

# New bent-core mesogens with carbon–carbon multiple linkages in the terminal chains†‡

Gerhard Pelzl, Maria G. Tamba, Sonja Findeisen-Tandel, Martin W. Schröder, Ute Baumeister, Siegmur Diele and Wolfgang Weissflog\*

Received 29th February 2008, Accepted 23rd April 2008

First published as an Advance Article on the web 15th May 2008

DOI: 10.1039/b803493a

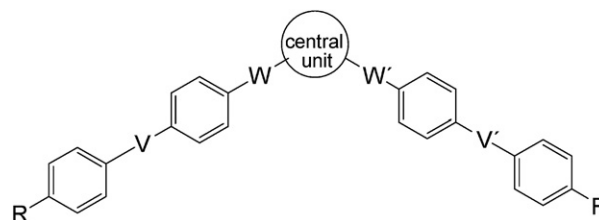
New five-ring bent-core mesogens have been synthesized in which terminal alkynyl chains are connected with the terminal rings of the aromatic core by means of oxycarbonyl groups, cinnamic esters groups or oxyacetic ester moieties. The insertion of C–C triple bonds in different positions of the terminal chains can change the mesophase behaviour and can result in an increase or decrease of the clearing temperatures in comparison to corresponding compounds with saturated chains. In addition, lateral substituents are attached to different positions of the central ring. The mesophase behaviour of the new compounds has been studied by polarizing microscopy, differential scanning calorimetry, X-ray experiments and electro-optical measurements. On the base of the experimental findings new relationships between the molecular structure and the mesomorphic properties have been obtained. Different polar phases (SmCP, Col, B<sub>7</sub>) could be proved, in some of these the polar (ferro- or antiferroelectric) switching takes place through a collective rotation of the molecules around their long axes. Interestingly, three compounds with terminal alkynyl chains form a mesophase with all textural features of a B<sub>7</sub> phase although these phases possess obviously a simple layer structure. For the first time it could be observed that helical filaments formed on slow cooling the isotropic liquid are stable to low temperatures. Some of these spirals can serve as nuclei in the growing process of ribbon-like and oval domains. Surprisingly, the helical pitch of the spirals can be exactly recovered in the equidistant stripes of these domains. It is also remarkable that all compounds derived from 2-methylisophthalic acid exhibit unusually high clearing temperatures and that the SmC phases of these compounds show polar switching about 50 K below the SmA–SmC transition temperature.

## Introduction

In 1996 Niori *et al.*<sup>1</sup> discovered that bent-core (banana-shaped) molecules without molecular chirality are able to form fluid smectic phases with polar order. Due to their intrinsic shape the molecules can be packed in the bent direction which leads to a long-range correlation of the lateral dipoles. Depending on the polar order correlation between adjacent layers ferroelectric or antiferroelectric phases can occur. From the new smectic phases 2D phases (columnar phases) can also be derived which are considered to be made from layer fragments (broken layers). In addition, in such smectic phases supramolecular chirality can occur although the constituent molecules are achiral.<sup>2,3</sup> Because of their unusual properties these new phases have attracted much attention and bent-core mesogens have been developed to a topical subfield of liquid crystal research.<sup>4–9</sup> The properties of the new phases formed by bent-core mesogens are not only interesting from the theoretical point of view, but also with

respect to possible practical applications. For example, they might be candidates for switchable nonlinear optical materials in high-modulation devices.<sup>10</sup>

The properties of these new phases formed by bent-core molecules ('banana phases') are clearly related to the molecular structure as summarized in recent reviews.<sup>4–9</sup> Most of the bent-core mesogens are characterized by five or more aromatic rings, which are linked by connecting groups V, W well known from calamitic mesogens, *e.g.* COO, CH=N, CH=CH, COS, N=N, as depicted in Scheme 1. In many cases the bending angle of about 120° results from the 1,3-disubstitution at the central phenyl ring. The central phenyl ring can be substituted by a naphthyl unit or by a five- or six-membered heterocyclic ring. There are examples, however, where the molecular bend is introduced by a single unit, like -O-, -S-, -CH<sub>2</sub>-, -CO-<sup>11,12</sup> or by a short odd-numbered spacer, which connects two calamitic



Scheme 1 General molecular design of bent-core mesogens.

Martin-Luther-Universität Halle-Wittenberg, Institut für Physikalische Chemie, Mühlpforte 1, 06108 Halle, Germany. E-mail: weissflog@chemie.uni-halle.de

† This paper is part of a *Journal of Materials Chemistry* theme issue on Liquid Crystals Beyond Display Applications. Guest editor: Carsten Tschierske.

‡ Electronic supplementary information (ESI) available: Further analytical data, tables and POM images. See DOI: 10.1039/b803493a

moieties to each other.<sup>13,14</sup> It is interesting to mention that also in the case of a central 1,3-phenylene fragment the bending angle can considerably deviate from 120°. This is a consequence of lateral substituents positioned in the neighbourhood of the connecting groups linked to the central phenyl ring, which can cause a change of the molecular shape from bent to a nearly calamitic shape.<sup>15,16</sup>

With respect to the present paper the wing groups **R** attached at both terminal phenyl rings are of special interest. They have a strong influence on the type and existence range of 'banana phases'. In the vast number of compounds reported up to now alkyloxy chains have been used. With an increasing number of carbon atoms in these chains a change of the mesophase type from SmC<sub>c</sub> (B<sub>6</sub>) to Col (B<sub>1</sub>) to SmCP phases was observed in several homologous series.<sup>17–19</sup> Terminal alkyl chains can also be directly connected to the outer phenyl rings,<sup>17,20</sup> or by means of sulfur.<sup>21,22</sup> The connection of an alkyl chain to each of the outer aromatic rings by means of carboxylic units was used by Bedel *et al.*<sup>23,24</sup> to prepare compounds with an unusual polymorphism as discussed below. These derivatives served as parent compounds for us in order to modify the terminal chains by the insertion of carbon–carbon multiple bonds.

The effect of microsegregation is of influence if terminal groups are introduced which are chemically incompatible with hydrocarbon and aromatic moieties.<sup>25</sup> Three different types of fragments capable of microsegregation were attached to bent-core mesogens: perfluoroalkyl chains,<sup>26,27</sup> oligo(siloxane)- and carbosilane-terminated chains,<sup>17,28,29</sup> and the tetra(ethylene glycol) fragment<sup>30</sup> in one example, only. The combination of a perfluoroalkyl and a siloxanyl-terminated chain in bent-core mesogens was also described.<sup>31</sup>

In some cases the terminal chains of bent-core mesogens were branched to prepare chiral banana-shaped liquid crystals.<sup>7</sup> These compounds are used to study the competition between molecular and supramolecular chirality. Takezoe *et al.*<sup>32</sup> inserted an additional oxygen atom in such methyl branched carbon chains. The combination of a long aliphatic chain attached to one terminal end with a polar group on the other end results in nematic and smectic phases with a high tendency to form biaxial phases.<sup>17</sup>

Only a few compound bearing carbon–carbon multiple bonds in one or both of the terminal chains have been reported. Most of these are intermediate products to prepare siloxane containing bent-core mesogens by hydrosilylation reaction of a corresponding  $\omega$ -alkenyl substituted compound. Depending on the chemical structure and functionality of the reaction partners monomeric,<sup>28,29</sup> dimeric,<sup>33,34</sup> dendrimeric and polymeric materials<sup>35,36</sup> containing bent-core moieties have been prepared. Furthermore, terminally acrylate and dienyl substituted monomers have been synthesized as intermediates for corresponding polymers containing bent-core mesogenic units.<sup>30,37–40</sup> Some references related to bent-core mesogens with carbon–carbon double bonds in the wing groups are listed in Table S1 (see ESI†). To our knowledge, bent-core mesogens with carbon–carbon triple bonds in the terminal alkyl chains have not been reported up to now.

In most cases the  $\omega$ -alkenyloxy substituted bent-core mesogens exhibit phase behaviour identical or similar to that of the corresponding alkyloxy terminated compounds. Some related pairs of compounds are listed in Table S2 (see ESI†). For these

examples the derivatives bearing undecenyoxy chains in both terminal positions exhibit the lower mesophase stability in comparison to the corresponding undecyloxy compounds which is indicated by the decrease of the clearing temperatures ( $\Delta T$ ) by –11 to –20 K. The larger the aromatic core the lower the effect of mesophase destabilization by the carbon–carbon double bond, however, the type of mesophase is not changed.

To study the influence of carbon–carbon triple bonds on the mesophase behaviour of bent-core mesogens, three series **A–C** of new compounds have been prepared. Esters of isophthalic acid served as basic mesogens. The alkyloxycarbonyl substituted homologous series **A** (Scheme 2, RY- = alkyloxycarbonyl) was the starting point of our study due to its unusual polymorphism and the occurrence of SmC<sub>G</sub> phases as reported by Bedel *et al.*<sup>23,24</sup>

In the new derivatives presented here, carbon–carbon triple bonds are inserted in different positions of the aliphatic chains, see Scheme 2. Both terminal wing groups are identical. Additionally in series **B** and **C**, the corresponding compounds with saturated alkyloxy chains have been synthesized for comparison. In series **A** the aliphatic chains (saturated or unsaturated) are linked to the aromatic core by means of oxycarbonyl groups (alkyloxycarbonyl, alkynyloxycarbonyl groups), in series **B** by an acrylate fragment (resulting in terminal cinnamic ester) and in series **C** by an oxyacetic ester moiety (giving terminal phenoxy acetic esters). Furthermore, lateral substituents **Z** (4-Br, 5-NO<sub>2</sub>, 2-CH<sub>3</sub>, 5-CH<sub>3</sub>) are attached to the central phenyl ring of the five-ring bent-core mesogens bearing tetradecyl and tetradecynyl chains, to study their influence on the mesophase behaviour. In a few examples, a lateral methyl group is attached to the middle phenyl rings in positions **X**. The alkyl and unsaturated hydrocarbon chains used are listed in Scheme 2.

## Experimental

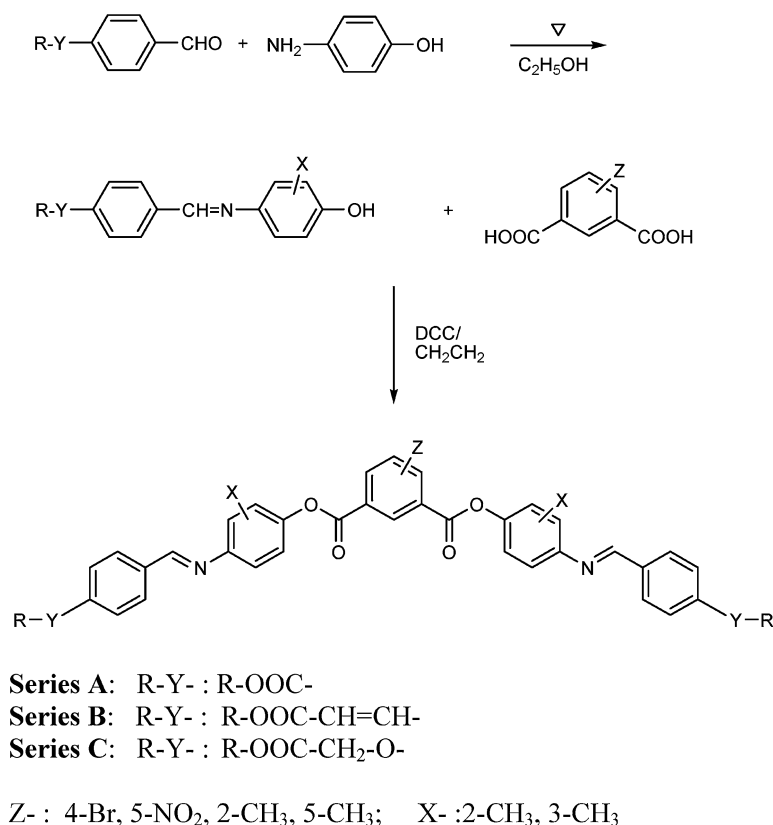
### Materials

The members of all three series were prepared as shown in Scheme 2. The synthesis corresponds to the preparation of the parent molecules reported by Bedel *et al.*<sup>24</sup>

Esterification of 4-formylbenzoic acid, 4-formylcinnamic acid and 4-formylphenoxyacetic acid with different long-chain alkanols and alkynols was performed in dichloromethane in the presence of dicyclohexylcarbodiimide and 4-dimethylaminopyridine as catalyst.

Condensation of these formyl substituted intermediates with 4-aminophenol and methyl substituted 4-aminophenols, respectively, in boiling ethanol with a few drops of acetic acid as catalyst yielded the corresponding 4-substituted benzylidene-aminophenols. This condensation also works with crude formyl compounds, which exhibit low melting temperatures in some cases. Reaction of isophthalic acid and laterally substituted isophthalic acids with two equivalents of the phenolic intermediates resulted in the final compounds which were recrystallized from DMF–ethanol and ethyl acetate several times.

