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## Liquid Crystals

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# The inverse phase sequence SmA–SmC in symmetric dimeric liquid crystals

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Seven homologous symmetric dimeric liquid crystals are presented where two three-ring mesogenic units are connected by a bis(carbonyloxy)alkylene spacer. For homologues with terminal heptyloxy, octyloxy and nonyloxy chains, the unusual phase sequence SmA–SmC with increasing temperature was detected by the study of the optical textures and by X-ray diffraction measurements. This unusual behaviour is discussed on the basis of the molecular structure of these compounds

## 1. Introduction

In liquid crystalline dimers two mesogenic groups are connected with a flexible spacer. The conformation and the phase behaviour of such compounds are significantly influenced by the structure and the length of the spacer as well as by the positions of the linking groups [1]. In the case of symmetric dimeric compounds where the mesogenic groups are terminally linked by a bis(carbonyloxy)-alkylene spacer a marked even–odd effect is reported. Dimers with an even-numbered spacer form SmA phases and/or nematic phases while analogous compounds with an odd-numbered spacer exhibit SmC phases [2, 3]. The smectic A phase is an intercalated one, the layer spacing of which is about half the molecular length. The structure of the SmC phase can be modified through its dependence on the length of the spacer and the length of the terminal chains.

If the length of the terminal chains is smaller than or comparable to the length of the spacer, an intercalated SmC structure of bent molecules is observed, characterized by a random mixing of the terminal chains and the spacer [2, 3]. In this structure the tilt direction of the mesogenic units alternates in passing from one layer to the next as indicated by the occurrence of singularities  $s = 1/2$  in the schlieren texture of this phase.

If the terminal chains are significantly longer than the spacer, the tails and the spacer can segregate from each other giving rise to a biaxial structure where the bent molecules are packed in the smectic layers with uniform bent direction [4, 5]. From electro-optical measurements, an antiferroelectric structure can be deduced characterized by an alternating direction of the spontaneous polarization.

If the lengths of the spacer and the terminal chains are between the cases mentioned above, two-dimensional frustrated smectic phases are observed [5].

In the case of symmetric dimeric compounds possessing a dioxyalkylene spacer, the phase behaviour is quite different [6, 7]. It was found that the SmA phase does not only occur in twins with an even-numbered spacer, but also in twins with an odd-numbered spacer, although the clearing temperatures are lower in the latter case. This SmA phase is not an intercalated one, and its layer spacing is nearly equal to the molecular length. The same is true for the SmC phase which generally appears in homologues with relatively long terminal chains [6, 7]. A special feature of these symmetric dimers is also the formation of undulated hexatic phases [7].

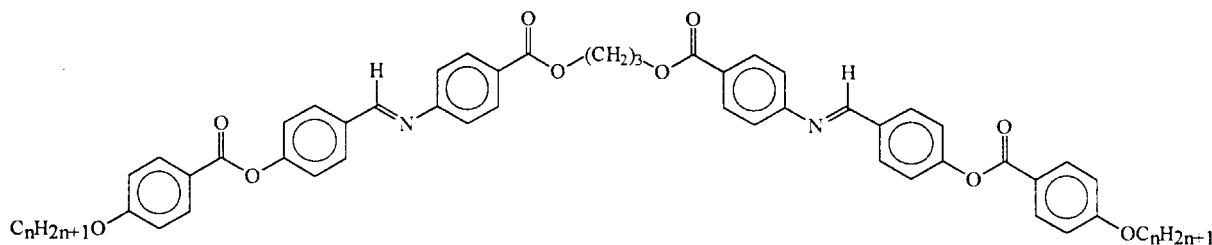
In this paper we present seven homologous symmetric dimeric liquid crystals where two three-ring mesogenic units are connected by a bis(carbonyloxy)propylene spacer. An unusual phase behaviour detected by microscopical investigations and X-ray measurements will be reported and discussed.

## 2. Materials

The transition temperatures and transition enthalpies of the substances studied are listed in the table.

