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A new class of bent-shaped mesogens exhibiting unusual mesophase behaviour

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Examples of a new class of bent-core compounds are presented, the central fragment of which consists of a benzoyl derivative of a secondary cyclic amine. The mesophase behaviour has been studied by differential scanning calorimetry, polarizing optical microscopy, X-ray diffraction and electro-optical measurements. It was found that the five-ring compounds form smectic CP or B₁ phases which are typical for bent-core mesogens. The six-ring compounds exhibit, in some cases, only conventional non-polar smectic phases; in other cases non-polar smectic phases as well as banana phases are seen. Of particular interest is the occurrence of a switchable uniaxial smectic A-like phase with an antiferroelectric structure.

1. Introduction

The study of liquid crystal phases formed by achiral bent-shaped molecules has grown rapidly in the last few years. The reason for this particular interest is not only the occurrence of new mesophases which differ from analogous mesophases of calamitic compounds, but also because some of the new mesophases show polar properties resulting from the bent molecules being tightly packed and aligned in the bend direction, giving rise to a spontaneous polarization of the smectic layers [1]. The most frequently observed smectic phase composed of bent molecules is the SmCP phase in which the polar packed molecules are tilted with respect to the layer normal. In this phase, which may be regarded as the polar variant of the SmC phase, the smectic layers possess C₂ symmetry. Depending on the stacking of the smectic layers, the SmCP phase may exhibit antiferroelectric or ferroelectric properties. It is remarkable that the combination of director tilt and polar packing leads to a chirality of the smectic layers although the constituent molecules are achiral [2]. In some rare cases the polar packed molecules are, on average, orthogonal with respect to the layer planes and a polar biaxial SmA phase results, designated as SmAP. This phase was predicted by Brand *et al.* [3] and experimentally shown to be an antiferroelectric variant by Eremin *et al.* [4] and Shreenivasa Murthy and Sadashiva [5]. Similar to

calamitic compounds, bent-core compounds are also able to form mesophases with a two-dimensional superstructure [6, 7]. This phase may be regarded as a columnar phase in which the columns are represented by layer fragments. In most cases reported in the literature these columnar phases (also designated as B₁) form a rectangular cell. Investigations on well oriented samples give evidence that the molecules are usually tilted within the layer fragments (SmCP-like layer fragments). There are also cases where the layer fragments are SmAP-like, which means that within the layer fragments the molecules are, on average, orthogonal with respect to the layer planes [8, 9].

In recent years a large number of bent-core compounds have been synthesized. The majority of these compounds consist of a central phenyl ring, with identical two-ring mesogenic units substituted in the 1,3-positions. In some cases the central fragment is a biphenyl or naphthalene ring. There are also asymmetric bent-core mesogens where the asymmetry is due to different linkage groups in the legs of the bent compound. The asymmetry of the molecules may also be due to different lengths of the legs. Recently Schröder *et al.* [10] described examples of a new class of asymmetric bent-core mesogens in which the central fragment consists of a benzoyl derivative of a secondary cyclic amine. In these compounds the bend of the molecule is not achieved by a 1,3-substitution of the central aromatic ring but by a carbonyl group which links the phenyl ring of one leg with the nitrogen of the piperidine or piperazine ring which

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is part of the second leg. In this paper we present 20 compounds of this new class that exhibit five or six rings.

The mesophase behaviour has been investigated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), X-ray diffraction (XRD) and electro-optical measurements. Depending on the molecular structure, these compounds are able to form polar smectic phases (characteristic for bent-core mesogens) as well as non-polar smectic phases (typical for calamitics). It will be shown that in some cases unusual phase sequences occur.

2. Experimental

2.1. Characterization

The phase transition temperatures were determined by DSC (DSC Pyris 1, Perkin-Elmer) and by POM (Leitz Orthoplan). The identification of the mesophases was based on microscopic examination of the optical textures and by XRD measurements. Powder-like samples were studied using Guinier methods or a home-made small angle device with a linear detector. The observation of field-induced texture changes and the measurement of switching polarization were carried out in commercially available glass cells (spacing: 5, 6 and 10 μm).

2.2. Synthesis

Structures, along with phase sequences, phase transition temperatures ($^{\circ}\text{C}$) and enthalpy changes (kJ mol^{-1} , in square brackets) of the synthesized compounds, are presented in tables 1–4. Depending on the connecting groups and lateral substituents, acylations were performed with selected acids with the use of DCC/DMAP, or by using the acid chlorides in the presence of triethylamine. The synthesis of the compounds starts from 4-hydroxyphenylpiperazine, 4-hydroxypiperidine or *N*-(2-hydroxyethyl)piperazine which react with selected two-ring acids.

2.2.1. Compounds 1 and 2. A substituted benzoylchloride (22 mmol), prepared from the corresponding benzoic acid by means of thionylchloride, was added to a solution of 10 mmol 4-hydroxypiperidine or *N*-(2-hydroxyethyl)piperazine and 25 mmol triethylamine in 50 ml toluene. The mixture was stirred for 12 h at room temperature and then heated at 60°C for 2 h. The precipitate of triethylamine hydrochloride was separated. After evaporating the solvent, the crude products were recrystallized from a DMF/ethanol mixture; yield 20–30%.

1a: $^1\text{H NMR}$: (200 MHz, CDCl_3 , δ/ppm): 0.88 (m, 6H, $2 \times \text{CH}_3$), 1.27–1.88 (m, 24H, $12 \times \text{CH}_2$), 3.59 (broad, 4H, piperidine), 3.89 (broad, 4H, piperidine), 4.03 (t, $^3J=6.4\text{ Hz}$, 4H, $2 \times \text{OCH}_2$), 5.29 (broad, 1H, piperidine), 6.96 (d, $^3J=8.9\text{ Hz}$, 4 Ar–H), 7.27 (d, $^3J=8.7\text{ Hz}$, 4 Ar–H), 7.49 (d, $^3J=8.5\text{ Hz}$, 4 Ar–H), 8.11 (dd, $^3J=8.7\text{ Hz}$, $^4J=2.1\text{ Hz}$, 4 Ar–H). Elemental analysis for $\text{C}_{49}\text{H}_{59}\text{NO}_9$: calcd: C 73.02, H 7.38, N 1.74; found C 72.82, H 7.51, N 1.63%. MS: m/z 805 (M^+).

2a: $^1\text{H NMR}$: (200 MHz, CDCl_3 , δ/ppm): 0.87 (m, 6H, $2 \times \text{CH}_3$), 1.24–1.84 (m, 28H, $14 \times \text{CH}_2$), 3.44 (broad, 4H, piperazine), 3.65 (broad, 4H, piperazine), 4.03 (t, $^3J=6.6\text{ Hz}$, 4H, $2 \times \text{OCH}_2$), 6.96 (d, $^3J=9.1\text{ Hz}$, 4 Ar–H), 7.27 (d, $^3J=8.7\text{ Hz}$, 4 Ar–H), 7.31 (d, $^3J=8.7\text{ Hz}$, 4 Ar–H), 7.48 (d, $^3J=8.5\text{ Hz}$, 4 Ar–H), 8.08 (m, 4 Ar–H). Elemental analysis for $\text{C}_{50}\text{H}_{62}\text{O}_9\text{N}_2$: calcd C 71.92, H 7.48, N 3.35; found C 71.66, H 7.52, N 3.38%. MS: m/z 834 (M^+).