In the following, the preparation of compound **C14-Me-2** is described in detail together with analytical data. Furthermore, NMR data are given for selected derivatives of all three series **A–C**. The short name of the final compounds is composed of the



Abbreviation of R	Chemical name of R	Chemical formula of R
12	dodecyl-1	—C <sub>12</sub> H <sub>25</sub>
12/in-9	9-dodecyn-1-yl	—(CH <sub>2</sub> ) <sub>8</sub> C≡CC <sub>2</sub> H <sub>5</sub>
14	tetradecyl-1	—C <sub>14</sub> H <sub>29</sub>
14/in-3	3-tetradecyn-1-yl	—CH <sub>2</sub> CH <sub>2</sub> C≡CC <sub>10</sub> H <sub>21</sub>
16	hexadecyl-1	—C <sub>16</sub> H <sub>33</sub>
16/in-7	7-hexadecyn-1-yl	—(CH <sub>2</sub> ) <sub>6</sub> C≡CC <sub>8</sub> H <sub>17</sub>
16/in-9	9-hexadecyn-1-yl	—(CH <sub>2</sub> ) <sub>8</sub> C≡CC <sub>6</sub> H <sub>13</sub>
16/in-11	11-hexadecyn-1-yl	—(CH <sub>2</sub> ) <sub>10</sub> C≡CC <sub>4</sub> H <sub>9</sub>

**Scheme 2** General formula of the new compounds showing the hydrocarbon chains of different length and structure and their linking to the aromatic core as well as the position and type of lateral substituents. Used terminal alkyl and alkynyl groups are listed together with their abbreviations.

character of the series, the abbreviation of the terminal hydrocarbon chains (given in Scheme 2), the lateral substituent Z and its position at the central isophthalic moiety.

## Procedure

### Bis[4-(4-*n*-tetradecyloxycarbonylmethoxybenzylideneamino)-phenyl] 2-methylisophthalate (C14-Me-2)

**Step 1: Tetradecyl 4-formylphenoxyacetate.** 1.8 g (0.01 mol) 4-formylphenoxyacetic acid and 2.4 g (0.011 mol) 1-tetradecanol were dissolved in 50 ml dichloromethane. 2.3 g (0.011 mol) dicyclohexylcarbodiimide and a small amount of 4-dimethylaminopyridine as catalyst were added and the mixture was allowed to stir at room temperature for about 24 h. Dicyclohexylurea was filtered off, the solvent evaporated and the residue recrystallized from ethanol. Yield: 2.90 g, 77.0%, white crystals,

mp 52.8 °C [ $\Delta H = 63.9 \text{ kJ mol}^{-1}$ ]. Elemental analysis: C<sub>23</sub>H<sub>36</sub>O<sub>4</sub>,  $M = 376.518$ : C 73.36, H 9.64 (calc.), 72.98, H 9.66% (found); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  0.86 (m, 3 H, CH<sub>3</sub>), 1.24–1.26 (m, 22 H, CH<sub>2</sub>), 1.63 (m, 2 H, ArOCH<sub>2</sub>COOCH<sub>2</sub>CH<sub>2</sub>), 4.19 (t, <sup>3</sup> $J = 6.7$  Hz, 2 H, ArOCH<sub>2</sub>COOCH<sub>2</sub>CH<sub>2</sub>), 4.69 (s, 2 H, ArOCH<sub>2</sub>COOCH<sub>2</sub>CH<sub>2</sub>), 6.99 (d, <sup>3</sup> $J = 8.7$  Hz, 2 H, Ar-H), 7.83 (d, <sup>3</sup> $J = 8.9$  Hz, 2 H, Ar-H), 9.88 (s, 1 H, CHO).

**Step 2: Tetradecyl 4-(4-hydroxyphenylaminomethyl)phenoxyacetate.** A solution of 3.76 g (0.01 mol) tetradecyl 4-formylphenoxyacetate, 1.1 g (0.01 mol) 4-aminophenol and a few drops of acetic acid in 50 ml ethanol were refluxed for two hours. After cooling to 10 °C the precipitate was separated and recrystallized from ethanol or heptane twice. Yield: 2.25 g, 48.2%, slightly yellow powder, mp 94.8 °C [ $\Delta H = 64.9 \text{ kJ mol}^{-1}$ ]. Elemental analysis: C<sub>29</sub>H<sub>41</sub>O<sub>4</sub>N ( $M_m = 467.62$ ) C 74.48, H 8.84,

N 3.00 (calc.); C 74.22, H 9.05, N 2.70% (found);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.86 (t,  $^3J = 6.8$  Hz, 3 H,  $\text{CH}_3$ ), 1.23–1.28 (m, 22 H,  $\text{CH}_2$ ), 1.62 (m, 2 H,  $\text{ArOCH}_2\text{COOCH}_2\text{CH}_2$ ), 4.19 (t,  $^3J = 6.7$  Hz, 2 H,  $\text{ArOCH}_2\text{COOCH}_2\text{CH}_2$ ), 4.66 (s, 2 H,  $\text{ArOCH}_2\text{COOCH}_2\text{CH}_2$ ), 5.54 (bs, 1 H, OH), 6.80 (d,  $^3J = 8.7$  Hz, 2 H, Ar–H), 6.95 (d,  $^3J = 8.8$  Hz, 2 H, Ar–H), 7.11 (d,  $^3J = 8.8$  Hz, 2 H, Ar–H), 7.80 (d,  $^3J = 8.8$  Hz, 2 H, Ar–H), 8.37 (s, 1 H,  $\text{CH}=\text{N}$ ).

**Step 3:** Bis[4-(4-*n*-tetradecyloxycarbonylmethoxybenzylideneamino)phenyl] 2-methylisophthalate (**C14-Me-2**). A mixture of 5.1 g (0.011 mol) tetradecyl 4-(4-hydroxyphenylamino-methyl)phenoxyacetate, 0.9 g (0.005 mol) 2-methylisophthalic acid, 2.3 g (0.011 mol) dicyclohexylcarbodiimide and a catalytic amount of 4-dimethylaminopyridine in 80 ml dichloromethane was stirred at room temperature for about 24 h. Precipitated dicyclohexylurea was separated, the dichloromethane evaporated and the crude materials purified by recrystallisation from DMF–ethanol and ethyl acetate several times. Yield: 2.05 g, 38.0% of slightly cream-coloured crystals. Melting behaviour: see Table 5 (later). Elemental analysis:  $\text{C}_{67}\text{H}_{86}\text{O}_{10}\text{N}_2$  ( $M_m = 1080.37$ ) C 74.48, H 8.02, N 2.59 (calc.); C 74.26, H 7.96, N 2.32% (found);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  0.86 (m, 6 H,  $\text{CH}_3$ ), 1.25–1.27 (m, 44 H,  $\text{CH}_2$ ), 1.64 (m, 4 H,  $\text{ArOCH}_2\text{COOCH}_2\text{CH}_2$ ), 2.90 (s, 3 H, Ar– $\text{CH}_3$ ), 4.20 (t,  $^3J = 6.7$  Hz, 4 H,  $\text{ArOCH}_2\text{COOCH}_2\text{CH}_2$ ), 4.68 (s, 4 H,  $\text{ArOCH}_2\text{COOCH}_2\text{CH}_2$ ), 6.98 (d,  $^3J = 8.9$  Hz, 4 H, Ar–H), 7.24 (m, 8 H, Ar–H), 7.45 (t,  $^3J = 7.1$  Hz, 1 H, Ar–H), 7.85 (d,  $^3J = 8.9$  Hz, 4 H, Ar–H), 8.19 (m, 2 H, Ar–H), 8.39 (s, 2 H,  $\text{CH}=\text{N}$ ).

Analytical data of further final products are given in ESI.†

## Physical measurements

The phase transition temperatures as well as the transition enthalpies were determined using a Perkin-Elmer Pyris 1 differential scanning calorimeter. The optical textures and the field-

induced texture changes were examined using a polarizing microscope (DMRXP, Leica) equipped with a hot stage HT80 and an automatic temperature controller (Mettler-Toledo). X-Ray investigations on non-oriented samples were performed using the Guinier film method and a small angle camera. Electro-optical measurements were done by a standard experimental set-up using commercially available sandwich cells (EHC Corp., Japan) with a cell thickness of 5, 6 or 10  $\mu\text{m}$ .

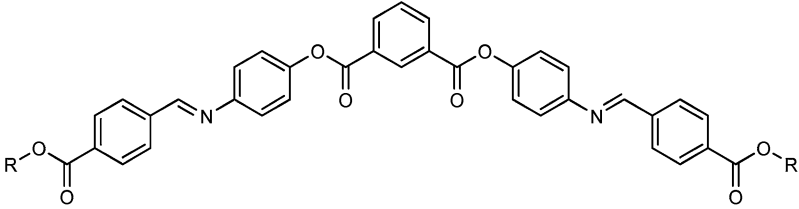
## Results

### Bent-core compounds A without and with a carbon–carbon triple bond in the terminal chains

Table 1 presents eight bent-core compounds which possess the same rigid core consisting of five benzene rings connected by ester and azomethine groups. The compounds without carbon–carbon multiple bonds in the terminal chains (**A12**, **A14**, **A16**) which have been already reported by Bedel *et al.*<sup>23,24</sup> show very interesting phase behaviour. As found by detailed X-ray investigations, compounds **A12** and **A14** form a mesophase with a smectic bilayer structure built up with two associated  $\text{SmC}_G$  layers and a synclinal arrangement of the tilted molecules. In addition, the layers are broken into single fragments which leads to a two-dimensional superstructure ( $\text{Sm}\bar{\text{C}}_S\text{G}_2\text{P}_A$ ). The longer-chained homologue **A16** exhibits smectic dimorphism. The low-temperature phase is an antiferroelectric  $\text{SmCP}_A$  phase whereas in the smectic high-temperature phase ( $\text{USmCP}_A$ ) the layers are undulated with an undulation period of about 150 Å.<sup>23,24</sup>

Compounds **A12/in-9**, **A14/in-3**, **A16/in-7**, **A16/in-9**, and **A16/in-11** contain carbon–carbon triple bonds within the terminal chains but depending on the used alkynol this triple bond is located in different positions of the terminal chain (see Scheme 2). For example, in compound **A14/in-3** the carbon–carbon triple bond

**Table 1** Influence of carbon–carbon multiple bonds inserted in terminal alkyl chains (series A)



No.	$\text{Cr}^a$	$\text{SmCP}_A$	polar $\text{SmC}$	Is	$\Delta T^b$
<b>A12</b>	• 174.4 [39.8]	—	• 182.7 <sup>c</sup> [21.1]	•	
<b>A12/in-9</b>	• 159.6 [62.1]	—	(• 147.5) <sup>d</sup> [17.5]	•	$\Delta T$ : –35 K
<b>A14</b>	• 169.6 [44.5]	—	• 176.9 <sup>c</sup> [21.1]	•	
<b>A14/in-3</b>	• 166.9 [61.1]	175.0 [0.3]	• 187.3 <sup>c</sup> [26.3]	•	$\Delta T$ : +10 K
<b>A16</b>	• 166.9 [43.7]	(• 153.7) [0.44]	• 172.6 <sup>c</sup> [19.5]	•	
<b>A16/in-7</b>	• 147.8 [60.5]	(• 131.1) [15.5]	—	•	$\Delta T$ : –41 K
<b>A16/in-9</b>	• 147.5 [62.4]	(• 132.1) [15.6]	—	•	$\Delta T$ : –40 K
<b>A16/in-11</b>	• 152.0 [63.4]	(• 138.1) [16.6]	—	•	$\Delta T$ : –34 K

<sup>a</sup> Some of the compounds show crystalline polymorphism. <sup>b</sup>  $\Delta T$ : Change of the clearing temperatures caused by insertion of the carbon–carbon triple bonds in carbon chains of the same length. <sup>c</sup>  $\text{Sm}\bar{\text{C}}_S\text{G}_2\text{P}_A$  phase.<sup>23</sup> <sup>d</sup>  $\text{B}_7'$  phase (only by polarizing optical microscopy (POM) studies). <sup>e</sup>  $\text{B}_7'$  phase.

