,4-substituted phenylene-based moiety as the mesogenic group in their core [1]. When this moiety is replaced with a five-membered heterocyclic system, for example thiophene, the geometry of the mesogen is changed, and this has a pronounced influence on mesomorphic phase formation. The sulphur atom also changes the polarity of the local bonds and the polarizability of the mesogenic group. Thus, the convenient combination of one or more phenylene and/or thiophene units connected by polar functional groups and spacers has led to the design of various nematogens [2–5] and smectogens exhibiting ferro-, ferri- and antiferro-electric phases [6–10]. Liquid crystalline bi- [11, 12], ter- [3, 7, 13], oligo- and polythiophenes [8, 9, 14, 15] have also been studied and have found application in the design of new photonic, and conductive polymers and in molecular devices. Fused thiophene-based cores, for example, benzothiophene [16] and thienothiophene [17], have also been incorporated in liquid crystalline molecules, although, high transition temperatures and a destabilization of mesomorphic properties were observed. On the other hand, we have found [18, 19] that even higher fused heterocycles can be successfully used in the design of new ferroelectric materials. Recently [20] it was shown that simple esters of [1]benzothieno[3,2-*b*][1]benzothiophene-2,7-dicarboxylic acid, a tetracyclic fused system, exhibit liquid crystalline properties. Long chain saturated and unsaturated esters were further studied [21] and it was found that due to the relatively large, flat and fully aromatic system having a high polarizability, the liquid crystalline phases exhibit interesting charge transport properties. These properties were attributed to the π-stacking of the aromatic cores which supports a lamello–columnar ordering. The term 'sanidics' was suggested for such mesogens instead of the more usual 'calamitics'.

Our interest in the chemistry of fused heterocyclic compounds [22–25] and their application in materials chemistry [26, 27] led us to develop methods for the introduction of alkyl and acyl groups into the [1]benzothieno[3,2-*b*][1]benzothiophene (**1**) core, see scheme 1 [28]. These methods enabled us to synthesize series of derivatives of heterocycle **1** with long acyl and alkyl chains attached in positions 2 and 7, i.e. along the long axis of the molecule. To continue our search for new liquid crystalline molecules, here we report the syntheses and physical studies of achiral and chiral derivatives of heterocycle **1** with the aim to broaden our knowledge of materials based on such a single ring system.

2. Experimental

2.1. *Characterization*

The melting points of crystalline intermediates were determined using a Leica VM TG block. Elemental analyses were carried out on a Perkin-Elmer 2400. IR

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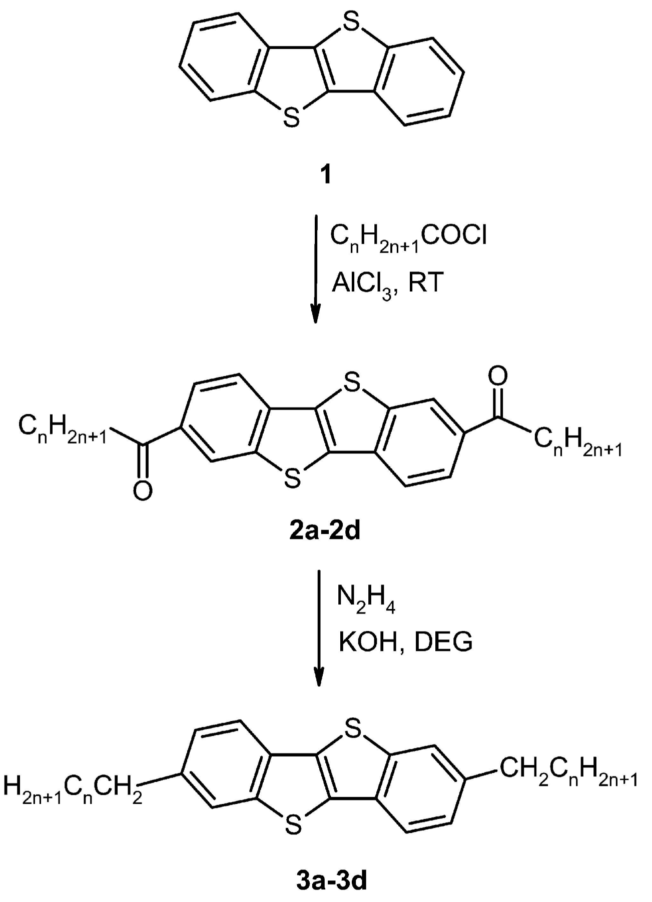


Scheme 1. Preparation of the achiral series **2** and **3**. **2**: **a**: $n = 5$; **b**: $n = 7$; **c**: $n = 9$; **d**: $n = 11$ **3**: **a**: $n = 6$; **b**: $n = 8$; **c**: $n = 10$; **d**: $n = 12$.

spectra were recorded on a Nicolet 740 FTIR spectrometer in chloroform, or as KBr disks. NMR spectra were measured on a Varian Gemini 300 HC (300 MHz for ^{1}H). Deuteriochloroform was used as the solvent and the solvent signal served as an internal standard.