2.2.2. Compounds 3, 4 and 5. A mixture of 2 mmol 4-hydroxyphenylpiperazine, 4 mmol selected benzoic acid, 4.8 mmol *N,N'*-dicyclohexylcarbodiimide and 4-dimethylaminopyridine as catalyst in 100 ml dichloromethane was stirred for 24 h at room temperature. The precipitate was separated. The solvent was evaporated and the crude products recrystallized from a DMF/ethanol mixture several times; yield 20–30 %.

3a: $^1\text{H NMR}$: (400 MHz, CDCl_3 , δ/ppm): 0.91 (m, 6H, $2 \times \text{CH}_3$), 1.30–1.82 (m, 16H, $8 \times \text{CH}_2$), 3.24 (broad, 4H, piperazine), 3.61 (broad, 4H, piperazine), 3.97 (t, $^3J=6.5\text{ Hz}$, 4H, $2 \times \text{OCH}_2$), 6.95 (m, 4 Ar–H), 7.14 (d, $^3J=8.9\text{ Hz}$, 4 Ar–H), 7.25 (m, 4 Ar–H), 7.52 (d, $^3J=8.3\text{ Hz}$, 4 Ar–H), 7.94 (d, $^3J=9.3\text{ Hz}$, 4 Ar–H), 8.00 (d, $^3J=8.3\text{ Hz}$, 4 Ar–H), 8.24 (d, $^3J=8.3\text{ Hz}$, 4 Ar–H), 8.50 (s, 1H, $\text{CH}=\text{N}$), 8.56 (s, 1H, $\text{N}=\text{CH}$). Elemental analysis for $\text{C}_{50}\text{H}_{56}\text{O}_5\text{N}_4$: calcd C 75.73, H 7.12, N 7.07; found C 75.8, H 7.12, N 7.11%. MS: m/z 792 (M^+).

4a: $^1\text{H NMR}$: (400 MHz, CDCl_3 , δ/ppm): 0.90 (m, 6H, $2 \times \text{CH}_3$), 1.31–1.81 (m, 16H, $8 \times \text{CH}_2$), 3.27 (broad, 4H, piperazine), 3.58 (broad, 4H, piperazine), 3.95 (t, $^3J=6.6\text{ Hz}$, 4H, $2 \times \text{OCH}_2$), 6.92 (dd, $^3J=9.1\text{ Hz}$, $^4J=2.7\text{ Hz}$, 4 Ar–H), 6.98 (d, $^3J=9.1\text{ Hz}$, 4 Ar–H), 7.15 (m, 4 Ar–H), 7.56 (d, $^3J=8.3\text{ Hz}$, 2H), 8.24 (d, $^3J=8.3\text{ Hz}$, 4 Ar–H), 8.23 (s, 4 Ar–H). Elemental analysis for $\text{C}_{50}\text{H}_{54}\text{O}_9\text{N}_2$: calcd C 72.62, H 6.58, N 3.39; found C 72.68, H 6.51, N 3.56%. MS: m/z 826 (M^+).

3. Results

3.1. Five-ring compounds

The phase behaviour of the five-ring compounds is summarized in tables 1 and 2. It can be seen from

Table 1. Phase behaviour and transition temperatures ($^{\circ}\text{C}$) of compounds **1**. The transition enthalpies (kJ mol^{-1}) are given in square brackets.

Compound	n	Cr	SmCP _A	I	
1a	8	•	128 [17.1]	•	
1b	9	•	124 [41.9]	•	
1c	10	•	110 [33.1]	(• 108) [16.4]	•
1d	11	•	110 [26.3]	• 114 [20.1]	•
1e	12	•	110 [30.5]	• 116 [21.7]	•
1f	16	•	113 [12.9]	• 118 [18.7]	•

Table 2. Phase behaviour and transition temperatures ($^{\circ}\text{C}$) of compounds **2**. The transition enthalpies (kJ mol^{-1}) are given in square brackets.

Compound	n	Cr	SmC-P _A	B ₁	I
2a	8	•	110 [53.5]	(• 88) [3.3]	•
2b	12	•	101 [19.4]	(• 96) [2.6]	•

table 1 that the short chain homologues of series **1** (**1a**, **1b**) do not exhibit a mesophase. The mesophase shown by the long chain homologues (**1c–1f**) was identified as a SmCP phase. It forms a non-specific texture on cooling the isotropic liquid. If the isotropic liquid is cooled in presence of an electric field a fan-shaped texture is obtained. The mesophase is switchable, the threshold field for compound **1c** is $2.5\text{--}3.5\text{ V}\mu\text{m}^{-1}$. The texture of the switched state clearly depends on the polarity of the applied field; furthermore, the

extinction crosses of circular domains rotate in reverse directions when the sign of the field is changed. The current response to a triangular voltage shows two peaks per half-cycle which suggests an antiferroelectric ‘homochiral’ ground state (figure 1). From the current response, a high switching polarization of 1000 nC cm^{-2} was determined. For compound **1f** the layer spacing d of the SmCP_A phase was found to be 45.7 \AA , which is smaller than the molecular length L ($\approx 65\text{ \AA}$). From the ratio d/L a tilt angle of about 45° may be estimated using $\cos\theta = d/L$. The switching polarization was found to be 450 nC cm^{-2} .

In series **2** the second nitrogen is connected with an aromatic ring via a $(\text{CH}_2)_2\text{OOC}$ spacer. Both compounds form a monotropic mesophase. The mesophase of compound **2a** was identified as a B₁ phase according to the characteristic mosaic texture observed. The mesophase of compound **2b** possesses a simple layer structure. The layer spacing d (39.8 \AA) was found to be smaller than the molecular length L ($\approx 52\text{ \AA}$), corresponding to a tilt angle of about 40° .

3.2. Six-ring compounds

In these compounds the second nitrogen atom of the piperazine ring is directly linked with a phenyl ring. In this way one leg of the bent molecules contains two, the other leg four rings, giving a strongly asymmetric structure. The members of series **3** and **4** are distinguished by the linkage group X and X' , respectively. In series **3** the linkage group is an azomethine group; in series **4** the linkage group is a carboxyl group.