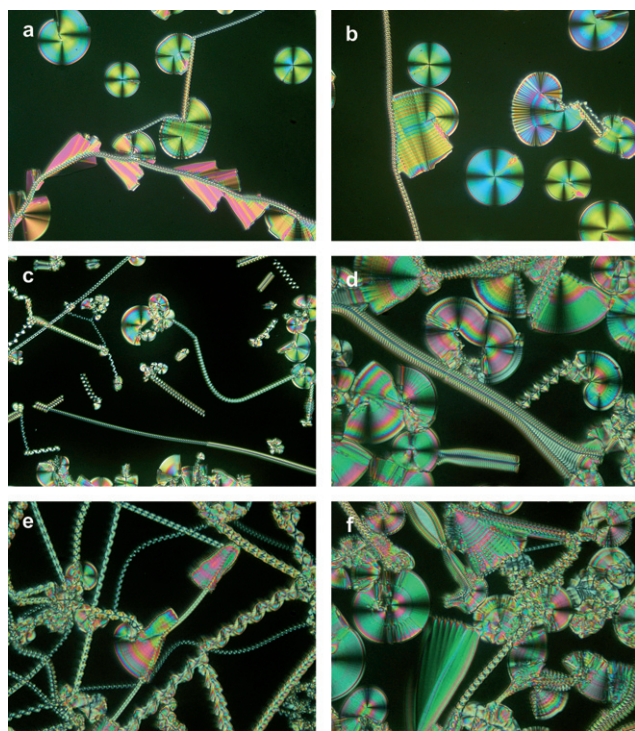
<sup>f</sup>  $\text{USmCP}_A$  phase.<sup>23</sup>



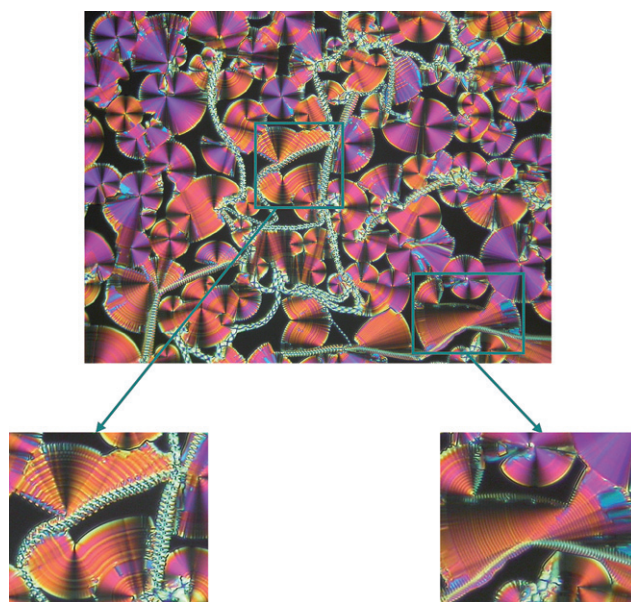
bonds are relatively near the terminal phenyl rings in contrast to the compounds **A12/in-9**, **A16/in-7**, **A16/in-9** and **A16/in-11**.

Compound **A12/in-9** forms a monotropic mesophase which could not be clearly identified because it immediately crystallizes after its formation. The occurrence of ribbon-like and screw-like nuclei is reminiscent of a  $B_7$  phase.

Compound **A14/in-3** where the triple bond is near the terminal rings possesses a clearing temperature which is higher by 10 K than in the corresponding compound without carbon–carbon triple bonds (**A14**). It follows from X-ray investigations on a non-aligned sample that this mesophase exhibits a simple smectic layer structure without in-plane order. The layer spacing  $d$  (50 Å) is clearly smaller than the molecule length  $L$  (60 Å) determined for a molecular model with a bending angle of  $120^\circ$ . From  $d$  and  $L$  the tilt angle  $\theta$  of about  $35^\circ$  could be estimated using the equation  $\cos\theta = d/L$ . On slow cooling of the isotropic liquid the texture shows circular and oval domains the extinction crosses of which are parallel to the crossed polarizers. In addition a lot of beautiful nuclei can appear: above all quite different kind of spiral nuclei indicating a helicoidal structure, furthermore ribbons with equally spaced lines and 2D periodic patterns, see Fig. 1 and 2. Additional examples are given in ESI† to allow the study of the texture formation in more detail. We observed for the first time that the screw-like helical domains do not disappear on cooling but remain stable up to the crystallization. It is also remarkable that banana leaf-like domains, circular and oval domains and ribbon-like domains can nucleate directly from the stable screw-like domains. Interestingly, the periodicity of the ribbon-like domain is the same as that in the basic screw-like domains, as demonstrated in Fig. 2. The different nuclei which



**Fig. 1** Nucleation of the  $B_7'$  phase of compound **A14/in-3**, which can be observed on different places of the microscopic samples. a, b: Sample thickness 6  $\mu\text{m}$ ; c–f: sample thickness 10  $\mu\text{m}$ .



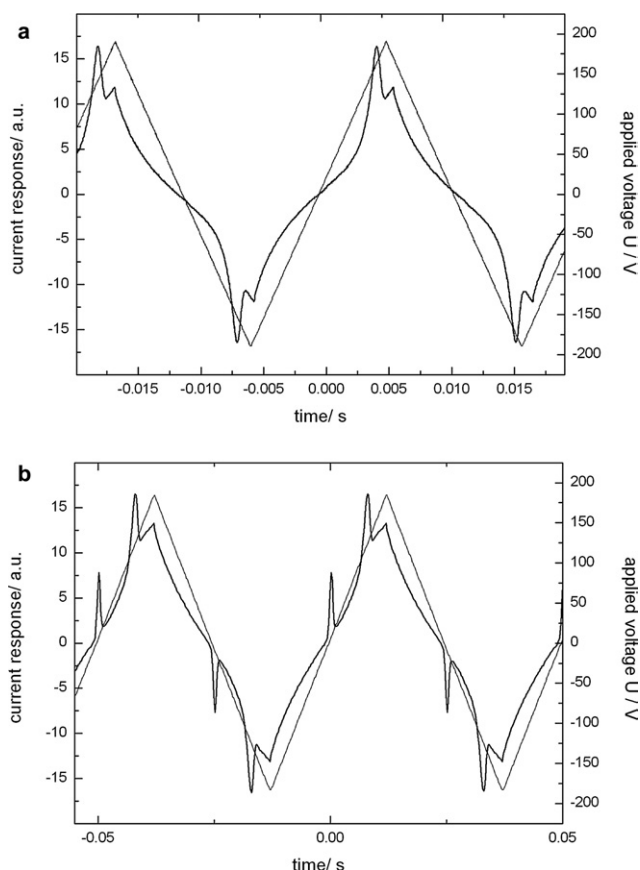
**Fig. 2** Nucleation of the  $B_7'$  phase of compound **A14/in-3**, which demonstrates the relation between the pitch of the spiral domains and the periodicity of the oval and ribbon-like domains (sample thickness 6  $\mu\text{m}$ ). The enlarged details support these connections.

occur simultaneously in different regions of the sample coalesce to a complex texture which is typical for  $B_7$  phases.

Above  $175^\circ\text{C}$  the application of a sufficiently high electric field ( $10\text{ V }\mu\text{m}^{-1}$ ) leads to the formation of a fan-like texture which is independent of the polarity of the applied field. If the field is removed the texture remains nearly unchanged, only the birefringence is slightly changed. This switching is accompanied by a current response with only one peak per half period of the applied field indicating a ferroelectric ground state ( $P_S = 380\text{ nC cm}^{-2}$ ) (Fig. 3a). The switching is obviously based on the collective rotation of the molecules around their long axes. At  $175^\circ\text{C}$  a phase transition takes place which is indicated by a small calorimetric peak. In the low-temperature phase the textures of the ground state and the switched states are clearly different and two current peaks per half period are observed (Fig. 3b).

At low fields ( $<2\text{ V }\mu\text{m}^{-1}$ ) the texture of switched states is different for an opposite polarity of the field. This points to a switching from an anticlinic antiferroelectric to a synclinic ferroelectric state ( $\text{SmC}_A\text{P}_A\text{--SmC}_S\text{P}_F$ ). Above  $2\text{ V }\mu\text{m}^{-1}$  the texture of the switched state is independent of the electric field which corresponds to a synclinic antiferroelectric ground state ( $\text{SmC}_S\text{P}_A$ ) which is switched into an anticlinic ferroelectric state ( $\text{SmC}_A\text{P}_F$ ) ( $P_S = 850\text{ nC cm}^{-2}$ ). It is remarkable that at lower temperature the distance between the current peaks becomes clearly closer and the threshold decreases to  $2\text{--}3\text{ V }\mu\text{m}^{-1}$ . Furthermore, the field-induced fan-shaped texture shows domains of opposite handedness, which was also reported for SmCP phases of other bent-core compounds.<sup>41</sup>

The isomeric compounds **A16/in-7**, **A16/in-9** and **A16/in-11** are only distinguished by the position of the carbon–carbon triple bond in the terminal chains. By supercooling, all these compounds form a monotropic mesophase which exhibits a fan-like texture with many defects. This mesophase crystallizes a few



**Fig. 3** Compound **A14/in-3**: (a) switching current response in the high-temperature phase obtained under a triangular wave field (383 V<sub>pp</sub>; 45 Hz) at 185 °C, sample thickness 5 μm; (b) switching current response in the SmCP<sub>A</sub> phase obtained under a triangular wave field (368 V<sub>pp</sub>; 20 Hz) at 174 °C.

minutes after its formation so that detailed measurements were impossible, however the time was sufficient to observe the textures as well as the field-induced changes of the textures. We found at electric fields of about 10 V μm<sup>-1</sup> that the grainy texture

transforms into a smooth fan-like texture which is independent of the polarity of the field. This finding suggests a field-induced transition SmC<sub>S</sub>P<sub>A</sub> to SmC<sub>A</sub>P<sub>F</sub>.

### Bent-core compounds **B** with and without triple bonds inserted in the alkyl chains of terminal cinnamic esters

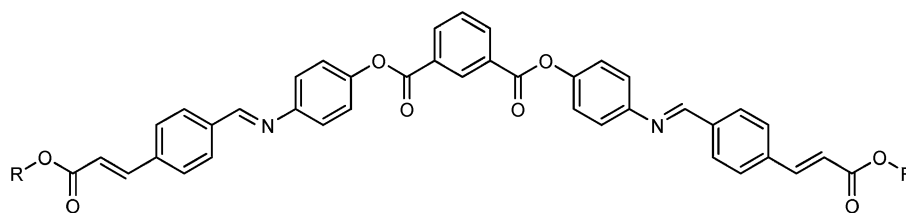
Compounds **B12**, **B12/in-9**, **B14**, **B14/in-3**, **B16**, **B16/in-7** presented in Table 2 have an analogous structure to the compounds **A12**, **A12/in-9**, **A14**, **A14/in-3**, **A16**, **A16/in-7**. The only difference in compounds **B** is an additional C≡C unit inserted between the carboxyl group and the outer phenyl rings which results in cinnamic esters. It is seen from Table 2 that the insertion of the cinnamic groups leads to a stabilization of the mesophases indicated by clearly higher clearing temperatures.

Compound **B12** which does not possess carbon–carbon triple bonds in the terminal chains forms a mesophase, the optical texture of which exhibits fan-like domains with irregular stripes perpendicular to the fans. According to X-ray investigations this mesophase could be identified as a smectic phase with a simple layer structure. The layer spacing *d* was found to be 51.4 Å which is clearly smaller than the molecular length *L* of the bent conformation (*L* = 63 Å) corresponding to a tilt angle *θ* of about 35°. Above a threshold field of about 2 V μm<sup>-1</sup> the smectic phase is switchable, *i.e.* the grainy texture is transformed into a smooth fan-shaped texture. The current response shows two peaks per half period of a triangular voltage. From the current response a switching polarization of 820 nC cm<sup>-2</sup> was determined. Since the textures of the switched states are equal for a different sign of the field an antiferroelectric ground state (SmC<sub>S</sub>P<sub>A</sub>) can be assumed which is switched into the ferroelectric state (SmC<sub>A</sub>P<sub>F</sub>).

The homologue **B14** also forms a smectic phase without in-plane order. The texture, the field-induced textures, the threshold field, the current response and the magnitude of the polarization (800 nC cm<sup>-2</sup>) are quite similar to those of the homologue **B12** discussed before.