It is seen that the short chained members, compounds 1–3, of the homologous series form only a SmC phase, whereas the member with the longest chain (7) exhibits a SmA phase. The homologues with intermediate length of the terminal chains (4–6) show smectic dimorphism, but in an unusual phase sequence where the SmC phase is the high temperature phase with respect to the SmA phase. Furthermore, the homologues 5 and 6 form a

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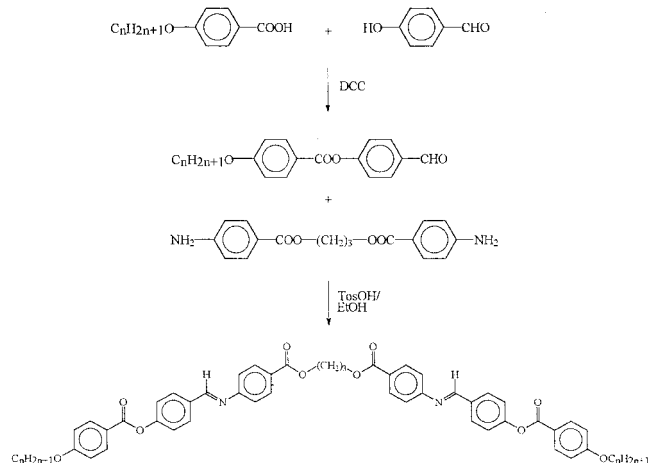
Table 1. Phase transition temperatures in °C and transition enthalpies [kJ mol<sup>-1</sup>].

Compound	<i>n</i>	Cr	E	SmA	SmC	N	I
1	4	• 177.9 [12.8]	• 207.6 [46.5]	—	• 268.7 [13.6]	—	•
2	5	• 166.5 [42.3]	• 174.4 [28.3]	—	• 258.8 [13.4]	—	•
3	6	• 142.2 [ 3.1]	• 177.0 [55.2]	—	• 252 [13.2]	—	•
4	7	• 154.2 [12.9]	• 169.5 [53.1]	• 181 [4.3]	• 244.5 [16.2]	—	•
5	8	• 155.3 [11.2]	• 168.6 [42.2]	• 205.4 [2.7]	• 237.5 [12.9] <sup>a</sup>	• 238.5 [-]	•
6	9	• 162.5 [15.3]	• 165.3 [37.6]	• 231 [14.6] <sup>a</sup>	• 232 [-]	• 233 [-]	•
7	10	• 150.9 [11.9]	• 167.3 [41.3]	• 232.1 [16.4]	—	—	•

<sup>a</sup> These values include the enthalpy contributions of the subsequent transitions

nematic phase in a small temperature range. Another interesting finding is the occurrence of a crystal E phase.

Synthetic route:



Esterification of 4-*n*-alkoxybenzoic acids with 4-hydroxybenzaldehyde was performed by means of dicyclohexylcarbodiimide/dimethylaminopyridine resulting in two-ring compounds bearing the reactive formyl group at one terminal position. The final products were prepared by condensation of these 4-formylphenyl 4-*n*-alkoxybenzoates with 1,3-propylene glycol bis-(4-aminobenzoate) [Aldrich] by heating under reflux in ethanol under nitrogen. Toluenesulphonic acid served as

catalyst. After cooling, the precipitates were separated off and recrystallized at least twice from toluene/heptane and finally from dimethylformamide. Representative of all the compounds, the analytical data are given for substance **5** (*n* = 8):