The mesophase of the homologues **3a** and **3b** exhibits a SmA-like fan-shaped texture or a strongly fluctuating

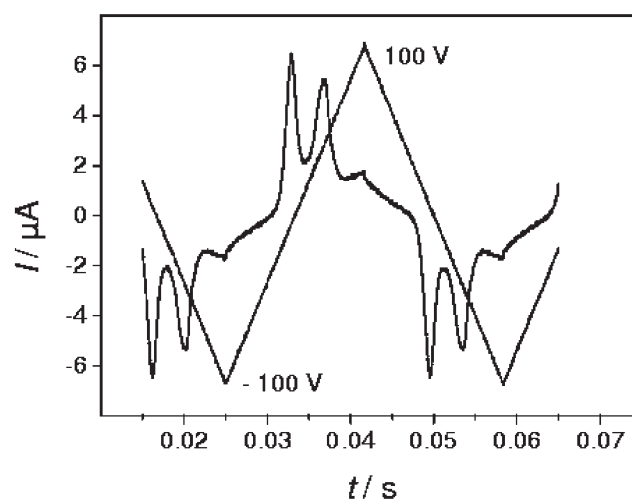
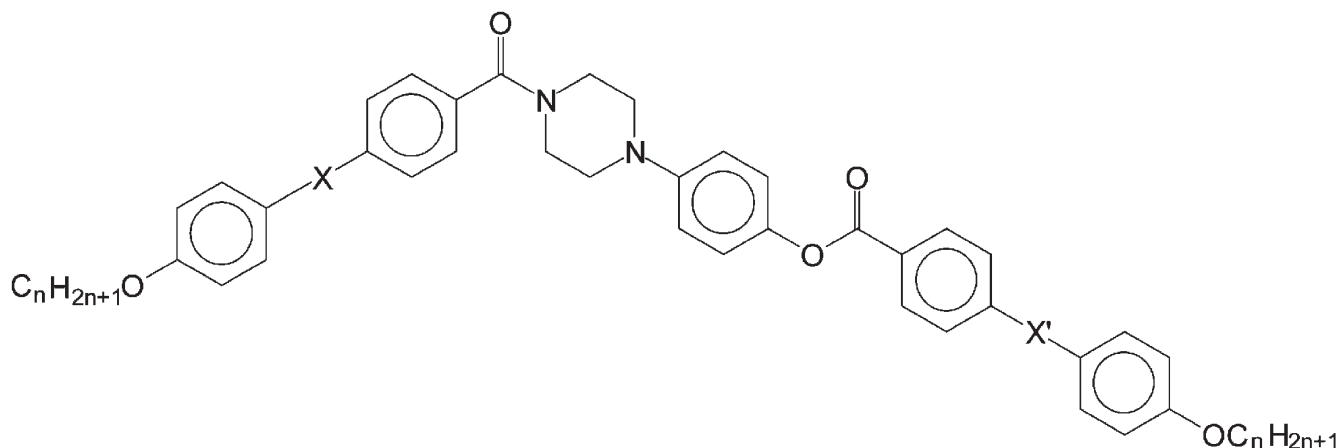


Figure 1. Switching current response in the SmCP_A phase of compound **1c** ($T=101^{\circ}\text{C}$, $U=200\text{ V}_{\text{PP}}$).

Table 3. Phase behaviour and transition temperatures ($^{\circ}\text{C}$) of the six-ring compounds **3** and **4**. The transition enthalpies (kJ mol^{-1}) are given in square brackets.



Compound	n	X	X'	Cr	SmA'	SmCP/ SmAP	SmX	SmA	I
3a	6	N=CH	CH=N	• 222 [13.3]	—	—	• 256 [13.8]	—	•
3b	8	N=CH	CH=N	• 230 [20.2]	—	—	• 258 [13.2]	—	•
3c	12	N=CH	CH=N	• 221 [23.3]	—	—	• 247 [2.7]	• 253 [10.7]	•
4a	6	OOC	COO	• 168 [31.9]	—	—	• 212 [0.7]	• 243 [6.1]	•
4b	8	OOC	COO	• 175 [22.2]	—	• 210 [0.7]	—	• 246 [8.4]	•
4c	12	OOC	COO	• 167 [20.1]	• 195 [0.7]	• 206 ^a	—	• 241 [8.6]	•

^aThe transition enthalpy could not be detected by DSC.

schlieren texture. In the fan-shaped texture some irregular stripes perpendicular to the fans arise on cooling the sample. Compound **3c** shows liquid crystalline dimorphism. The high temperature phase may be assigned as a SmA phase indicated by typical fan-shaped texture and homeotropic textures. The texture of the low temperature phase is quite similar to that of the short chain homologues. Unfortunately, structural investigations or electro-optical measurements were impossible because of the high temperatures involved. From the schlieren texture we deduce that this phase is biaxial, but the schlieren and fan-shaped textures are not typical for a SmC phase.

For the members of series **4** the high temperature phase is a SmA phase. If the fan-shaped texture is cooled into the low temperature phase, the texture remains almost unchanged. On the other hand, if the homeotropic SmA texture is cooled the low temperature phase forms a strongly fluctuating schlieren texture

(figure 2) which is quite similar to that of the biaxial smectic phase of compounds **3a** or **3b**.

For compound **4a**, when the biaxial phase is formed from the SmA fan-shaped texture the texture is not markedly changed. Above a threshold of about $6 \text{ V } \mu\text{m}^{-1}$ the fan-shaped texture of the SmX phase may be switched into a fan-shaped texture with different interference colours. In the case of compound **4a** the switching is not polar. In contrast, for compound **4b** the fan-shaped texture of the low temperature phase forms irregular stripes perpendicular to the fans, and the biaxial phase shows a current response with two peaks per half-cycle of the applied triangular voltage, which suggests a SmCP phase with an antiferroelectric groundstate.

The dodecyloxy homologue **4c** exhibits three smectic phases. The high temperature phase is SmA. On cooling, the SmA phase transforms at 206°C into a biaxial smectic phase which displays a weakly birefringent schlieren texture or a SmA-like smooth fan-shaped

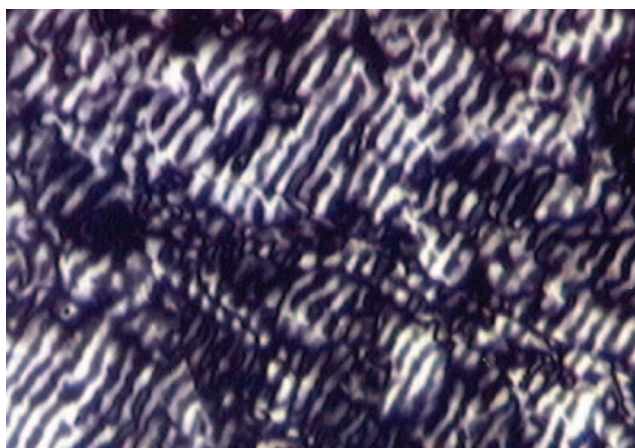


Figure 2. Optical texture of the fluctuating schlieren texture of compound **4a** ($T=185^{\circ}\text{C}$).