All the final products were studied using DSC (Perkin–Elmer Pyris Diamond); cooling and heating rates of 5 K min^{-1} were used. The samples were placed in a nitrogen atmosphere and hermetically closed in aluminium pans; sample mass was 5–8 mg.

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

The complex permittivity ε^* was measured using a Schlumberger 1260 impedance analyser in the frequency range 100 Hz–1 MHz. The length of the helical pitch p was measured from the diffraction of He-Ne laser light on dechiralization lines.

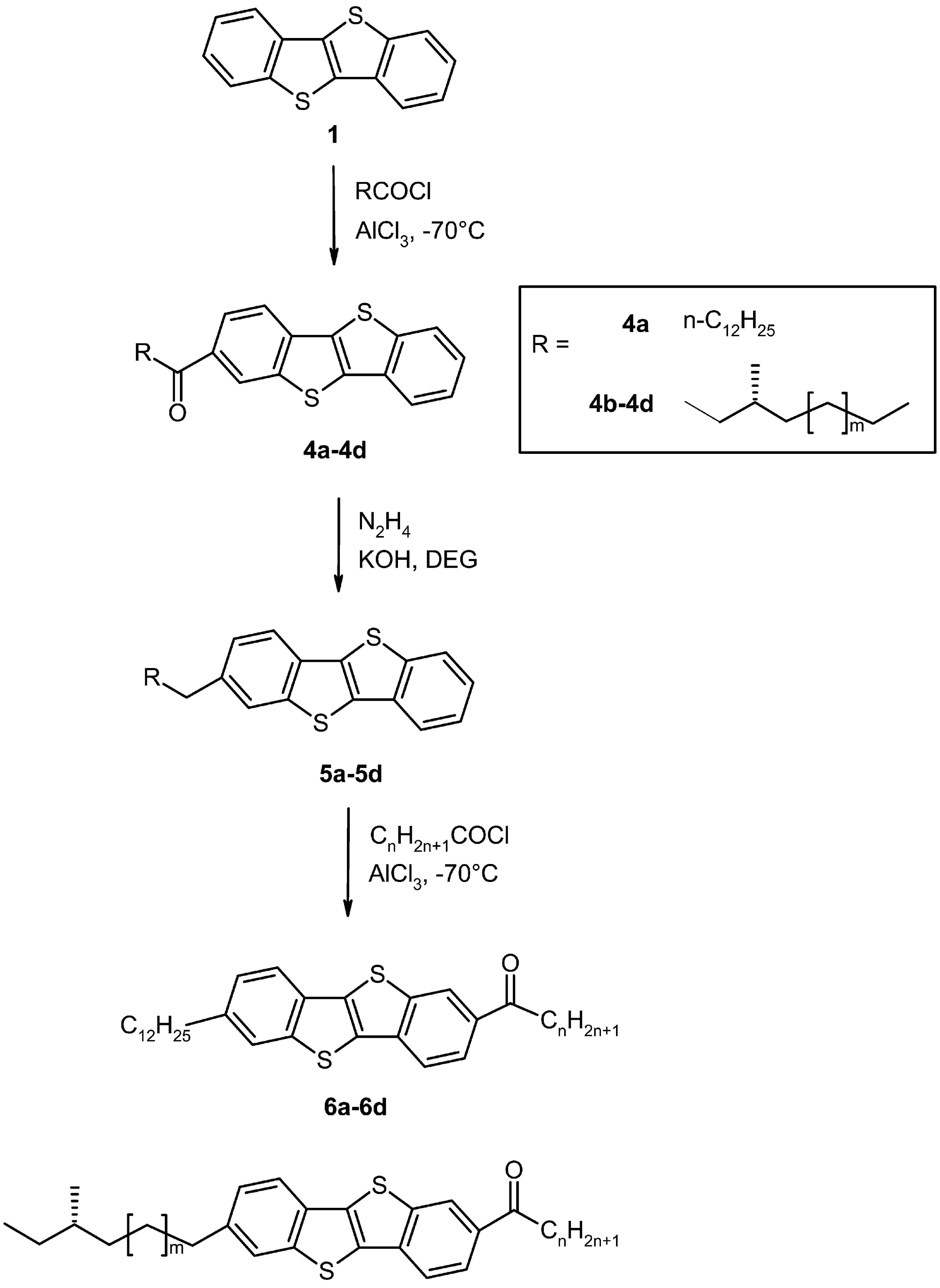
The spontaneous polarization $\mathbf{P}_S$ was determined from the hysteresis loops detected during switching at a frequency of 60 Hz and an electric field 40 V μm^{-1}. The frequency is sufficiently high that direct switching between two saturated ferroelectric states occurs without restoring the antiferroelectric state at the zero electric field. In such a case the single hysteresis loop is observed [29]. Spontaneous tilt angle θ_S was determined on unwinding the helicoidal structure by a square wave field of 10 V μm^{-1}, 0.1 Hz, by measuring the angular difference between the extinction positions of opposite unwound structures.