In contrast to the lower homologues compound **B16** forms two mesophases. The high-temperature phase displays a mosaic

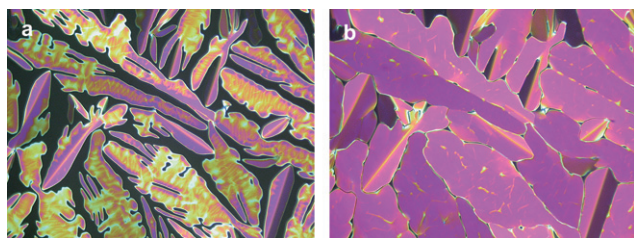
**Table 2** Influence of carbon–carbon triple bonds inserted in the alkyl chains of terminal cinnamic esters (series **B**)



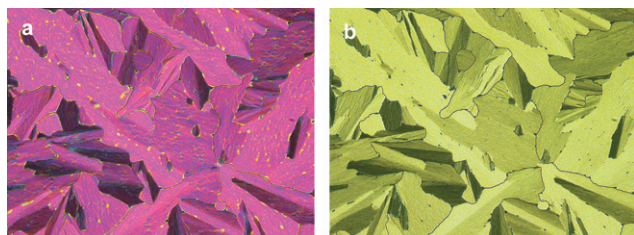
No.	Cr <sup>a</sup>	SmCP <sub>A</sub>	ColP <sub>A</sub>	Is	ΔT <sup>b</sup>
<b>B12</b>	• 170.6 [60.8]	• 224.2 [23.1]	—	•	
<b>B12/in-9</b>	• 162.1 [30.6]	• 197.3 [19.5]	—	•	ΔT: -27 K
<b>B14</b>	• 160.3 [52.1]	• 216.9 [17.2]	—	•	
<b>B14/in-3</b>	• 189.2 [68.5]	• 225.4 <sup>c</sup> [28.1]	—	•	ΔT: +9 K
<b>B16</b>	• 167.2 [44.6]	• 197.1 [0.3]	• 214.8 [22.4]	•	
<b>B16/in-7</b>	• 158.2 [35.9]	• 179.8 <sup>d</sup> [18.6]	—	•	ΔT: -35 K

<sup>a</sup> Some of the compounds show crystalline polymorphism. <sup>b</sup> ΔT: Change of the clearing temperatures caused by insertion of the carbon–carbon triple bonds in carbon chains of the same length. <sup>c</sup> B<sub>7</sub>' phase according to textural features. <sup>d</sup> SmCP<sub>F</sub> phase.

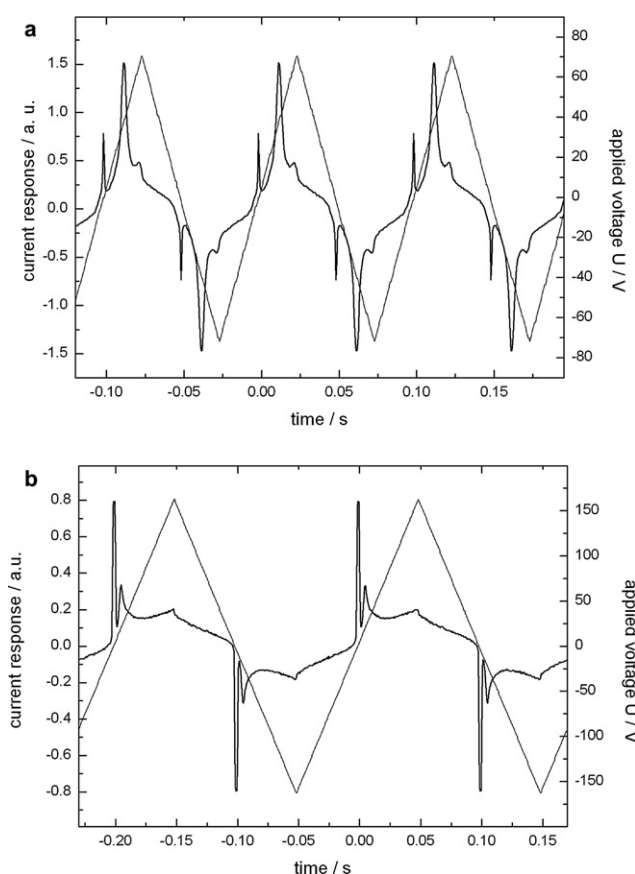




**Fig. 4** High-temperature phase of compound **B16**: (a) growth of dendritic domains observed on cooling of the isotropic liquid (212 °C); (b) mosaic texture at 200 °C.



**Fig. 5** Microscopic texture of the high-temperature phase of compound **B16** at 205 °C: (a)  $U = 0$  V; (b)  $U = \pm 75$  V.



**Fig. 6** Compound **B16**: (a) switching current response in the high-temperature phase obtained under a triangular wave field (144  $V_{pp}$ ; 10 Hz) at 207 °C, sample thickness 5  $\mu\text{m}$ ; (b) switching current response in the  $\text{SmCP}_A$  phase obtained under a triangular wave field (325  $V_{pp}$ ; 5 Hz) at 167 °C.

texture which indicates a columnar phase (Fig. 4a,b). Unfortunately, this phase could not be classified by X-ray studies because of the high temperature range of the mesophase.

At electric fields above  $10 \text{ V } \mu\text{m}^{-1}$  the original texture can be switched to a texture of a changed birefringence which is independent of the polarity of the field (Fig. 5). The current response shows two peaks per half period of a triangular voltage which points to an antiferroelectric ground state (Fig. 6a). The spontaneous polarisation was found to be  $320 \text{ nC cm}^{-2}$ .

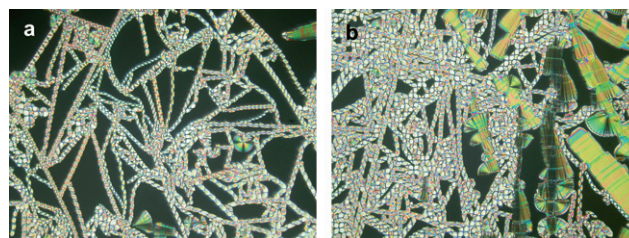
The low-temperature phase which forms a paramorphic texture of the high-temperature phase is a smectic phase with a simple layer structure which also shows a polar switching. The threshold of the switching is clearly decreased ( $2 \text{ V } \mu\text{m}^{-1}$ ) and the current response (also two peaks per half period, see Fig. 6b) as well as the optical picture of the switching are quite similar to those of the  $\text{SmCP}_A$  phases of the lower homologues. In the low-temperature phase the switching polarization  $P_S$  is slightly enhanced ( $420 \text{ nC cm}^{-2}$ ).

The mesophase behavior of compound **B12/in-9** is not markedly different from that of compound **B12**. This means it forms a  $\text{SmC}_s\text{P}_A$  phase with similar textures and similar field-induced texture change. Also the layer spacing (49 Å) and the tilt angle (about  $40^\circ$ ) are of the same order of magnitude. Interestingly, similar to compound **A14/in-3** the field-induced fan-shaped texture shows complementary regions of opposite handedness.

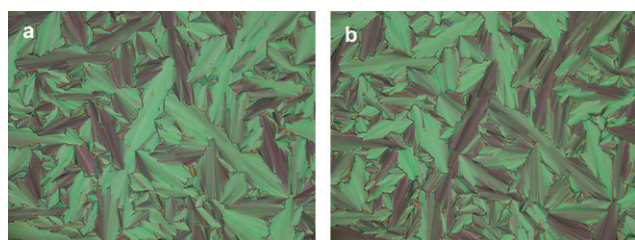
The mesophase of the higher homologue **B14/in-3** is also a tilted smectic phase with a layer spacing of 52.3 Å, which corresponds to a tilt angle of about  $35^\circ$ . This phase forms textural features which are also reminiscent of a  $B_7$  phase. On cooling the isotropic liquid beside birefringent domains with stripes helical domains also appear which are different from those observed for **A14/in-3** (Fig. 7). Also in this case the screw-like domains are stable on further cooling.

By application of an electric field above  $2 \text{ V } \mu\text{m}^{-1}$  this texture is transformed into a smooth  $\text{SmA}$ -like fan-shaped texture which is independent of the sign of the field and relaxes into a grainy texture. The current response indicates an antiferroelectric ground state, the polarization was found to be  $350 \text{ nC cm}^{-2}$ . Similar to the compounds **A14/in-3** and **B12/in-9** the field-induced fan-shaped texture shows regions of opposite handedness visible by a decrossing of the polarizers (Fig. 8).

The mesophase of compound **B16/in-7** exhibits a fan-like texture. At electric fields above  $15 \text{ V } \mu\text{m}^{-1}$  the smectic phase shows a switching which is accompanied by a small change of the birefringence, but the textures of the switched state are independent of the sign of the applied field. This switching is a polar one because by current response measurements one peak per half



**Fig. 7** Compound **B14/in-3**: (a) nucleation of the smectic phase on slow cooling the isotropic liquid, (b) texture of the smectic phase at 208 °C.



**Fig. 8** Field-induced fan-shaped texture in the smectic phase of compound **B14/in-3** at 190 °C observed by rotating one polarizer (a) by +25° and (b) by –25° from the crossed position.

period could be recorded from which a polarization of 190 nC cm<sup>-2</sup> was determined. The bistable character of the switching and the current response measurements indicate a ferroelectric ground state. The field-induced texture change suggests that the switching is based on the collective rotation of the molecules around their long axes. Also in this case domains of opposite handedness can be distinguished in the field-induced fan-shaped texture. Another interesting finding should be mentioned: By application of a strong electric field (40 V μm<sup>-1</sup>) an enhancement of the clearing temperature of about 2 K could be observed. Such an effect has already been described for several bent-core mesogens.<sup>42,43</sup>

#### Influence of lateral substituents on the mesophase behaviour of tetradecyl and tetradecynyl substituted five-ring compounds (in series A)

The compounds listed in Table 3 are derived from the compounds **A14** and **A14/in-3** but in addition to the parent

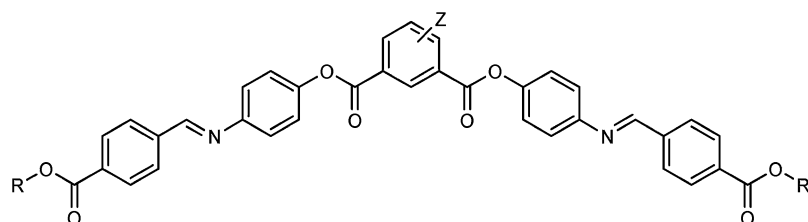
compounds they possess lateral substituents in the 2, 4 or 5 position of the central core.

In most cases (**A14-NO<sub>2</sub>**, **A14/in-3/NO<sub>2</sub>**, **A14-Me-5**, **A14/in-3/Me-5**) the lateral substituents cause the loss of liquid-crystalline properties. On supercooling the isotropic liquid of the compounds **A14-Br** and **A14/in-3/Br**, a birefringent texture could be observed by means of polarizing microscopy which is reminiscent of a SmCP phase. Due to the high tendency to crystallize further investigations could not be realized. Surprisingly, in the compounds **A14-Me-2** and **A14/in-3/Me-2** where a methyl group is introduced in the 2-position of the central phenyl ring the mesophase is strongly stabilized in comparison to the non-substituted compounds, visible by the enhancement of the clearing temperatures by about 35 K. This could be related to a significant enhancement of the opening angle between the molecular wings of the bent-core mesogens.

On cooling the isotropic liquid of compound **A14-Me-2**, a focal conic or homeotropic texture appears at 214 °C and a broken fan-shaped texture or a schlieren texture occurs on cooling below 203 °C, see Fig. 9. These textures indicate a smectic A and a smectic C phase, respectively.

In contrast to the SmA phase, the SmC phase shows at lower temperatures a clear switching although the texture and birefringence do not markedly change. In the isotropic as well as in both smectic phases a broad diffuse peak could be recorded per half period of an applied triangular voltage, which is obviously due to ionic conductivity. Surprisingly, about 50 K below the transition from the SmA to the SmC phase a clear reproducible additional peak arises which points to a polar switching with a switching polarisation of 130 nC cm<sup>-2</sup>. This switching is obviously based on the collective rotation of the molecules around their long axes, but we can not distinguish between

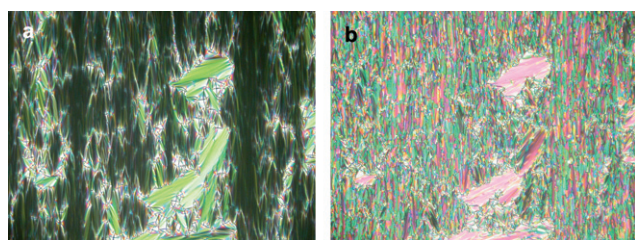
**Table 3** Influence of lateral substituents on the mesophase behaviour of tetradecyl- and tetradecynyl substituted five-ring compounds (series A—laterally substituted)



No.	Z	Cr <sup>a</sup>	SmCP	Polar SmC	SmA	Is
R = -C <sub>14</sub> H <sub>29</sub>						
<b>A14</b>	H	• 169.6 [44.5]	—	• 176.9 <sup>b</sup> [21.1]	—	•
<b>A14-Br</b>	4-Br	• 148.7 [63.7]	(141.9) <sup>c</sup> [19.6]	—	—	•
<b>A14-NO<sub>2</sub></b>	5-NO <sub>2</sub>	• 196.7 [59.0]	—	—	—	•
<b>A14-Me-2</b>	2-CH <sub>3</sub>	• 100.5 [71.8]	—	• 203 <sup>d</sup> [—] <sup>e</sup>	• 214.4 [8.3]	•
<b>A14-Me-5</b>	5-CH <sub>3</sub>	• 151.4 [55.5]	—	—	—	•
R = -CH <sub>2</sub> CH <sub>2</sub> -C≡C-C <sub>10</sub> H <sub>21</sub>						
<b>A14/in-3</b>	H	• 166.9 [61.1]	175.0 [0.3]	• 187.3 <sup>f</sup> [26.3]	—	•
<b>A14/in-3/Br</b>	4-Br	• 166.3 [71.4]	(161.5) [—] <sup>e</sup>	—	—	•
<b>A14/in-3/NO<sub>2</sub></b>	5-NO <sub>2</sub>	• 206.6 [63.5]	—	—	—	•
<b>A14/in-3/Me-2</b>	2-CH <sub>3</sub>	• 118.6 [35.1]	—	• 186 <sup>d</sup> [—] <sup>e</sup>	• 221.4 [10.0]	•
<b>A14/in-3/Me-5</b>	5-CH <sub>3</sub>	• 151.7 [33.2]	—	—	—	•

<sup>a</sup> Some compounds show crystalline polymorphism. <sup>b</sup> SmC<sub>s</sub>G<sub>2</sub>P<sub>A</sub> phase.<sup>23</sup> <sup>c</sup> SmCP phase (studied only by POM). <sup>d</sup> SmC phase which shows about 50 K below the SmA–SmC transition an antiferroelectric switching. <sup>e</sup> Only by POM studies. <sup>f</sup> B<sub>7</sub>' phase.