texture. It is remarkable that at 195°C a phase transition takes place where the fan-shaped texture does not change and the schlieren texture becomes homeotropic again, indicating a uniaxial structure. If the glass substrates are sheared, birefringent grainy islands arise within the homeotropic texture. X-ray investigations indicate that all three smectic phases possess no in-plane order. Interestingly not only the intermediate biaxial smectic phase but also the uniaxial low temperature phase, designated as SmA' , show electro-optical switching. In the biaxial smectic phase the birefringence of the fan-shaped texture is changed by the electric field but this effect is independent of the polarity of the field. In the low temperature SmA -like phase the character of the switching is different. The switched state relaxes into a grainy texture after removal of the field. In some regions the texture of the switched state depends on the sign of the field, see figures 3(a) and 3(b). We found that the biaxial smectic phase, as well as the low temperature uniaxial smectic phase, show a current response with two peaks per half-cycle of the applied triangular voltage, indicating an antiferroelectric ground state, figure 3(c). The threshold field is rather low ($\approx 2\text{--}4\text{ V}\mu\text{m}^{-1}$). The switching polarization was found to be 310 nC cm^{-2} in the biaxial phase and 250 nC cm^{-2} in the low temperature phase (SmA').

3.3. Laterally substituted six-ring compounds

Compounds **5** are derived from the basic six-ring molecule **3b** and differ only by the lateral substituents on the terminal rings. As seen from table 4 compound **5a** forms a SmA phase, only; compound **5b** shows smectic dimorphism. The high temperature phase was identified as a SmA phase. The low temperature phase

exhibits similar textures and electro-optical behaviour analogous to compound **4b**, indicating a $\text{SmA}\text{--}\text{SmCP}_A$ or $\text{SmA}\text{--}\text{SmAP}_A$ phase sequence. The other compounds listed in the table show some unusual mesophase behaviour.

In compound **5c** three mesophases can be identified by calorimetry and by microscopy. The high temperature phase is a SmA phase which on cooling at 191°C forms a biaxial phase with a fluctuating schlieren texture, whereas the fan-shaped texture of the SmA phase remains unchanged, figure 4(a). At 185°C the schlieren texture again becomes homeotropic indicating a SmA -like phase, figure 4(b). Between 130 and 120°C a very weakly birefringent schlieren appears within the homeotropic texture. This schlieren texture may also be induced by mechanical shearing of the substrates. If the schlieren texture is heated, the transition into the homeotropic texture takes place between 155 and 160°C . It should be noted that the layer spacing is the same in the three smectic phases (45.3 \AA). The fan-shaped texture of the biaxial smectic phase can be switched, as indicated by a slight colour change while the textures of the switched state are independent of the polarity of the field. A polar switching could not be detected, however, neither in the biaxial phase (SmC or SmA_b) nor in the homeotropic low temperature phase (SmA').

Besides the SmA phase, compound **5d** exhibits a biaxial low temperature phase; if this is formed from the homeotropically oriented SmA phase a weakly birefringent texture with mosaic-like domains arises, see figure 5(a). At this transition the fan-shaped texture of the SmA phase, figure 5(b), is not markedly changed; if it takes place in the presence of a strong d.c. field, however, a texture is formed which is reminiscent of a mosaic texture of a columnar phase, figure 5(c). This phase shows a weak switching effect at sufficiently high electric fields ($15\text{--}20\text{ V}\mu\text{m}^{-1}$) but a current response indicating a polar structure could not be detected. It was found by XRD measurements that the layer spacing d of the SmA phase is 45.7 \AA (184°C). At the transition into the low temperature phase the d -value slightly increases (46.2 \AA at 180°C ; 46.4 \AA at 164°C). It is remarkable that in the low temperature phase a satellite of low intensity occurs behind the first order Bragg reflection, suggesting a one-dimensional layer undulation with a period of about 165 \AA perpendicular to the layer normal.

Compound **5e** forms three smectic phases. The high temperature phase is a SmA which exhibits a homeotropic or characteristic fan-shaped texture, figure 6(a). At 189°C a phase transition takes place with an associated calorimetric peak. At this transition slight