2.2. *Synthesis*

An effective method [28] for the selective introduction of acyl and alkyl chains in positions 2 and 7 of heterocycle **1** is based on Friedel–Crafts acylation. This method can be used to introduce either one or two chains, depending on the reaction conditions. Diacylation of **1** at room temperature afforded diketones **2a**–**2d** in moderate yields (scheme 1). Reduction of diketones **2a**–**2d** with hydrazine hydrate under Huang–Minlon conditions was found to be successful, giving the dialkyl derivatives **3a**–**3d** in high yield. In contrast, monoacylation using several long chain achiral and chiral acyl chlorides occurred at low temperature, giving the corresponding monoketones **4a**–**4d** (scheme 2). Their subsequent reduction gave rise to alkyl derivatives **5a**–**5d**. Acylation of the 2-alkyl derivatives **5a**–**5d** proceeded selectively and the corresponding 7-alkyl-2-acyl derivatives **6a**–**6d** and **7a**–**7g** were obtained. Thus, four new series of 2,7-disubstituted [1]benzothieno[3,2-*b*][1]benzothiophenes were synthesised.

2.2.1. *1,1′-([1]Benzothieno[3,2-b][1]benzothiophene-2,7-diyl)bisdodecanone (**2d**)*

To a stirred solution of **1** (500 mg; 2.08 mmol) in dry dichloromethane (50 ml), aluminium chloride (1.5 g, 11.25 mmol) was added at $-10°\mathrm{C}$. The solution was cooled to $-70°\mathrm{C}$ and dodecanoyl chloride (2.5 ml, 10.48 mmol) was added dropwise. After 1 h, the temperature was allowed to rise to room temperature and stirring was continued for 48 h. The reaction mixture was then diluted with water (10 ml); the deposited solid was filtered off and washed with methanol (2×10 ml). Crystallization from toluene afforded 579 mg (46%) of pure product **2d**. For $C_{38}H_{52}O_2S_2$ (604.96) calculated: C 75.45%, H 8.66%, S 10.60%; found: C 75.40%, H 8.55%, S 10.53%. ^{1}H NMR: 8.58 d, 2 H, $J(1,3) = 1.1$ (H-1); 8.09 dd, 2 H, $J(1,3) = 1.1$, $J(3,4) = 8.2$ (H-3); 7.99 d, 2 H, $J(3,4) = 8.2$ (H-4); 3.08 t, 4 H, $J = 7.1$ (CH_2);



Scheme 2. Preparation of the achiral series **6** and chiral series **7**. **6**: **a**: $n = 5$; **b**: $n = 7$; **c**: $n = 9$; **d**: $n = 11$ **7**: **a**: $m = 1$, $n = 5$; **b**: $m = 1$, $n = 6$; **c**: $m = 1$, $n = 7$; **d**: $m = 1$, $n = 8$; **e**: $m = 1$, $n = 9$; **f**: $m = 1$, $n = 10$; **g**: $m = 1$, $n = 11$; **h**: $m = 3$, $n = 5$; **i**: $m = 3$, $n = 7$; **j**: $m = 3$, $n = 9$; **k**: $m = 5$, $n = 5$; **l**: $m = 5$, $n = 7$; **m**: $m = 5$, $n = 9$.

1.80 m, 4 H ($\mathrm{CH_2}$); 1.19–1.45 m, 32 H; 0.89 t, 6 H ($\mathrm{CH_3}$). IR: 2 959 m (C–H), 2 915 s (C–H), 2 848 s (C–H), 1 682 s (C=O).

Compounds **2a**–**2c** were prepared by analogous methods.

2.2.2. *2,7-Didodecyl[1]benzothieno[3,2-b][1]benzothiophene (**3d**)*

To a stirred suspension of **2d** (280 mg, 0.46 mmol) in diethylene glycol (15 ml), potassium hydroxide (100 mg, 1.78 mmol) and hydrazine hydrate (0.5 ml of 80% aq. solution, 8.23 mmol) were added successively. The reaction mixture was then heated to 120°C for 1 h and to 220–230°C for another 5 h; it was cooled to room temperature and the resulting precipitate filtered off and washed with methanol (2 × 15 ml). After purification by column chromatography (silica gel, eluent hexane) product **3d** was obtained in a yield of 239 mg (90%). For $\mathrm{C_{38}H_{56}S_2}$ (577.0) calculated: C 79.10%, H 9.78%, S 11.11%; found: C 79.03%, H 9.88%, S 11.13%. ^{1}H NMR: 7.75 d, 2 H, $J(3,4) = 8.3$ (H-4); 7.69 d, 2 H, $J(1,3) = 1.4$ (H-1); 7.26 dd, 2 H, $J(3,4) = 8.3$, $J(1,3) = 1.4$ (H-3); 2.76 t, 4 H, $J = 7.7$ ($\mathrm{CH_2}$); 1.70 m, 4 H ($\mathrm{CH_2}$); 1.35 m, 8 H ($\mathrm{CH_2}$); 1.27 m, 28 H ($\mathrm{CH_2}$); 0.89 t, 6 H, $J = 6.8$ ($\mathrm{CH_3}$). IR: 2 917 s (C–H), 2 849 s (C–H).