**Fig. 9** Compound **A14-Me-2**: (a) fan-shaped texture of the SmA phase (206 °C) and (b) broken fan-shaped texture of the SmC phase (182 °C).

ferroelectric and antiferroelectric properties. We also observed a similar polar current response in the SmC phase of the 2-methyl-substituted compound **A14/in-3/Me-2**, and also for corresponding derivatives in series **B** (see below, **B14-Me-2** and **B14/in-3/Me-2**).

#### Influence of lateral substituents on the mesophase behaviour of tetradecyl- and tetradecynyl substituted compounds containing terminal cinnamic ester groups (in series B)

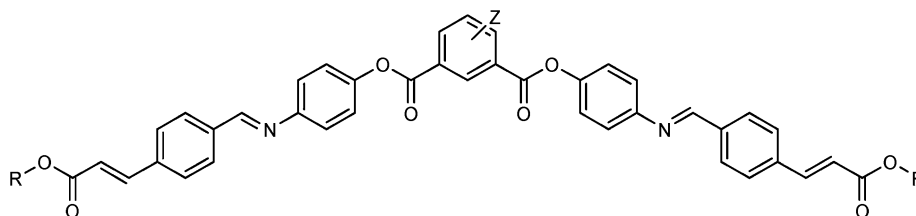
Table 4 presents compounds which are derived from the parent compounds **B14** and **B14/in-3**. The additional carbon–carbon double bond of the cinnamic group gives rise to a considerable enhancement of the clearing temperatures of the 2-methyl substituted compounds **B14-Me-2** and **B14/in-3/Me-2** compared with the corresponding compounds of series **A**, the clearing temperatures are enhanced by about 55 K. Similar to the analogous **A** compounds the 5-NO<sub>2</sub> and 5-CH<sub>3</sub> substituted compounds **B14-NO<sub>2</sub>**, **B14/in-3/NO<sub>2</sub>**, **B14-Me-5** and **B14/in-3/Me-5** do not form a mesophase.

Unlike the analogous compounds without cinnamic groups the 4-bromine substituted compounds **B14-Br** and **B14/in-3/Br** form enantiotropic mesophases. Compound **B14-Br** possesses two mesophases. The high-temperature phase exhibits a texture with fan-like and mosaic domains (Fig. 10a), but X-ray studies on a partially oriented sample point to a simple layer structure.

At electric fields above 5 V μm<sup>-1</sup> a noticeable switching is visible although the texture is only slightly changed (Fig. 10b). From the current response two peaks per half period could be recorded (Fig. 10c). This result points to a switching from an antiferroelectric ground state into corresponding ferroelectric states. The transition into the low-temperature phase is indicated by a DSC signal and a minor change of the texture, whereas the X-ray pattern remains nearly unchanged as can be seen from the 2D patterns of a partially surface-aligned sample in the two phases in Fig. 11. The layer spacing *d* determined from the small angle reflections slightly increases with decreasing temperature (55.5, 56.0, and 57.1 Å at 180, 170, and 150 °C, respectively). The tilt angle of the molecules with respect to the layer normal calculated from the positions of the maxima of the outer diffuse scattering amounts to about 25° in both phases. The only visible difference between the high and low temperature patterns is a stronger intensity of the layer reflections of higher order at lower temperature, which may be attributed to a sharper definition of the layers.

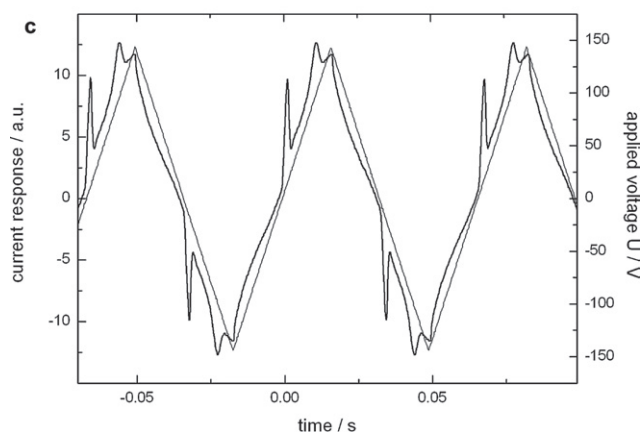
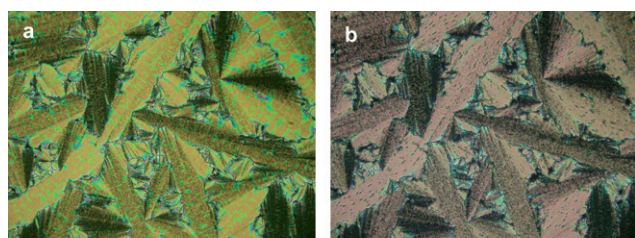
By application of an electric field (1.5–2.0 V μm<sup>-1</sup>) the texture of the low-temperature phase is transformed into a smooth fan-shaped texture which relaxes into a grainy fan-shaped texture after removing the field (Fig. 12a,b). It follows from X-ray and electro-optical measurements that the low-temperature phase is a polar tilted SmC phase which is synclinic and antiferroelectric (SmC<sub>S</sub>P<sub>A</sub>). The current response is shown in Fig. 12c. In both

**Table 4** Influence of lateral substituents on the mesophase behaviour of tetradecyl- and tetradecynyl substituted five-ring compounds containing terminal cinnamic ester groups (series **B**—laterally substituted)

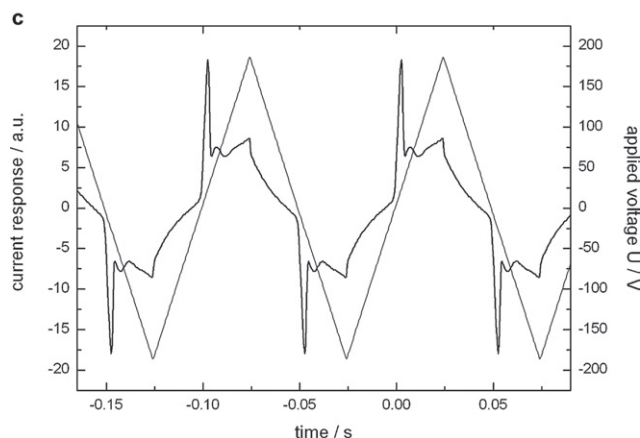
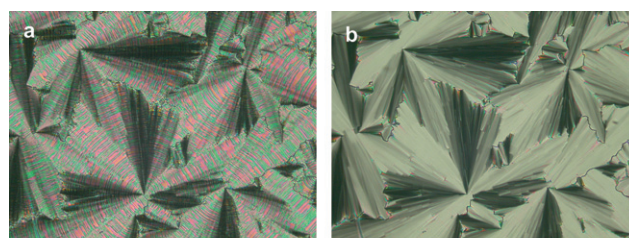


No.	Z	Cr	SmCP <sub>A</sub>	SmC <sub>X</sub>	SmA	Is
R = -C <sub>14</sub> H <sub>29</sub>						
<b>B14</b>	H	• 160.3 [52.1]	• 216.9 [17.2]	—	—	•
<b>B14-Br</b>	4-Br	• 142.2 [44.8]	• 178.6 [0.3]	185.9 <sup>a</sup> [20.6]	—	•
<b>B14-NO<sub>2</sub></b>	5-NO <sub>2</sub>	• 204.5 [54.7]	—	—	—	•
<b>B14-Me-2</b>	2-CH <sub>3</sub>	• 107.2 [42.5]	—	• 251.1 <sup>c</sup> [0.07]	• 269 [8.9]	•
<b>B14-Me-5</b>	5-CH <sub>3</sub>	• 186.5 [46.6]	—	—	—	•
R = -CH <sub>2</sub> CH <sub>2</sub> -C≡C-C <sub>10</sub> H <sub>21</sub>						
<b>B14/in-3</b>	H	• 189.2 [68.5]	—	• 225.4 <sup>d</sup> [28.1]	—	•
<b>B14/in-3/Br</b>	4-Br	• 163.6 [39.5]	• 194.2 [24.6]	—	—	•
<b>B14/in-3/NO<sub>2</sub></b>	5-NO <sub>2</sub>	• 213.6 [56.6]	—	—	—	•
<b>B14/in-3/Me-2</b>	2-CH <sub>3</sub>	• 120.2 [46.2]	—	• 230 <sup>c</sup> [—] <sup>b</sup>	• 272.0 [10.3]	•
<b>B14/in-3/Me-5</b>	5-CH <sub>3</sub>	• 192.6 [60.5]	—	—	—	•

<sup>a</sup> The texture is reminiscent of a Col phase, but X-ray studies point to a simple layer structure. <sup>b</sup> Phase transition from microscopic observation. <sup>c</sup> SmC phase which shows about 50 K below the SmA–SmC transition an antiferroelectric switching. <sup>d</sup> B<sub>7</sub>′ according to textural features.



**Fig. 10** Compound **B14-Br**: microscopic textures of the high-temperature phase at 181 °C. (a)  $U = 0$  V, (b)  $U = \pm 68$  V, sample thickness 6  $\mu\text{m}$ ; (c) switching current response in the high-temperature phase obtained under a triangular wave field (282  $V_{\text{pp}}$ ; 15 Hz) at 181 °C, sample thickness 10  $\mu\text{m}$ .



**Fig. 12** Compound **B14-Br**: microscopic texture of the  $\text{SmCP}_A$  phase at 145 °C. (a)  $U = 0$  V, (b)  $U = \pm 37$  V, sample thickness 6  $\mu\text{m}$ ; (c) switching current response in the  $\text{SmCP}_A$  phase obtained under a triangular wave field (372  $V_{\text{pp}}$ ; 10 Hz) at 145 °C, sample thickness 10  $\mu\text{m}$ .

polar phases the switching polarization is nearly the same (800  $\text{nC cm}^{-2}$ ).

According to X-ray investigations the mesophase of compound **B14/in-3/Br** could also be classified as a tilted smectic phase ( $d = 55.8 \text{ \AA}$ ) which shows a polar switching. The threshold field, the current response and the field-induced texture change are similar to the low-temperature phase of compound **B14-Br** so that the switching can be interpreted by a field-induced transition  $\text{SmC}_S\text{P}_A$  to  $\text{SmC}_A\text{P}_F$  ( $P_S = 300 \text{ nC cm}^{-2}$ ).

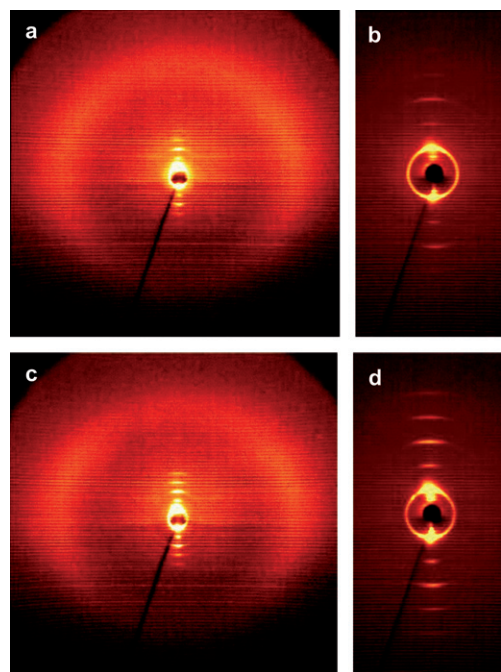
#### Bent-core compounds with and without multiple bonds inserted in the alkyl chains of terminal phenoxyacetic esters (series C)

Table 5 presents the transition temperatures and transition enthalpies of laterally substituted bent-core mesogens with phenoxy acetic ester groups in the terminal molecular fragments.