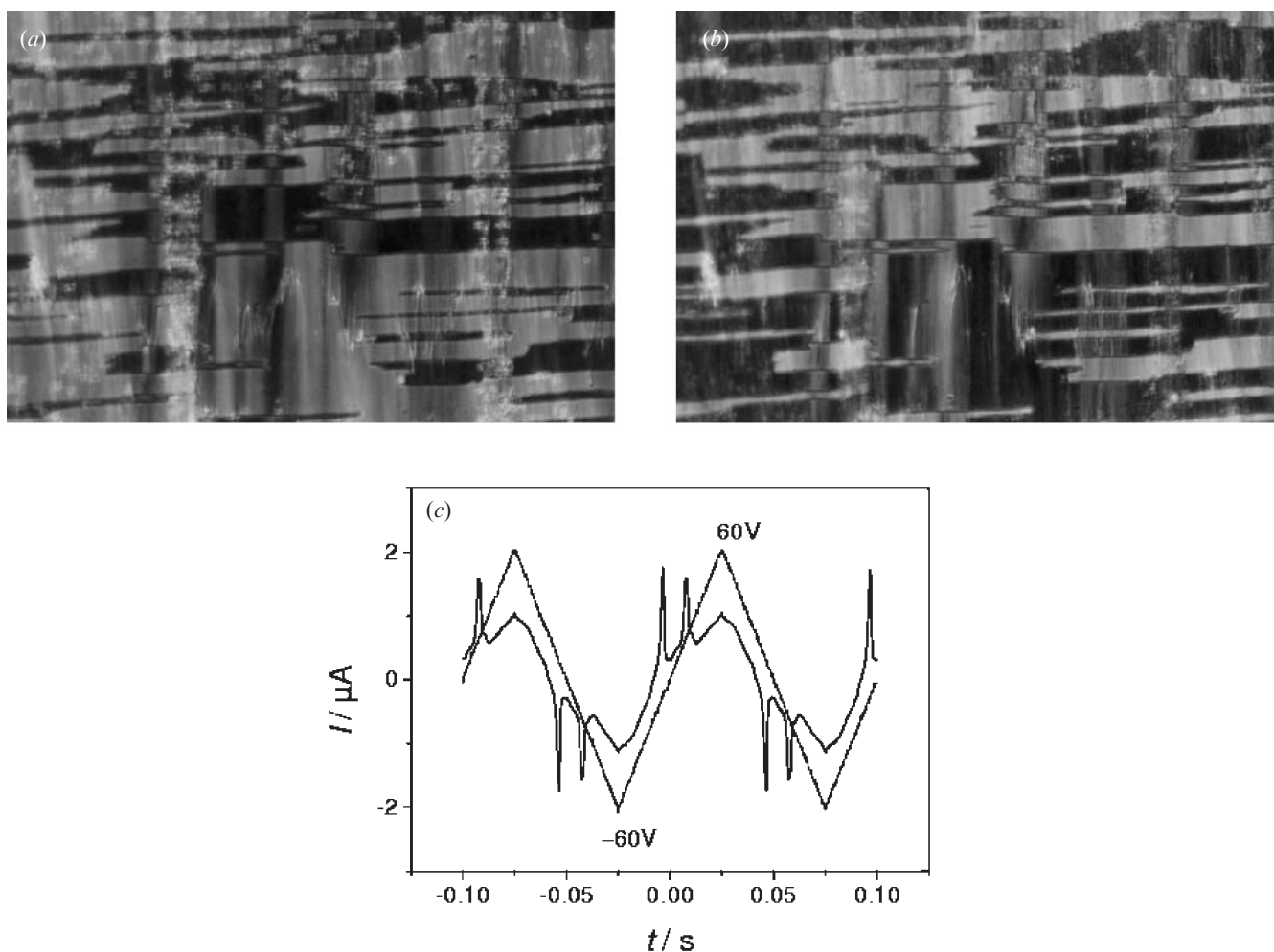


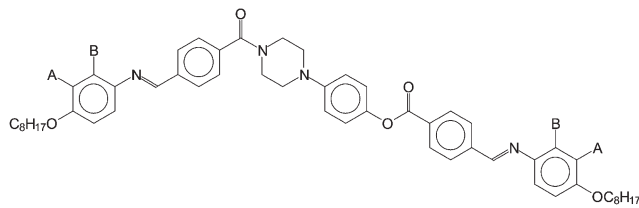
Figure 3. SmA' phase of compound **4c**: (a) optical textures of the switched states $+3 \text{ V } \mu\text{m}^{-1}$, $T=186^\circ\text{C}$; (b) $-3 \text{ V } \mu\text{m}^{-1}$, $T=186^\circ\text{C}$; (c) switching current response ($T=160^\circ\text{C}$, $U=120 \text{ V}_{\text{PP}}$).

but reproducible motions within the homeotropic texture can be observed. In particular, in thicker samples grainy birefringent islands arise which can be destroyed by mechanical stress. On very fast cooling, almost the whole sample is covered with grainy birefringent islands, figure 7(a). The phase transition between the SmA and the homeotropic low temperature phase is also visible by a clear colour change of the fan-shaped texture, figure 6(b). At 182°C the homeotropic texture transforms into a weakly birefringent scale-like schlieren texture, figure 7(b), and the fan-shaped texture forms a grainy texture, figure 6(c). The occurrence of the schlieren texture is an indication of a biaxial phase. This transition is accompanied by a very small calorimetric peak (transition enthalpy 0.1 kJ mol^{-1}). If the biaxial phase is heated, the reverse transition into the uniaxial intermediate phase (SmA'') does not take place. At 189°C the biaxial phase transforms into the SmA phase. X-ray studies show that all these smectic phases

have liquid-like order within the layer. The layer spacing d was found to be 44 \AA in the SmA phase; it decreases continuously on cooling into the low temperature SmA'' phase and into the SmCP_A phase ($d=42 \text{ \AA}$ at 173°C). The intermediate SmA-like phase (SmA''), as well as the biaxial low temperature phase, show an electro-optical response which clearly points to an antiferroelectric groundstate (figure 8). The switching polarization in the SmA'' phase was found to be 550 nC cm^{-2} (186°C). It increases significantly in the SmCP_A phase (780 nC cm^{-2} at 180°C).

Compound **5f** shows a smectic trimorphism. In contrast to the other compounds of series **5** all three smectic phases are biaxial. The high temperature phase forms a fan-shaped texture or a schlieren texture with singularities exhibiting four brushes. During the transition at 156°C the fan-shaped texture remains unchanged, but in the schlieren texture the fluctuations disappear and the

Table 4. Phase behaviour and transition temperatures ($^{\circ}\text{C}$) of the laterally substituted compounds **5**. The transition enthalpies (kJ mol^{-1}) are given in square brackets.



Compound	A	B	Phases
5a	OCH ₃	H	Cr 144 SmA 175 I [33.0] [5.3]
5b	F	H	Cr 187 SmAP _A /SmCP _A 238 SmA 246 I [24.9] [0.7] [9.6]
5c	Br	H	Cr 154 SmA' 185 SmC/SmA _b 191 SmA 215 I [2.7] [0.02] [0.02] [1.1]
5d	CN	H	Cr 163 Sm _{und} 182 SmA 190 I [41.5] [0.5] [9.0]
5e	CH ₃	H	Cr 160 SmCP _A 182 SmA'' 189 SmA 199 I [52.3] [0.1] [2.9] [4.9]
5f	H	CH ₃	Cr 148 (SmCP _A ' 147) SmCP _A 156 SmC 193 I [19.7] ^{aa} [10.6]

^aA calorimetric peak could not be detected by DSC.

schlieren texture displays a type of fan-like superstructure. At 149°C the fan-shaped texture becomes grainy and the schlieren texture again fluctuates (figure 9). It should be noted the transitions at 156 and 149°C could not be detected by calorimetric measurements. X-ray experiments show that the layer spacing d is almost independent of the temperature (44.4 – 44.6 Å) in all three smectic phases.

In the SmC phase a weak electro-optical response is observed which is due to a Fredericksz transition. At about 155°C the character of the switching is changed, and in both tilted low temperature phases an antiferroelectric groundstate was demonstrated ($P_S = 520 \text{ nC cm}^{-2}$).

4. Discussion

The five-ring compounds (tables 1 and 2) form mesophases which are typical for bent-core mesogens, namely the anticlinic SmCP_A phase (SmC_AP_A) or the columnar B₁ phase. In the six-ring compounds the additional phenyl ring in the longer wing of the molecule leads to a larger molecule length and makes the

molecule more asymmetric. The greater molecular length causes a strong enhancement of the melting and clearing temperatures in comparison with those of the five-ring compounds. The high temperature range of the mesophases prevents or strongly complicates structural investigations by X-ray or physical measurements. Nevertheless, the SmA phase could be clearly assigned on the basis of the characteristic textures (fan-shaped texture, homeotropic texture) observed.

The textures of the SmX phase (compounds **3a–3c**, **4a**, **5c**) are not characteristic of a SmC phase, but are compatible with a biaxial SmA (SmA_b) or an anticlinic SmC phase (SmC_A). The textures of the low temperature phase of compounds **4b**, **4c**, **5b**, and **5c** are similar to those of the SmX phase, but these phases show polar switching. Since the texture of the switched state is independent of the polarity of the applied field we cannot distinguish between a SmAP_A or a SmCP_A phase. Such a distinction would be only possible from X-ray measurements on oriented samples.

An interesting feature is the occurrence of an undulating smectic phase which is found in compound **5d** as the low temperature phase. X-ray measurements show that the period of the undulation is about 165 Å.