Compounds **3a**–**3c** were prepared by the same procedure.

2.2.3. *(S)-1-([1]Benzothieno[3,2-b][1]benzothiophen-2-yl)-4-methylhexan-1-one (**4b**)*

A stirred solution of compound **1** (2.0 g, 8.32 mmol) in dichloromethane (200 ml) was cooled to −20°C and aluminium chloride (3.4 g, 25.5 mmol) was added in one portion. After cooling to −78°C, (*S*)-4-methylhexanoyl chloride [30] (1.0 ml, 6.53 mmol) was added dropwise within 10 min and the mixture was stirred for 4 h at −70°C, decomposed with water (200 ml) and diluted with dichloromethane to dissolve the entire solid. The organic layer was separated and washed with water (2 × 200 ml) and brine (200 ml) then dried over anhydrous magnesium sulphate. Solvent was removed under vacuum and the resulting solid recrystalized from toluene to afford 1.21 g (52.6%) of pure product. The mother liquor was chromatographed on silica gel (eluent hexane/toluene 3/1) to recover 670 mg of starting material and 400 mg (17.4%) of **4b**. The overall yield was 1.61 g (70%) (calculated on acyl chloride), m.p. 181.7–183.0°C. ^{1}H NMR: 8.56 d, 1 H, $J(1,3) = 1.6$ (H-1); 8.07 dd, 1 H, $J(1,3) = 1.6$, $J(3,4) = 8.2$; 7.98–7.91 m, 3 H (H-4, H-6, H-9); 7.51–7.41 m, 2 H (H-7, H-8); 3.15–3.00 m, 2 H, $J = 7.3$ ($\mathrm{CH_2CO}$); 1.80 m, 1 H; 1.60 m, 1 H; 1.45 m, 2 H; 1.25 m, 1 H; 1.00–0.87 m, 6 H. IR: 2 960 s (C–H), 2 930 s (C–H), 2 858 s (C–H), 1 677 m (C=O), 1 590 m, 1 464 m.

Compounds **4a**, **4c** and **4d** were prepared in the same manner.

2.2.4. *(S)-2-(4-methylhexyl)[1]benzothieno[3,2-b][1]benzothiophene (**5b**)*

A mixture of **4b** (1.2 g, 3.40 mmol), potassium hydroxide (0.5 g, 8.91 mmol), hydrazine hydrate (1.3 ml of 80% aq. solution, 21.4 mmol) and diethylene glycol (30 ml) was heated to 100–110°C for 1 h. The temperature was then raised to 210–220°C and held for 5 h. The precipitate formed was filtered off and washed with methanol (2 × 15 ml). Column chromatography on silica gel (eluent hexane) afforded pure product **5b** in a yield of 1.1 g (95%). For analytical purposes a sample was recrystallized from methanol/toluene (2/1), m.p. 77.7–79.6°C. ^{1}H NMR: 7.92 d, 1 H, $J(6,7) = 7.7$ (H-6); 7.84 dd, 1 H, $J(7,9) = 1.7$, $J(8,9) = 7.7$ (H-9); 7.79 d, 1 H, $J(3,4) = 8.2$ (H-4); 7.73 s, 1 H (H-1); 7.46 ddd, 1 H, $J(7,9) = 1.7$, $J(6,7) = 7.7$, $J(7,8) = 8.2$ (H-7); 7.39 ddd, 1 H, $J(6,8) = 1.7$, $J(8,9) = 7.7$, $J(7,8) = 8.2$ (H-8); 7.29 dd, 1 H, $J(1,3) = 1.7$, $J(3,4) = 8.2$ (H-3); 2.75 t, 2 H, $J = 7.7$ ($\mathrm{CH_2}$); 1.80–1.60 m, 2 H ($\mathrm{CH_2}$); 1.45–1.30 m, 3 H ($\mathrm{CH_2}$); 1.30–1.10 m, 2 H; 0.86 m, 6 H ($\mathrm{CH_3}$).

Compounds **5a**, **5c** and **5d** were prepared by analogous methods.

2.2.5. *1-(7-Dodecyl[1]benzothieno[3,2-b][1]benzothien-2-yl)dodecan-1-one (**6d**)*