This minor structural modification in comparison to analogous compounds shown in Tables 2 and 3 leads, in general, to the loss of liquid-crystalline properties.

The exceptions are the 2-methyl substituted compounds **C14-Me-2** and **C14/in-3/Me-2** which form mesophases at relatively low temperatures. As seen from Table 5, compound **C14/Me-2** forms two mesophases, a nematic phase and on further cooling a smectic phase which shows—depending on the experimental conditions—a schlieren texture, a fan-like texture (Fig. 13) or a texture with circular domains in which the extinction crosses are parallel to the crossed polarizers.

X-Ray diffraction measurements on a powder-like sample using the Guinier film method showed the first-order layer reflection for the smectic phase at  $d = 45.7 \text{ \AA}$  along with an outer diffuse scattering between 130 and 115 °C on cooling.

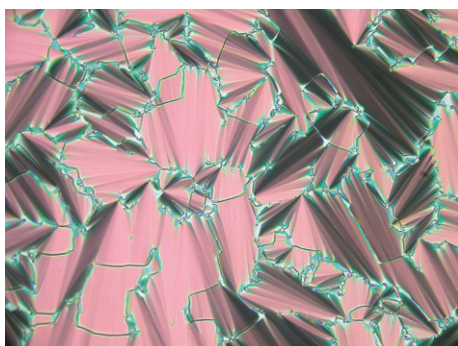


**Fig. 11** 2D X-ray patterns of a partially surface-aligned sample of **B14-Br**: (a), (b) high temperature phase at 180 °C, (c), (d) low temperature phase at 150 °C; (a) and (c) full scattering range, (b) and (d) small angle region.

**Table 5** Melting behaviour of laterally substituted bent-core mesogens with phenoxy acetic acid ester groups in both terminal positions (series C—laterally substituted)

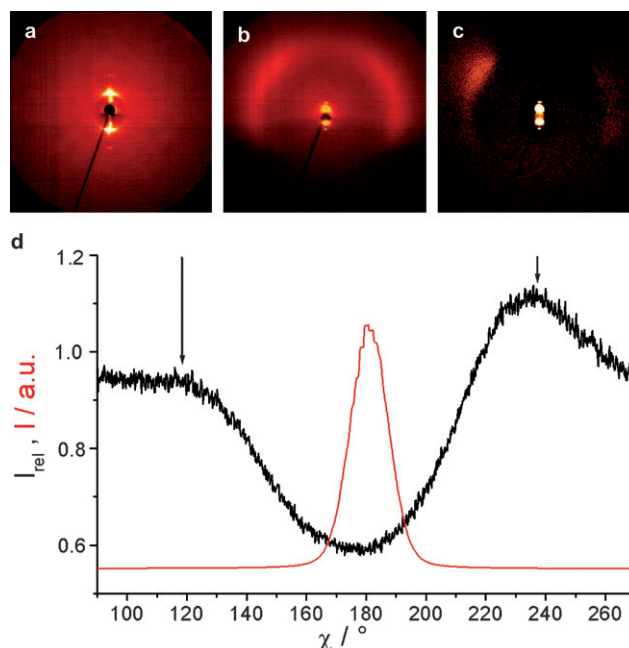
No.	Z	Cr <sup>a</sup>	Col	SmCP <sub>A</sub>	N	Is
R = -C <sub>14</sub> H <sub>29</sub>						
<b>C14</b>	H	• 158.8 [109.7]	—	—	—	•
<b>C14-Br</b>	4-Br	• 143.6 [99.0]	—	—	—	•
<b>C14-NO<sub>2</sub></b>	5-NO <sub>2</sub>	• 155.8 [53.2]	—	—	—	•
<b>C14-Me-2</b>	2-CH <sub>3</sub>	• 121.7 [79.6]	—	• 137.2 [5.8]	• 139.0 [1.2]	•
<b>C14-Me-5</b>	5-CH <sub>3</sub>	• 134.8 [52.5]	—	—	—	•
R = -CH <sub>2</sub> CH <sub>2</sub> -C≡C-C <sub>10</sub> H <sub>21</sub>						
<b>C14/in-3</b>	H	• 170.8 [107.2]	—	—	—	•
<b>C14/in-3/Br</b>	4-Br	• 150.7 [98.6]	—	—	—	•
<b>C14/in-3/NO<sub>2</sub></b>	5-NO <sub>2</sub>	• 154.1 [51.2]	—	—	—	•
<b>C14/in-3/Me-2</b>	2-CH <sub>3</sub>	• 122.8 [48.4]	—	• 135.1 [10.1]	—	•
<b>C14/in-3/Me-5</b>	5-CH <sub>3</sub>	• 151.6 [67.7]	—	—	—	•

<sup>a</sup> Some compounds show crystalline polymorphism.

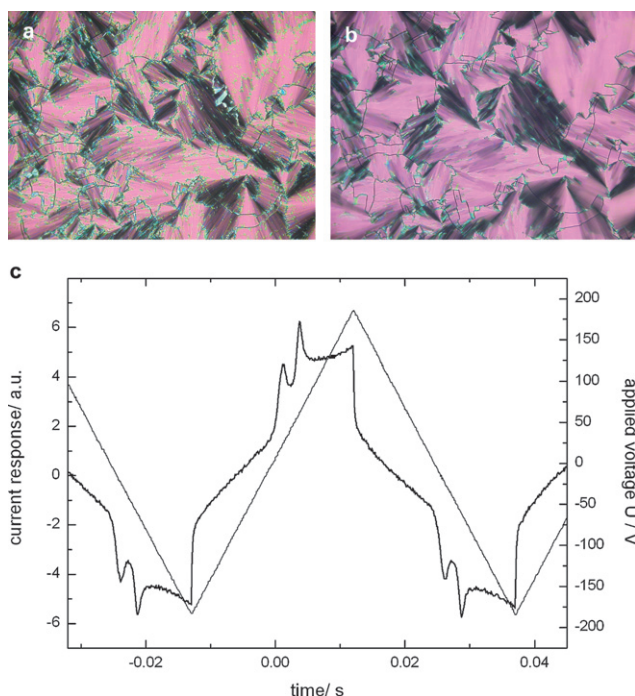
**Fig. 13** Microscopic texture of the SmCP phase of compound **C14-Me-2** at 132 °C, sample thickness 5 μm.

The 2D X-ray patterns of the nematic phase aligned in a magnetic field shows beside the usual outer diffuse scattering a second one at  $d = 4.6$  Å which can be attributed to cybotactic groups of the smectic C type in the nematic phase, where the long molecular axes have a 32° tilt with respect to the normal of the layer fragments.

Fig. 14a shows the 2D X-ray pattern of a surface aligned sample for the smectic phase of compound **C14-Me-2**. The layers are aligned parallel to the surface of the sample and, hence, the layer reflections are found on the meridian. The maxima of the outer diffuse scattering in the corresponding wide-angle pattern (Fig. 14b) are situated at about 30° above the equator indicating a 30° tilt of the long molecular axes with respect to the layer normal in the smectic phase. The obvious difference in the intensities of the scattering maxima to the left and to the right of the meridian gives a hint to a synclinic arrangement of the molecules in different layers (Fig. 14c and d). An estimate of the

**Fig. 14** X-Ray patterns of a surface-aligned sample of compound **C14-Me-2** in the smectic phase: a) small angle region at 128 °C on cooling, b) original wide angle pattern at 122 °C on cooling, c) the same wide angle pattern as in b), but the scattering of the isotropic liquid has been subtracted to enhance the visibility of the intensity difference for the maxima of the outer diffuse scattering to the left and to the right of the meridian, d)  $\chi$ -scans for the diffuse scattering at 122 °C in the wide angle region [black line, maxima at about  $\chi = 120$  and  $240^\circ$ , black arrows,  $I_{\text{rel}}$  for the outer scattering:  $I_{\text{rel}} = I(120^\circ)/I(145^\circ, \text{isotropic liquid})$ ] and in the small angle region (red line, maximum on the meridian at  $\chi = 180^\circ$ ).





**Fig. 15** Compound **C14-Me-2**: microscopic texture of the smectic phase at 127 °C. (a)  $U = 0$  V, (b)  $U = \pm 50$  V, sample thickness 5  $\mu\text{m}$ ; (c) switching current response of the smectic phase obtained under a triangular wave field (369  $\text{V}_{\text{pp}}$ ; 20 Hz) at 123 °C, sample thickness 5  $\mu\text{m}$ .

effective molecular length in the smectic phase  $L_{\text{eff}}$  from the layer distance  $d = 46$  Å and the tilt angle  $\tau = 30^\circ$  yields  $L_{\text{eff}} = d/\cos \tau = 53$  Å.

The application of electric fields of  $25\text{--}35$   $\text{V } \mu\text{m}^{-1}$  leads to a slight change of the birefringence, but the textures of the switched states do not change upon reversal of the field polarity (Fig. 15a,b). This switching is accompanied by two clearly separated repolarization current peaks in each half period of the

applied triangular voltage which is typical for switching from antiferroelectric to ferroelectric (Fig. 15c). The study of the optical textures during the switching indicates a switching mechanism which is characterized by the rotation of the molecules around the long axes ( $P_s = 650$   $\text{nC cm}^{-2}$ ).

The X-ray diffraction patterns of **C14/in-3/Me-2** in the liquid-crystalline phase closely resemble those for the smectic phase of **C14/Me-2**. The Bragg reflections on the meridian reveal approximately the same layer spacing of 46.1 Å, but the tilt angle derived from the outer diffuse scattering is considerably smaller at  $18^\circ$ , leading to an effective molecular length of only 48.5 Å.

### Influence of lateral methyl groups attached to the middle phenyl rings of both molecular legs

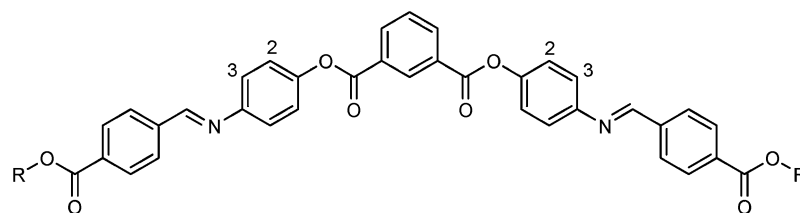
Starting from the compounds **A14** and **A14/in-3** a methyl group was laterally attached to positions 2 and 3, respectively, of both middle phenyl rings in the legs of the bent-core molecules. Although the clearing temperatures of the starting compounds are very high, a monotropic mesophase could only be found for the 2-methyl-substituted compounds **A14-X-2** and **A14/in-3/X-2**, see Table 6. The mesophase destabilization effect amounts to about 80 K, the microscopically observed textures are reminiscent of a polar smectic C phase (SmCP). Electrooptical measurements and further studies were not possible due to a high crystallization tendency.

## Discussion

### Linking of the terminal alkyl chains to the outer phenyl rings by different connecting groups

Comparing the series **A** and **B** of the new bent-core compounds it is not unexpected that the replacement of ester linking groups ( $-\text{COO}-$ ) with acrylester units ( $-\text{CH}=\text{CH}-\text{COO}-$ ) in the terminal chains leads to a stabilization of the mesophases. This is obviously the result of an enlargement of the more rigid central

**Table 6** Influence of methyl groups laterally attached to the positions 2 or 3 of the middle phenyl rings on the mesophase behaviour of tetradecyl- and tetradecynyl substituted compounds (series **A**)



No.	X	$\text{Cr}^a$	SmCP <sub>A</sub>	polar SmC	Is
R- = $-\text{C}_{14}\text{H}_{29}$					
<b>A14</b>	H	• 169.6 [44.5]	—	• 176.9 <sup>b</sup> [21.1]	•
<b>A14-X-2</b>	2-CH <sub>3</sub>	• 109.4 [92.6]	(• 94.8) <sup>c</sup> [15.7]	—	•
<b>A14-X-3</b>	3-CH <sub>3</sub>	• 106.6 [27.7]	—	—	•
R- = $-\text{CH}_2\text{CH}_2-\text{C}\equiv\text{C}-\text{C}_{10}\text{H}_{21}$					
<b>A14/in-3</b>	H	• 166.9 [61.1]	• 175.0 [0.3]	• 187.3 <sup>b</sup> [26.]	•
<b>A14/in-3/X-2</b>	2-CH <sub>3</sub>	• 129.6 [74.2]	(• 104.8) <sup>c</sup> [17.4]	—	•
<b>A14/in-3/X-3</b>	3-CH <sub>3</sub>	• 122.1 [44.4]	—	—	•

<sup>a</sup> Some compounds show crystalline polymorphism. <sup>b</sup> Sm $\tilde{\text{C}}_5\text{G}_2\text{P}_A$  phase. <sup>c</sup> Assignment only by POM.

core by the additional HC=CH- groups which are in conjugation with the outer phenyl rings.