Another interesting phenomenon is the existence of two SmA phases in the sequences SmA'–SmA_b/SmC–SmA (compound **5c**), SmA'–SmCP_A/SmAP_A–SmA (compound **4c**) or SmCP_A–SmA''–SmA (compound **5e**). Surprisingly, in compounds **4c** and **5e** the low temperature SmA phase shows antiferroelectric switching like the SmCP_A phase. In the case of compound **5e** the switching of the fan-shaped texture is accompanied by a small increase of birefringence but the switching polarization is relatively high. In compound **4c** the textures of the field-induced ferroelectric states depend on the polarity of the field, which cannot be interpreted in terms of a uniaxial structure; see figure 4 (a) and 4 (b).

A polar electro-optical response of a uniaxial smectic phase formed by bent-core molecules was first reported by Dantlgraber *et al.* [11] and Pocięcha *et al.* [12]. In the first case the molecules within the smectic layers are tilted but there is obviously no correlation between the layers, so that the overall structure is uniaxial. For the ferroelectric uniaxial smectic phase presented in [12] the ferroelectric properties result from a random direction of the layer polarization within a specific smectic layer.

To date we have no convincing explanation for the polar switching of the uniaxial smectic phases of compounds **4c** and **5c**. It should be noted, however, that the transition enthalpy between the switchable SmA and the SmCP_A phase is rather low (0.7 kJ mol^{-1} for compound **4c** and 0.02 kJ mol^{-1} for compound **5c**), indicating only

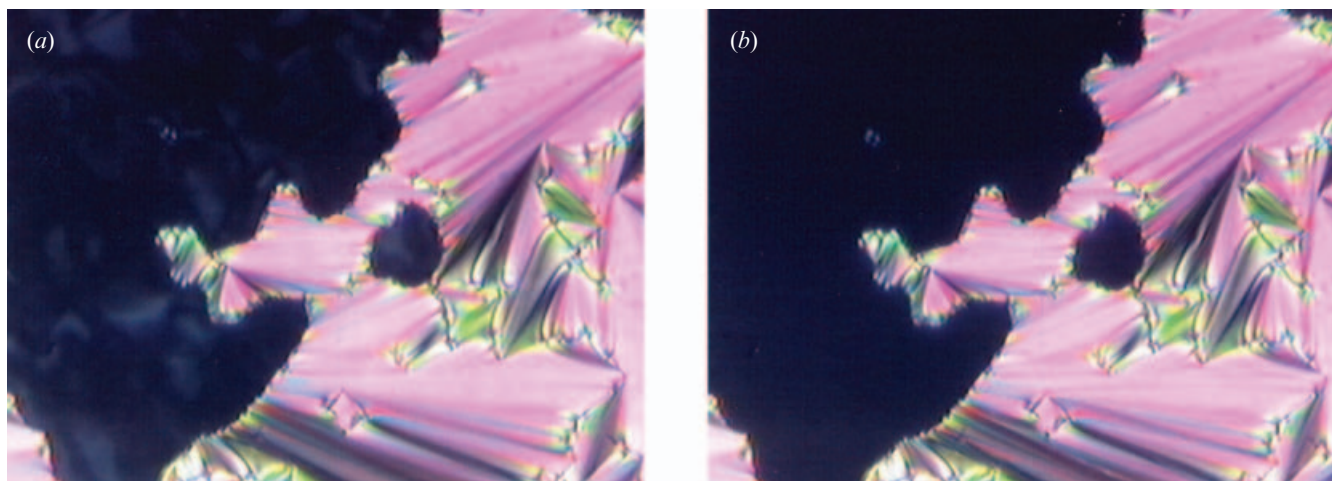


Figure 4. Texture: (a) of the SmC/SmA_b phase ($T=187^{\circ}\text{C}$), (b) of the low temperature SmA phase ($T=178^{\circ}\text{C}$) of compound **5c**.

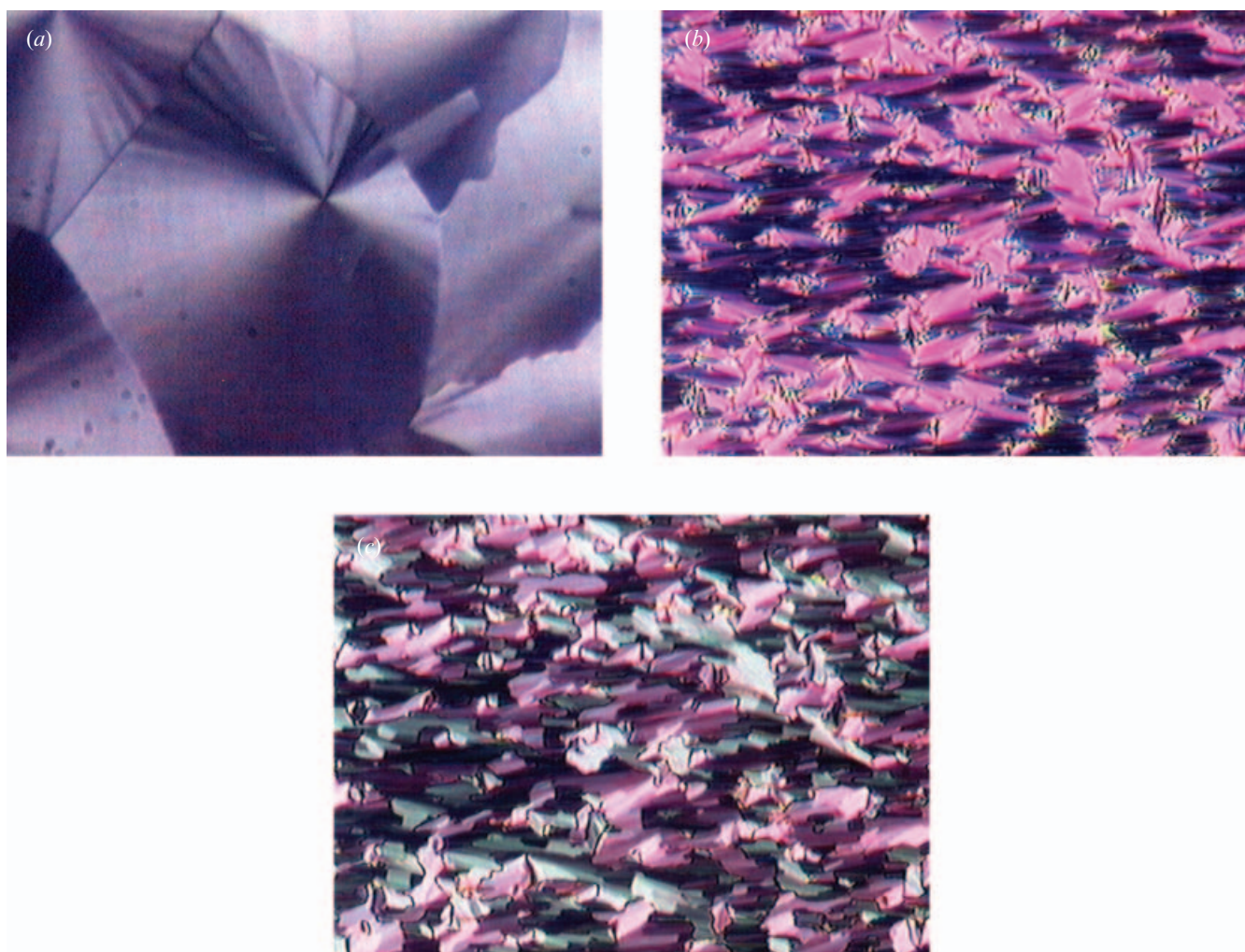


Figure 5. Compound **5d**: (a) texture of the undulated smectic phase obtained on cooling the homeotropic SmA phase; (b) fan-shaped texture of the SmA phase ($T=185^{\circ}\text{C}$); (c) texture of the undulated smectic phase obtained after applying of an electric field ($15\text{--}20\text{ V }\mu\text{m}^{-1}$, $T=180^{\circ}\text{C}$).