To a stirred solution of **5a** (180 mg, 0.443 mmol) in dry dichloromethane (15 ml), aluminium chloride (200 mg, 1.50 mmol) was added at −10°C; the solution was cooled to −78°C and dodecanoyl chloride (0.35 ml, 1.50 mmol) was added dropwise. The mixture was stirred for 4 h and the reaction was then quenched by addition of water (10 ml). The organic layer was separated, washed with water (15 ml) and brine (15 ml) then dried over anhydrous magnesium sulphate. The residue after evaporation was purified by column chromatography (silica gel, eluent toluene/hexane 1/3) to afford 223 mg (85%) of **6d**. For $\mathrm{C_{38}H_{52}O_2S_2}$ (604.96) calculated: C 75.45%, H 8.66%, S 10.60%; found: C 75.40%, H 8.68%, S 10.69%. ^{1}H NMR: 8.53 s, 1 H (H-1); 8.05 d, 1 H, $J(3,4) = 8.3$ (H-4); 7.89 d, 1 H, $J(8,9) = 8.5$ (H-9); 7.82 d, 1 H, $J(3,4) = 8.3$ (H-3); 7.73 s, 1 H (H-6); 7.31 d, 1 H, $J(8,9) = 8.5$ (H-8); 3.07 t, 2 H, $J = 7.5$ ($\mathrm{COCH_2}$); 2.78 t, 2 H, $J = 7.5$ ($\mathrm{CH_2}$); 1.83–1.67 m, 4 H ($\mathrm{CH_2}$); 1.27 m, 34 H; 0.89 t, 6 H, $J = 6.4$ ($\mathrm{CH_3}$). IR: 2 918 s (C-H), 2 859 s (C-H), 1 679 m (C=O).

Compounds **6a**–**6c**, **6e** and **7a**–**7m** were prepared by analogous methods.

3. Results

The phase transition temperatures and associated enthalpies were determined using DSC. A typical DSC trace is shown in figure 1 for both heating and cooling runs of the chiral substance **7d**. The SmA–SmC$_{\mathrm{A}}^{*}$ phase transition is accompanied by a very low enthalpy change whereas, the other transitions exhibit much higher enthalpy

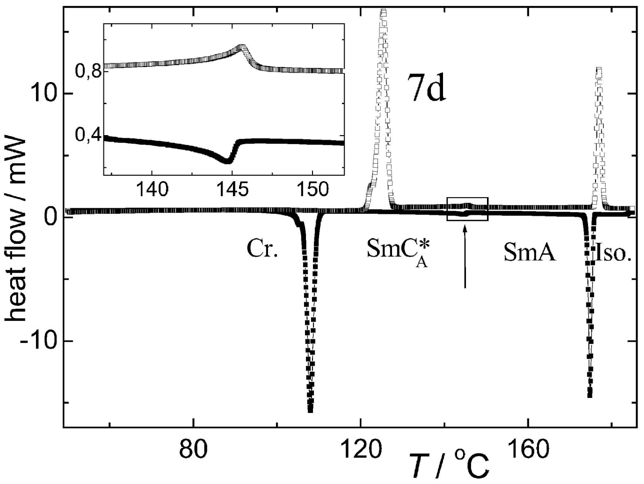


Figure 1. DSC traces recorded on subsequent heating and cooling runs for compound **7d**. The inset shows the SmA–SmC_A^* phase transitions; the arrow denotes the SmA–SmC_A^* phase transition.

values. The mesophases were identified from texture observations using the polarizing microscope. The phases, transition temperatures and associated enthalpy changes are summarized in table 1 for the non-chiral series **2**, **3**, and **6** and in table 2 and figure 2 for chiral series **7**.

3.1. *Properties of chiral intermediates*

Interestingly, two of the intermediate chiral ketones, **4c** and **4d**, containing only one chain exhibit liquid crystalline properties. In the case of **4c** a SmA phase (128–163°C), and for **4d** a low temperature SmX phase (70–121°C) and a SmA phase (121–166°C) have been found.

3.2. *Properties of the non-chiral series*

A broad SmA phase appears in all the compounds studied except for **2b**, which does not exhibit a SmA phase. In a number of homologues from series **2** and **6** a low temperature smectic phase denoted as SmX was found. This phase was not studied in detail and may be the same in the various compounds studied. The presence of a carbonyl group as the linking group between the molecular core and aliphatic chain increases both the melting and clearing points, the increase being higher when two carbonyl groups are present (cf. series **2** and **6** in table 1). The increase of the clearing point is greater, which leads to a wide temperature range SmA phase in the **2** and **6** series. It should be noted, however, that the transition to the isotropic phase in these series is often accompanied by a slow decomposition of the material. **6d** shows a wide (20 K) SmC phase.

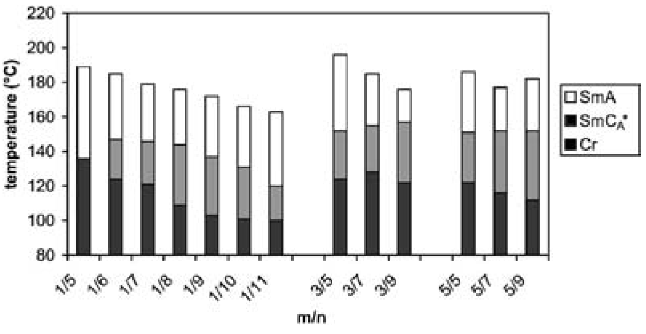


Figure 2. Phase behaviour of the chiral series **7**. The numbers n and m represent the number of carbon atoms in the achiral and chiral chains, respectively.