The destabilization or disappearance of mesophases by using a -OCH<sub>2</sub>COO- moiety between the aliphatic chains and the terminal rings is also not surprising because in calamitic compounds phenoxy acetic esters are also often not liquid crystalline. There are only a few examples of calamitic molecules containing a -OCH<sub>2</sub>COO- connecting group which are able to form mesophases, *e.g.* references 44–46. Liquid crystalline behaviour has been reported for some oligomeric and discotic mesogens.<sup>47,48</sup>

Bearing this in mind, however, the enantiotropic mesophase behaviour found for derivatives of the 2-methylisophthalic acid is very surprising.

### Comparison of alkyl and alkynyl substituted bent-core mesogens

In the last column of Tables 1 and 2,  $\Delta T$  values are given. Together with the transition temperatures listed in Tables 3–6, these values express the change of the clearing temperatures of compounds bearing terminal alkyl chains and terminal alkynyl chains, respectively. As one can see, the effect is different depending on the length of the alkyl chains and on the position of the multiple bonds in the chains. In most cases a strong decrease of the mesophase stability can be observed for the unsaturated compounds. Comparing corresponding compounds in Tables 1–6, the changes of the clearing temperatures caused by the triple bonds are summarized in Table 7.

The compounds with 3-tetradecyn-1-yl chains show a slight decrease up to a clear increase of the clearing points, whereas the other alkynyl chains cause a strong decrease of the mesophase stability. The difference is the position of the triple bond which is relatively near to the terminal aromatic phenyl rings in the case of the 3-tetradecyn-1-yl chains. This unusual tendency could also be confirmed for the laterally substituted compounds (Tables 3, 4, 6). The increase of the clearing temperatures  $\Delta T$  amounts to 4–21 K by the replacement of a carbon–carbon bond by a carbon–carbon triple bond within the tetradecyl chain. Only for the phenoxyacetic ester compounds (**C14-Me-2** and **C14/in-3/Me-2**) was a slight decrease of the clearing temperature ( $\Delta T = -4$  K) observed (Table 7).

### Influence of lateral substituents

In the series under study the introduction of lateral groups gave expected and unexpected results depending on the steric and electronic properties as well as the position of the lateral substituents at the parent molecule. The loss of the liquid crystalline properties by groups like methyl and nitro in the

5-position of the central phenyl ring was also found for other bent-core mesogens. For five-ring bent-core mesogens, only a few compounds, for example 5-fluoro-, 5-methyl- and 5-methoxy-substituted compounds, have been reported to be liquid crystalline.<sup>43,49,50</sup>

The significant stabilisation of mesophases by a methyl substituent in the 2-position is surprising and unexpected, especially the strong enhancement of the clearing temperatures in comparison with analogous non-substituted compounds. In series **C**, for example, only for the 2-methyl-substituted derivative mesophases could be observed. On the other hand, in the original series of banana-shaped liquid crystals, derived from resorcinol, the introduction of a methyl group in the 2-position often changes the polymorphism, but the clearing temperatures are of the same order of magnitude.<sup>4,51</sup> We can assume that the attachment of a methyl group in the case of isophthalic acid leads to a clear increase of the bending angle which can probably explain the unusual increase of the clearing temperature, but also the occurrence of nematic, SmA and SmC phases which are typical for calamitic mesogens.

Halogen atoms, like chlorine or bromine, attached to the 4-position of the central phenyl ring can result in mesophases characteristic of rod-like molecules, but also in polar smectic phases, typical for bent-core compounds, depending on the chemical structure of the whole molecule.<sup>43,52,53</sup> In the new series, for all 4-bromo-substituted derivatives (Tables 3, 4) smectic phases have been observed. The polar nature of two of the smectic phases has been proved by electrooptical measurements.

As shown in Table 5, the attachment of methyl groups to the positions 2 or 3 of the middle phenyl rings—which means in the legs of the molecules—is clearly disadvantageous. That finding is in agreement with general structure–property relationships reported for bent-core mesogens.

### Mesophase structures and electro-optical behaviour

It follows from X-ray and electro-optical investigations that most liquid crystalline compounds presented here exhibit a SmCP<sub>A</sub> phase which generally occurs in a synclinic variant (SmC<sub>S</sub>P<sub>A</sub>). In this case, the switching into a ferroelectric state takes place in the usual way by the director rotation around the tilt cone. Three compounds (**A14/in-3**, **B16**, **B14-Br**) form a polar high-temperature phase in addition to the SmC<sub>S</sub>P<sub>A</sub> phase. The high-temperature phase of compound **B16** could not be investigated by X-ray measurements because of the high transition temperatures (>197 °C). In the cases of compounds **A14/in-3** and **B14-Br** the X-ray studies indicate a simple layer structure. But we observed a polar switching which is clearly distinguished from that of the SmCP<sub>A</sub> low-temperature phase. For compound **A14/in-3** the textures of the switched state are independent of the polarity of the field and nearly identical with that of the field-off state. This finding suggests that the switching mechanism is based on the collective rotation of the molecules around their long axes. In addition, it was found that the high-temperature phase possesses a ferroelectric ground state, whereas the high-temperature phases of compounds **B16** and **B14-Br** show an antiferroelectric switching. In these compounds the textures of the switched state are also independent of the polarity of the electric field, but different from that of the field-off state. In this case it is

**Table 7** Increase or decrease of the clearing temperatures ( $\Delta T$ ) caused by the replacement of saturated alkyl chains by alkynyl groups

Dodec-1-yl to 9-dodecyn-1-yl: $\Delta T^a = -27$ K to $-35$ K
Tetradec-1-yl to 3-tetradecyn-1-yl: $\Delta T^b = -4$ K to $+21$ K
Hexadec-1-yl to 7-hexadecyn-1-yl: $\Delta T^c = -41$ K
Hexadec-1-yl to 9-hexadecyn-1-yl: $\Delta T^c = -40$ K
Hexadec-1-yl to 11-hexadecyn-1-yl: $\Delta T^c = -34$ K

<sup>a</sup> Comparison of two pairs. <sup>b</sup> Of seven pairs. <sup>c</sup> Of one pair, only.

difficult to decide if the switching is based on the director rotation around the tilt cone or on the rotation of the molecules around their long axes.

In our X-ray studies we did not observe additional reflections in the small angle region which would suggest a 2D structure, a double-layer structure or an undulated structure of the high-temperature phase as reported by Bedel *et al.*<sup>23,24</sup> for the parent compounds of series **A** having saturated terminal alkyl chains.

An interesting dimorphism was found for compound **C14-Me-2**. Beside a nematic phase which forms cybotactic smectic clusters, an anticlinic tilted smectic phase with an antiferroelectric polar switching occurs. The anticlinic structure is indicated by the extinction crosses in circular domains which are parallel to the crossed polarizers. The dimorphism nematic–SmCP<sub>A</sub> transition is not unknown for bent-core mesogens<sup>53</sup> but it is unusual for this phase sequence that the switching mechanism of the SmCP<sub>A</sub> phase is obviously based on the collective rotation of the molecules around the molecular long axes.

In this context it should be emphasized that in the SmC phase of the 2-methyl-substituted compounds **A14-Me-2** and **A14/in-3/Me-2**, **B14-Me-2** and **B14/in-3/Me-2** we found at lower temperatures a clear polar switching which obviously takes place by the same mechanism as found for the SmC-like phase of compound **C14-Me-2**.

### B<sub>7</sub> Phases and smectic layers with local C<sub>1</sub> symmetry

The mesophases of three compounds with terminal alkynyl chains (**A12/in-9**, **A14/in-3**, **B14/in-3**) exhibit textural features of a B<sub>7</sub> phase; for example spiral filaments of different shape, myelinic-like domains, banana leaf-like domains, ribbon-like domains or circular domains, which can simultaneously occur in the same sample (see Fig. 1–2). It is known from the literature that B<sub>7</sub> modifications can adopt an undulated layer structure (designated as B<sub>7</sub>') or a 2D (columnar) structure (designated as B<sub>7</sub>).<sup>54–57</sup> It was shown that the escape from the macroscopic polar order (SmC<sub>5</sub>P<sub>F</sub>) leads to a splay of the polarization giving rise to the undulation or breaking of the smectic layers.<sup>56</sup> In the ferroelectric domains stripes with preferred polarization splay arise which are separated by defect walls visible as periodic structures of polarization splay defects. As shown by Coleman *et al.*<sup>56</sup> the splay polarization is also an essential precondition for the formation of helical filament structures which are observed during the growth of the B<sub>7</sub>' or B<sub>7</sub> phase from the isotropic liquid. Obviously the twist deformation of the filaments is caused by the helical winding of the polarization modulation.

It follows from X-ray experiments that the B<sub>7</sub> modification of compounds **A14/in** and **B14/in** does not possess a 2D columnar structure, but only a simple layer organization. On the other hand, we found no hint of an undulated layer structure (B<sub>7</sub>') which would be indicated by satellites of weak intensity behind the 001 layer reflections. But if the undulation period is relatively long it is difficult to detect it. Note that also Pyc *et al.*<sup>58</sup> reported B<sub>7</sub> modifications with a simple layer structure.

Regardless whether the smectic phases of compound **A14/in-3** or **B14/in-3** has a simple layer structure or an undulated layer structure with a long period, the optical textures point unambiguously to a B<sub>7</sub>-like phase, particularly since we observed a variety of textural features which result from splay polarization

defects. For example, we observed about ten kinds of spiral germs indicating a helicoidal structure as well as domains with equally spaced stripes and 2D periodic patterns (Fig. 1, 2). It should be emphasized that the spiral domains do not disappear on cooling but remain stable up to the crystallization. To our knowledge this is the first observation of this behaviour. It is also remarkable that in some cases the nucleation of circular or ribbon-like domains starts directly at certain spiral filaments (see Fig. 1b, 2). The period of the stripe pattern agrees with the pitch of the corresponding helical filament. In this context it should be noted that Dantlgraber *et al.* found for a seven-ring bent-core mesogen a correlation between the sense of the helical filaments and the chirality (handedness) of the surrounding optically isotropic dark conglomerate domains.<sup>59</sup> There are only a few papers in which the nucleation of the B<sub>7</sub> phase is investigated.<sup>60–63</sup> Furthermore, it should be mentioned that this texture can be transformed into a fan-like texture by application of a moderate electric field.

The presented Fig. 1–2 and additional figures in the ESI† demonstrate that the compounds **A14/in-3** and also **B14/in-3** are suitable objects to study the nucleation process of the B<sub>7</sub> phases in more detail.

Another aspect should be discussed which concerns the local structure of B<sub>7</sub> phases. From results of electro-optical studies reported in the literature<sup>64,65</sup> it has been suggested that B<sub>7</sub>' phases are composed of layers with C<sub>1</sub> symmetry (SmC<sub>G</sub> structure) in which the layers have polarization components in and out of the layer planes.<sup>66</sup> From X-ray diffraction measurements we found no evidence of a double layer structure of the B<sub>7</sub> phases of compounds **A14/in-3** and **B14/in-3** as reported by Bedel *et al.*<sup>23</sup> for the compounds **A12**, **A14**, and **A16**. Such a double layer structure would be a clear indication for a C<sub>1</sub> symmetry of the smectic layers. But recently it was shown in a theoretical study by Bailey and Jakli<sup>67</sup> that steric and electrostatic features of the bent molecules can not only lead to a polarization splay modulation and a spontaneous layer bending but also cause a symmetry reduction of the smectic layers from C<sub>2</sub> to local C<sub>1</sub>.

We observed in the field-induced fan-shaped texture of compounds **A14/in-3** and **B14/in-3** domains of opposite handedness which points to a partial twist of the structure (see Fig. 8). It is interesting that the same chiral domains have been reported in the fan-shaped texture of a polar tilted smectic phase of a bent-core mesogen for which a SmC<sub>G</sub> structure was assumed because of the unusual electro-optical properties.<sup>41</sup> This could be a hint that in the B<sub>7</sub>' phase under discussion a local C<sub>1</sub> symmetry of the smectic layers also exists.