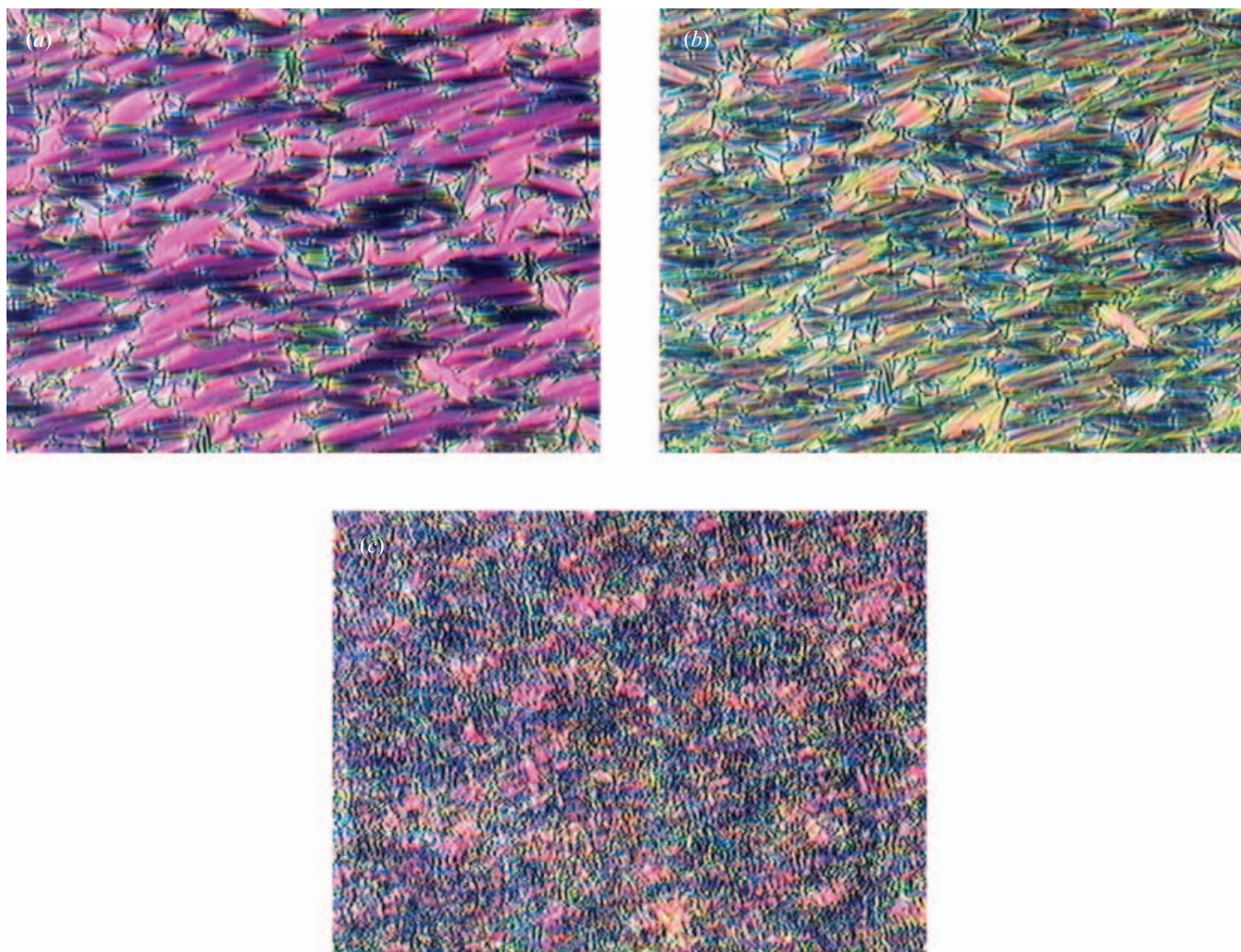


Figure 6. Compound **5e**: (a) fan-shaped texture of the SmA phase ($T=195^{\circ}\text{C}$); (b) fan-shaped texture of the SmA' phase ($T=187^{\circ}\text{C}$); (c) 'Grainy' texture of the SmCP_A phase ($T=180^{\circ}\text{C}$).

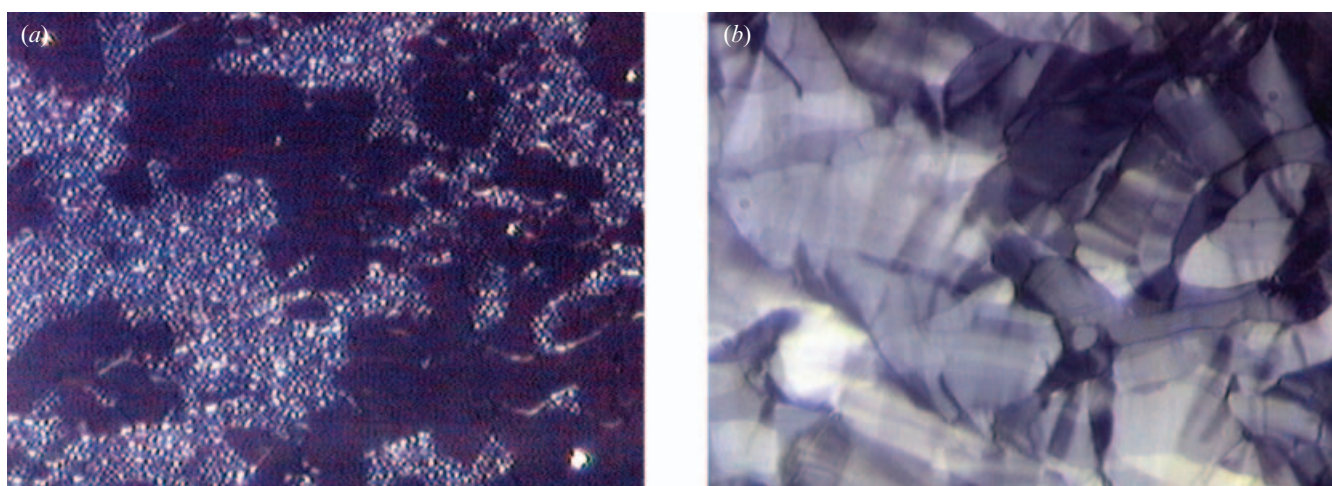


Figure 7. Compound **5e**: (a) homeotropic texture of the SmA' phase with grainy islands ($T=185^{\circ}\text{C}$); (b) scale-like texture of the SmCP_A phase ($T=175^{\circ}\text{C}$).