The dialkyl compounds **3** exhibit only a SmA phase and over a narrower temperature range when compared with series **2** and **6**, the clearing point being about 120°C.

3.3. *Properties of the chiral series*

The compounds in the chiral series **7** exhibit SmA and antiferroelectric SmC_A^* phases (see figure 1 for a typical DSC trace and table 2 and figure 2 for a comparison of the properties of series **7**). The only exception is **7a** (with the shortest achiral and chiral chains), which

Table 1. Transition temperatures T_{tr} (°C) and corresponding transition enthalpies ΔH (J g^{-1}) measured using DSC on cooling at a rate 5 K min^{-1} for the non-chiral series **2**, **3** and **6**.

Compound	M.p. ΔH	Cr	T_{tr} ΔH	SmX	T_{tr} ΔH	SmC	T_{tr} ΔH	SmA	T_{tr} ΔH	I
2a	188 + 17	•	158 – 18	—		—		•	238 – 48	•
2b	170 + 20	•	143 – 20	•	214 – 57	—		—		•
2c	162 + 20	•	136 – 25	•	198 – 44	—		•	244 – 21	•
2d	155 + 18	•	134 – 22	•	187 – 38	—		•	227 – 14	•
3a	115 + 80	•	108 – 81	—		—		•	119 – 17	•
3b	110 + 73	•	98 – 74	—		—		•	126 – 17	•
3c	110 + 83	•	97 – 87	—		—		•	122 – 19	•
3d	112 + 85	•	105 – 88	—		—		•	117 – 18	•
6a	123 + 56	•	100 – 15	•	126 – 11	—		•	200 – 12	•
6b	119 + 42	•	116 – 29	—		—		•	190 – 20	•
6c	125 + 52	•	122 – 43	—		—		•	183 – 20	•
6d	134 + 54	•	130 – 51	—		•	150 – 0.15	•	174 – 21	•

Table 2. Transition temperatures T_{tr} (°C) and corresponding transition enthalpy changes ΔH (J g^{-1}) measured using DSC on cooling at a rate 5 K min^{-1} for the chiral series **7**. The letters *m* and *n* denote the length of the non-chiral and chiral chains, respectively, $\mathbf{P}_S$ (nC cm^{-2}) is spontaneous polarization measured 10 K below the transition to the SmC$_A^*$ phase.

Compound	*m*/*n*	M.p. ΔH	Cr	T_{tr} ΔH	SmC$_A^*$	T_{tr} ΔH	SmA	T_{tr} ΔH	I	$\mathbf{P}_S$ [nC cm^{-2}]
7a	1/5	137 + 31	•	136 – 25	—		•	189 – 4.6	•	—
7b	1/6	134 + 30	•	124 – 22.9	•	147 – 0.15	•	185 – 47.8	•	32
7c	1/7	130 + 42	•	121 – 41	•	146 – 0.14	•	179 – 13	•	26
7d	1/8	125 + 29	•	109 – 45	•	144 – 0.44	•	176 – 20	•	27
7e	1/9	121 + 55	•	103 – 52	•	137 – 0.3	•	172 – 17	•	50
7f	1/10	119 + 47	•	101 – 43	•	131 – 0.18	•	166 – 16	•	37
7g	1/11	110 + 38	•	100 – 25	•	120 – 0.01	•	163 – 12	•	54
7h	3/5	124 + 28.7	•	115.5 – 28.6	•	152 – 6.7	•	196 – 25.0	•	[a]
7i	3/7	128 + 34.0	•	114 – 23.3	•	155 – 0.5	•	184.5 – 18.5	•	[a]
7j	3/9	122 + 48.5	•	108.5 – 38.9	•	157 – 0.5	•	176 – 18.0	•	[a]
7k	5/5	122 + 24.7	•	114.3 – 25.5	•	151 – 3.7	•	186 – 19.8	•	[a]
7l	5/7	116 + 25.9	•	107 – 27.4	•	151.5 – 5.1	•	177 – 18.3	•	35
7m	5/9	112 + 40.5	•	102.5 – 41.0	•	152 – 0.6	•	172 – 18.0	•	40

[a] $\mathbf{P}_S$ could not be measured.

forms only the SmA phase. In figure 2 the crystallization temperatures taken from the DSC traces are used as the low temperature limits of the SmC$_A^*$ phase. These temperatures were reproducible for each compound and can be used to compare the compounds, because the same cooling rate and sample weight was used in all the DSC measurements. The antiferroelectric nature of the SmC phase has been confirmed by the switching properties using a triangular wave field of 20 V µm^{-1} and a frequency below 10 Hz. Under these conditions two distinct peaks in the polarization reversal current are clearly seen (see figure 3), which are a characteristic of antiferroelectric switching. The field is not sufficiently high for complete switching so that the saturated double hysteresis loop cannot be observed. In higher fields a strongly non-linear increase of the electric conductivity occurs, probably due to the field decomposition of the materials in such low frequencies. The dielectric study described later corroborates the assignment of the antiferroelectric nature of the observed phases.