### References

- 1 T. Niori, F. Sekine, J. Watanabe, T. Furukawa and H. Takezoe, *J. Mater. Chem.*, 1996, **6**, 1213.
- 2 D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Körblova and D. M. Walba, *Science*, 1997, **278**, 1924.
- 3 H. R. Brand, P. E. Cladis and H. Pleiner, *Eur. Phys. J. B*, 1998, **6**, 347.
- 4 G. Pelzl, S. Diele and W. Weissflog, *Adv. Mater.*, 1999, **11**, 909.
- 5 R. Amaranatha Reddy and C. Tschierske, *J. Mater. Chem.*, 2006, **16**, 907.
- 6 M. B. Ros, J. L. Serrano, M. R. de la Fuente and C. L. Folcia, *J. Mater. Chem.*, 2005, **15**, 5093.
- 7 H. Takezoe and Y. Takanishi, *Jpn. J. Appl. Phys.*, 2006, **45**, 597.
- 8 M. Hird, *Liq. Cryst. Today*, 2005, **14**, 9.
- 9 J. Mieczkowski and J. Matraszek, *Pol. J. Chem.*, 2005, **79**, 179.



- 10 R. Macdonald, F. Kentischer, P. Warnick and G. Heppke, *Phys. Rev. Lett.*, 1998, **81**, 4408; S. W. Choi, Y. Kinoshita, B. Park, H. Takezoe, T. Niori and J. Watanabe, *Jpn. J. Appl. Phys.*, 1998, **37**, 3408; J. Ortega, J. A. Gallastegui, C. L. Folcia, J. Etxebarria, N. Gimeno and M. B. Ros, *Liq. Cryst.*, 2004, **31**, 579.
- 11 J. Thisayukta, Y. Nakayama and J. Watanabe, *Liq. Cryst.*, 2000, **27**, 1129.
- 12 (a) M. W. Schröder, S. Diele, G. Pelzl, U. Dunemann, H. Kresse and W. Weissflog, *J. Mater. Chem.*, 2003, **13**, 1877; (b) M. W. Schröder, G. Pelzl, U. Dunemann and W. Weissflog, *Liq. Cryst.*, 2004, **31**, 633; (c) U. Dunemann, M. W. Schröder, G. Pelzl, S. Diele and W. Weissflog, *Liq. Cryst.*, 2005, **32**, 151.
- 13 K. Pelz, W. Weissflog, U. Baumeister and S. Diele, *Liq. Cryst.*, 2003, **30**, 1151.
- 14 Y. Takanishi, M. Toshimitsu, M. Nakata, N. Takada, T. Izumi, K. Ishikawa, H. Takezoe, J. Watanabe, Y. Takahashi and A. Iida, *Phys. Rev. E*, 2006, **74**, 051703.
- 15 A. Eremin, H. Nadasi, G. Pelzl, S. Diele, H. Kresse, W. Weissflog and S. Grande, *Phys. Chem. Chem. Phys.*, 2004, **6**, 1290.
- 16 I. Wirth, S. Diele, A. Eremin, G. Pelzl, S. Grande, L. Kovalenko, N. Panchenko and W. Weissflog, *J. Mater. Chem.*, 2001, **11**, 1672.
- 17 See corresponding references in the reviews 4–9.
- 18 W. Weissflog, I. Wirth, S. Diele, G. Pelzl, H. Schmalfuss, T. Schoss and A. Würflinger, *Liq. Cryst.*, 2001, **28**, 1603.
- 19 R. Amaranatha Reddy and B. K. Sadashiva, *Liq. Cryst.*, 2003, **30**, 1031.
- 20 T. Sekine, T. Niori, M. Sone, J. Watanabe, S. W. Choi, Y. Takanishi and H. Takezoe, *Jpn. J. Appl. Phys.*, 1997, **36**, 6455.
- 21 (a) G. Heppke, D. D. Parghi and H. Sawade, *Liq. Cryst.*, 2000, **27**, 313; (b) I. Dierking, H. Sawade and G. Heppke, *Liq. Cryst.*, 2001, **28**, 1767.
- 22 J. Ortega, M. R. de la Fuente, J. Etxebarria, C. L. Folcia, S. Diez, J. A. Gallastegui, N. Gimeno, M. B. Ros and M. A. Perez-Jubindo, *Phys. Rev. E*, 2004, **69**, 011703.
- 23 J. P. Bedel, J. C. Rouillon, J. P. Marcerou, H. T. Nguyen and M. F. Achard, *Phys. Rev. E*, 2004, **69**, 061702.
- 24 J. P. Bedel, J. C. Rouillon, J. P. Marcerou, M. Laguerre, H. T. Nguyen and M. F. Achard, *Liq. Cryst.*, 2001, **28**, 1285.
- 25 C. Tschierske, *J. Mater. Chem.*, 1998, **8**, 1485.
- 26 L. Kovalenko, W. Weissflog, S. Grande, S. Diele, G. Pelzl and I. Wirth, *Liq. Cryst.*, 2000, **27**, 683.
- 27 D. Shen, A. Pegenau, S. Diele, I. Wirth and C. Tschierske, *J. Am. Chem. Soc.*, 2000, **122**, 1593.
- 28 Ch. Keith, R. Amaranatha Reddy, M. Prehm, U. Baumeister, H. Kresse, J. Lorenz, Chao, H. Hahn, H. Lang and C. Tschierske, *Chem.-Eur. J.*, 2007, **13**, 2556.
- 29 R. Amaranatha Reddy, U. Baumeister, C. Keith, H. Hahn, H. Lang and C. Tschierske, *Soft Matter*, 2007, **3**, 558.
- 30 J. Barbera, I. de Francisco, P. Forcen, N. Gimeno, L. Monreal, M. B. Ros and J. L. Serrano, 9th International Ferroelectric Liquid Crystal Conference, 2003, Dublin, book of abstracts, p. 87.
- 31 Y. Zhang, M. Wand, M. J. O'Callaghan, C. M. Walker and W. Thurmes, *Ferroelectrics*, 2006, **344**, 11.
- 32 K. Nishida, W. J. Kim, S. K. Lee, S. Heo, J. G. Lee, K.-T. Kang, Y. Takanishi, K. Ishikawa, J. Watanabe and H. Takezoe, *Jpn. J. Appl. Phys.*, 2006, **45**, L329.
- 33 R. Achten, A. Koudijs, M. Giesbers, A. T. M. Marcelis, E. J. R. Sudhölter, M. W. Schröder and W. Weissflog, *Liq. Cryst.*, 2007, **34**, 59.
- 34 B. Kosata, G.-M. Tamba, U. Baumeister, K. Pelz, S. Diele, G. Pelzl, G. Galli, S. Samaritani, E. V. Agina, N. I. Boiko, V. P. Shibaev and W. Weissflog, *Chem. Mater.*, 2006, **18**, 691.
- 35 R. Achten, A. Koudijs, M. Giesbers, R. Amaranatha Reddy, T. Verhulst, C. Tschierske, A. T. M. Marcelis and E. J. R. Sudhölter, *Liq. Cryst.*, 2006, **33**, 681; Ch. Keith, G. Dantlgraber, R. Amaranatha Reddy, U. Baumeister, M. Prehm, H. Hahn, H. Lang and C. Tschierske, *J. Mater. Chem.*, 2007, **17**, 3796.
- 36 Ch. Keith, R. Amaranatha Reddy and C. Tschierske, *Chem. Commun.*, 2005, 871.
- 37 X. Chen, K. K. Tenneti, C. Y. Li, Y. Bai, X. Wan, X. Fan, Q.-F. Zhou, L. Rong and B. S. Hsiao, *Macromolecules*, 2007, **40**, 840.
- 38 J. Barbera, N. Gimeno, L. Monreal, R. Pinol, M. B. Ros and J. L. Serrano, *J. Am. Chem. Soc.*, 2004, **126**, 7190.
- 39 C.-D. Keum, A. Kanazawa and T. Ikeda, *Adv. Mater.*, 2001, **13**, 321.
- 40 A. C. Sentman and D. L. Gin, *Angew. Chem.*, 2003, **115**, 1859.
- 41 G. Pelzl, M. W. Schröder, A. Eremin, S. Diele, B. Das, S. Grande, H. Kresse and W. Weissflog, *Eur. Phys. J. E*, 2006, **21**, 293.
- 42 V. Bourny, V. Lorman, J. Pavel, B. Mettout and H. T. Nguyen, *Ferroelectrics*, 2002, **276**, 127.
- 43 W. Weissflog, M. W. Schröder, S. Diele and G. Pelzl, *Adv. Mater.*, 2003, **15**, 630.
- 44 M. Marcos, E. Melendez and J. L. Serrano, *An. Quim., Ser. C*, 1983, **79**, 422.
- 45 M. Coden, S. Miyake, S. Takenaka and S. Kusabayashi, *J. Phys. Chem.*, 1984, **88**, 2387.
- 46 E. L. Steiger and H. J. Dietrich, *Mol. Cryst. Liq. Cryst.*, 1972, **16**, 279.
- 47 K. Zab, D. Joachimi, O. Agert, B. Neumann and C. Tschierske, *Liq. Cryst.*, 1995, **18**, 489.
- 48 H. Bengs, M. Ebert, O. Karthaus, B. Kohne, K. Praefcke, H. Ringsdorf, J. H. Wendorff and R. Wüstefeld, *Adv. Mater.*, 1990, **2**, 141.
- 49 S. Umadevi, S. Radhika and B. K. Sadashiva, *Liq. Cryst.*, 2006, **33**, 139.
- 50 J. Mieczkowski, J. Szydłowska, J. Matraszek, D. Pocięcha, B. Donnio and D. Guillon, *J. Mater. Chem.*, 2002, **12**, 3392.
- 51 A. Eremin, I. Wirth, S. Diele, G. Pelzl, H. Schmalfuss, H. Kresse, H. Nadasi, K. Fodor-Csorba, E. Gacs-Baitz and W. Weissflog, *Liq. Cryst.*, 2002, **29**, 775.
- 52 W. Weissflog, H. N. Shreenivasa Murthy, S. Diele and G. Pelzl, *Philos. Trans. R. Soc. London, Ser. A*, 2006, **364**, 2657.
- 53 G. Pelzl and W. Weissflog in *Thermotropic Liquid Crystals – Recent Advances*, ed. A. Ramamoorthy, Springer, 2007, p. 1.
- 54 G. Pelzl, S. Diele, A. Jakli, C. Lischka, I. Wirth and W. Weissflog, *Liq. Cryst.*, 1999, **26**, 135.
- 55 G. Pelzl, M. W. Schröder, U. Dunemann, S. Diele, W. Weissflog, C. Jones, D. Coleman, N. A. Clark, R. Stannarius, Y. Li, B. Das and S. Grande, *J. Mater. Chem.*, 2004, **14**, 2492.
- 56 D. A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Y. Takanishi, E. Körblova, D. R. Link, R.-F. Shao, W. G. Jang, J. E. MacLennan, O. Mondainn-Monval, C. Boyer, W. Weissflog, G. Pelzl, L.-C. Chien, J. Zasadzinski, J. Watanabe, D. M. Walba, H. Takezoe and N. A. Clark, *Science*, 2003, **301**(29), 1204.
- 57 G. Pelzl, S. Diele, A. Jakli and W. Weissflog, *Liq. Cryst.*, 2006, **33**, 1513.
- 58 P. Pyc, J. Mieczkowski, D. Pocięcha, E. Gorecka, B. Donnio and D. Guillon, *J. Mater. Chem.*, 2004, **14**, 2374.
- 59 G. Dantlgraber, Ch. Keith, U. Baumeister and C. Tschierske, *J. Mater. Chem.*, 2007, **17**, 3419.
- 60 A. Jakli, C. Lischka, W. Weissflog, G. Pelzl and A. Saupe, *Liq. Cryst.*, 2000, **27**, 1405.
- 61 Y. Yusuf, Y. Hidaka, S. Kai, H. R. Brand, P. E. Cladis, W. Weissflog and G. Pelzl, *Ferroelectrics*, 2002, **276**, 171.
- 62 Y. A. Nastishin, M. F. Achard, H. T. Nguyen and M. Klemen, *Eur. Phys. J. E*, 2003, **12**, 581.
- 63 M. F. Achard, M. Klemen, Y. A. Nasishin and H. T. Nguyen, *Eur. Phys. J. E*, 2005, **16**, 37.
- 64 A. Jakli, D. Krüerke, H. Sawade and H. Heppke, *Phys. Rev. Lett.*, 2001, **86**, 5715.
- 65 A. Eremin, S. Diele, G. Pelzl, H. Nadasi and W. Weissflog, *Phys. Rev. E*, 2003, **67**, 021702.
- 66 H. R. Brand, P. E. Cladis and H. Pleiner, *Eur. Phys. J. B*, 1998, **6**, 347.
- 67 C. Bailey and A. Jakli, *Phys. Rev. Lett.*, 2007, **99**, 207801.