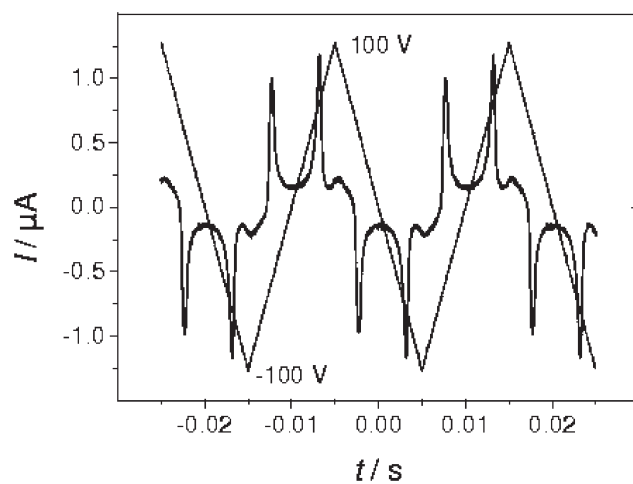


Figure 8. Switching current response in the SmCP_A phase of compound **5e** ($T=155^\circ\text{C}$, $U=200 \text{ V}_{\text{pp}}$).

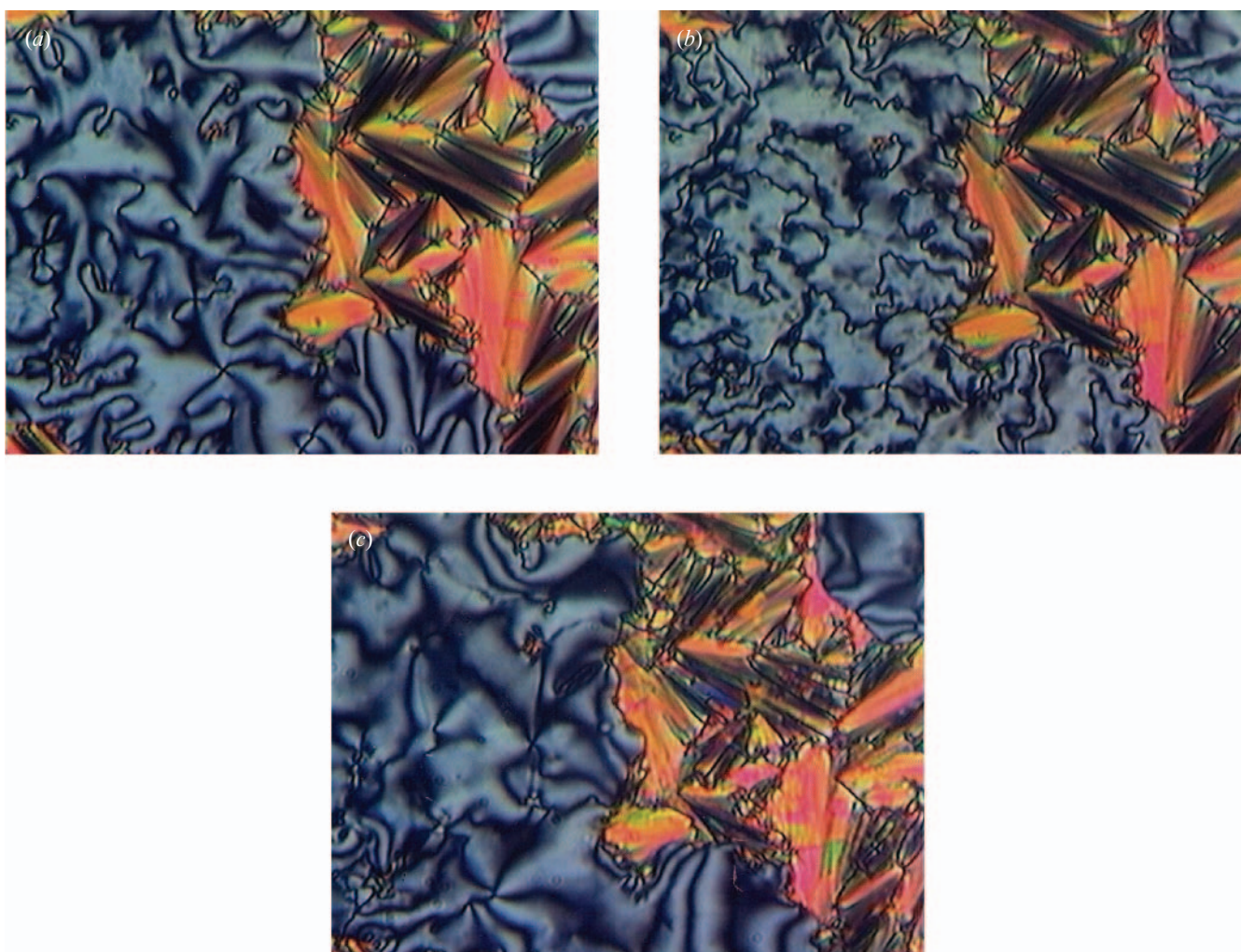


Figure 9. Optical texture of the smectic phases of compound **5f**: (a) SmC phase ($T=172^\circ\text{C}$); (b) SmCP_A phase ($T=155^\circ\text{C}$); (c) SmCP_A' phase ($T=140^\circ\text{C}$).

minor structural differences. Furthermore, the low temperature SmA phase of compound **5e** occurs only on cooling the SmA high temperature phase and is suppressed on heating the SmCP_A phase. In compound **4c** islands of a birefringent schlieren texture can be induced within the homeotropic sample. Therefore one can imagine that a biaxial structure is induced by a field-induced tilt, or by a field-induced alignment of randomly distributed polar clusters (SmAP) within the smectic layers.

Comparing the five- and six-ring compounds it is clear that the five-ring compounds form mesophases typical for bent molecules whereas six-ring compounds exhibit both banana phases and conventional smectic phases. Six-ring compounds form in some cases only non-polar smectic phases, in other cases banana-phases as well as non-polar smectic phases. The absence of polar smectic phases is an indication that the molecules are more or less stretched. The occurrence of both banana and conventional smectic phases for the same compound can be understood if the bending angle is relatively high ($\approx 140^\circ$ – 150°) and decreases with decreasing temperature. The relationship between a temperature-dependent bending angle and the occurrence of polymorphism variants with banana phases and non-polar smectic phases has been thoroughly studied in symmetric five-ring bent-core mesogens [13, 14]. Unfortunately, we were unable to determine the bending angle and its temperature dependence for the compounds under discussion.

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