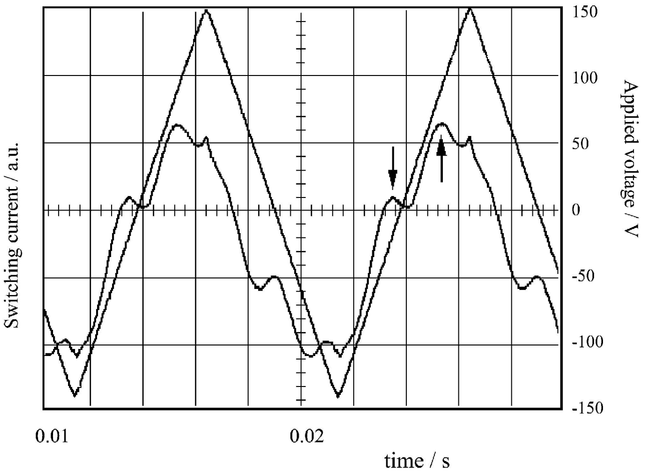


Figure 3. Polarization reversal current measured in the SmC$_A^*$ phase 10°C below the SmA–SmC$_A^*$ phase transition for compound **7c**. The two peaks, which characterize antiferroelectric switching, are indicated by arrows. The applied triangular electric field is 20 V µm^{-1}, 10 Hz.

The dependence of the phase transition temperatures on the length of the chiral and achiral chains is seen in figure 2.

In the optical texture observed for the SmC$_A^*$ phase dechiralization lines are present, which reflects the helicoidal structure. The temperature dependence of the pitch of the helix in the SmC$_A^*$ phase is qualitatively the same for all the compounds studied. Specifically, it increases rapidly on cooling at temperatures just below the SmA–SmC$_A^*$ phase transition temperature, T_c, and reaches a saturation value on further cooling (see figure 4). The pitch length in the saturated state increases linearly on increasing the

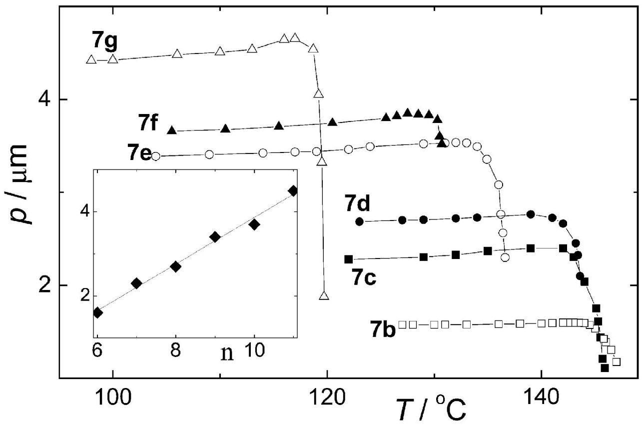


Figure 4. Temperature dependence of the helical pitch length *p* of the chiral compounds with the same length chiral chain ($m = 1$). In the inset the linear dependence of *p* on the achiral chain length is shown.

number of carbon atoms (n) in the achiral chain, from $p=1.7\,\mu\mathrm{m}$ for $n=6$ to $p=4.2\,\mu\mathrm{m}$ for $n=11$.

The frequency dispersion of the complex permittivity was measured for a range of temperatures in the SmA and SmC$^*_\mathrm{A}$ phases. In the majority of compounds no mode could be detected because of the small permittivity and high relaxation frequency of the modes, which interfered with the cut-off cell frequency [31]. In other compounds, the dispersions exhibited only one dielectrically active mode within the whole temperature and frequency range studied. The dispersions were analysed using the Cole–Cole equation, giving the basis parameters, relaxation frequency f_r and dielectric strength $\Delta\varepsilon$ of this mode:

$$\varepsilon^*(f)-\varepsilon_\infty=\frac{\Delta\varepsilon}{1+(\mathrm{i}f/f_\mathrm{r})^{(1-\alpha)}}+\mathrm{i}Af^n$$

where α is the distribution parameter of the mode, and A and n are fitting parameters.

In figures 5(a) and 5(b) the temperature dependence of f_r and $\Delta\varepsilon$ are shown for **7c** and **7e**. Figure 5(a) shows a maximum in $\Delta\varepsilon$ and a kink in $f_\mathrm{r}(T)$ at the phase transition T_c, while in figure 5(b) no anomalies in f_r and $\Delta\varepsilon$ at T_c are evident. The value of $\Delta\varepsilon$ in the SmC$^*_\mathrm{A}$ phase is very low, confirming that this phase is antiferroelectric.

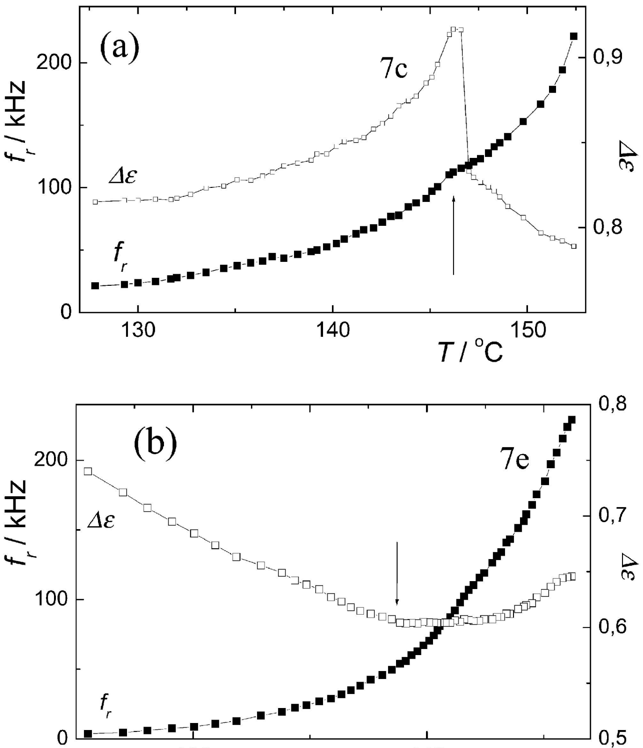


Figure 5. The fitted relaxation frequency and dielectric strength in the vicinity of the SmA–SmC$^*_\mathrm{A}$ phase transition for (a) **7c** and (b) **7e**. The arrow indicates the SmA–SmC$^*_\mathrm{A}$ phase transition.

The temperature dependence of the spontaneous tilt angles, θ_S shown in figure 6, are typical as the SmC$^*_\mathrm{A}$ phase is approached on cooling the SmA phase. A similar temperature dependence is found for the spontaneous polarization $\mathbf{P}_\mathrm{S}$, the values of which differ for different homologues. The values of $\mathbf{P}_\mathrm{S}$ measured at a temperature 10 K below T_c are shown in table 2 for selected compounds. For the other compounds $\mathbf{P}_\mathrm{S}$ could not be measured because of the rather high conductivity, which increased under the application of the switching electric field, probably due to the slight decomposition of the materials. No systematic correlation of the $\mathbf{P}_\mathrm{S}$ values with the length of the alkyl chain is found.

4. Discussion and conclusions

Four series of [1]benzothieno[3,2-b][1]benzothiophene derivatives have been synthesized. In the non-chiral series it was found that the carbonyl group linking the core and the alkyl chain increases both the melting and clearing temperatures. As expected, lengthening the alkyl chain generally leads to lower clearing temperatures, but this effect is weak and not well defined. It should be noted that the mesomorphic properties of the achiral series **2**, **3** and **6** resemble the properties of the known dialkylesters [32] of heterocycle **1**.

The introduction of a chiral chain leads to a substantial change in the LC properties. The compounds in the chiral series exhibit a rather wide antiferroelectric SmC$^*_\mathrm{A}$ phase, on cooling the SmA phase. The DSC and dielectric studies show that the SmA–SmC$^*_\mathrm{A}$ phase transition changes in character when the length of the acyl and alkyl chains differs. It is second order in nature for some compounds which exhibit a small transition enthalpy change. In these compounds a maximum in dielectric strength is observed at the phase transition caused by the contribution of the fluctuation of the molecular tilt, which becomes soft in the vicinity of the transition (soft mode) [33]. Higher

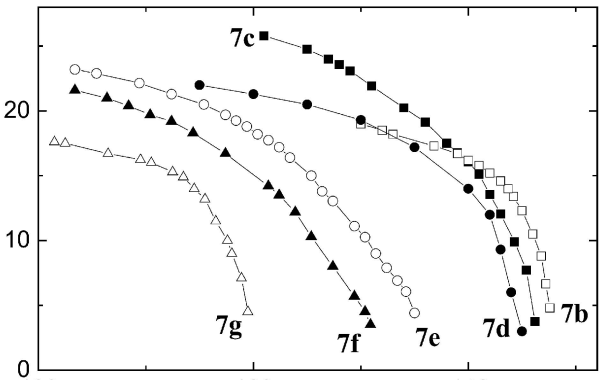


Figure 6. Temperature dependences of spontaneous tilt angle θ_S for compounds **7b**–**7g**.

transition enthalpy changes reflect a greater departure of the phase transition from being second order in nature, and the transition becomes strongly first order. In these compounds the fluctuation of the molecular tilt is not soft at the transition and therefore its contribution to the permittivity is negligible.

The pitch length in the saturated state increases linearly on increasing the number of carbon atoms in the achiral chain. The values of the spontaneous polarization are rather moderate.

The physical properties of the materials studied reveal that the heterocycle moiety can be used as the core for liquid crystal materials. The addition of a chiral chain introduces antiferroelectic phases. The appearance of such phases is somewhat surprising when comparing the molecular structure of these materials with known antiferroelectric systems. The alignment and packing of the heterocyclic system **1** in the layers seems to play an important role. The next stage in the design of these materials will focus on lowering the transition temperatures while maintaining the range and type of the liquid crystalline phases. A detailed X-ray investigation of the molecular organization in the smectic phases will be the subject of further research.

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