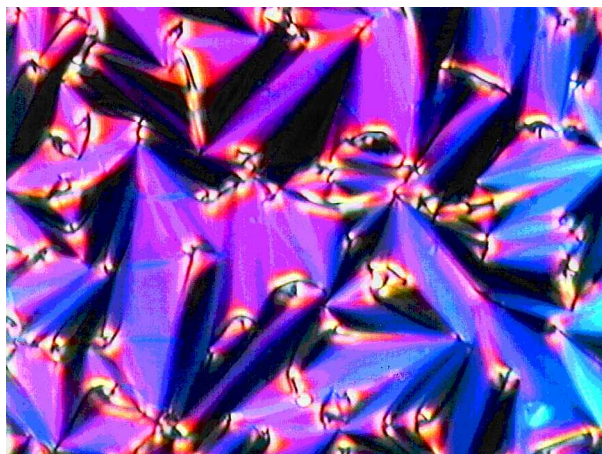
C<sub>61</sub>H<sub>66</sub>N<sub>2</sub>O<sub>10</sub> (987.20) Calc. C 74.22 H 6.74 N 2.84%  
Found C 74.19 H 6.38 N 2.92%.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ = 8.43 (s, 2H, CH=N), 8.13 (d, 4H, Ar-H, *J* = 8.9 Hz), 8.06 (d, 4H, Ar-H, *J* = 8.4 Hz), 7.96 (d, 4H, Ar-H, *J* = 8.6 Hz), 7.34 (d, 4H, Ar-H, *J* = 8.6 Hz), 7.18 (d, 4H, Ar-H, *J* = 8.2 Hz), 6.97 (d, 4H, Ar-H, *J* = 8.8 Hz), 4.54 (t, 4H, OCH<sub>2</sub>, *J* = 6.1 Hz), 4.05 (t, 4H, OCH<sub>2</sub>, *J* = 6.5 Hz), 2.3 (m, 2H, CH<sub>2</sub>), 1.83 (m, 4H, OCH<sub>2</sub>CH<sub>2</sub>), 1.31 (m, 20H, CH<sub>2</sub>), 0.9 (m, 6H, CH<sub>3</sub>).

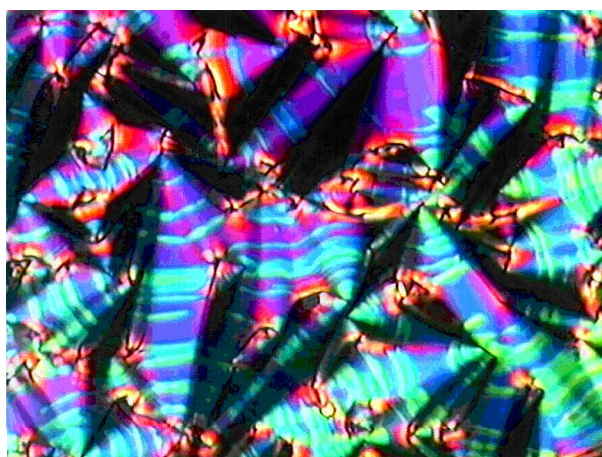
### 3. Experimental

The transition temperatures were determined using a Perkin Elmer DSC 7 differential scanning calorimeter and a Leitz Orthoplan polarizing optical microscope equipped with a Linkam THM 600 hot stage.

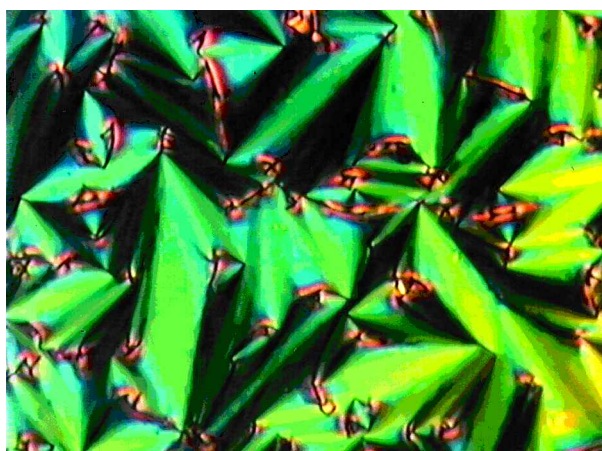
X-ray diffraction measurements were performed on both powder and aligned samples. For the powder samples a Guinier camera or a Guinier goniometer fitted with a bent quartz monochromator (Huber, Germany) was used. X-ray measurements on oriented samples were performed



(a)



(b)



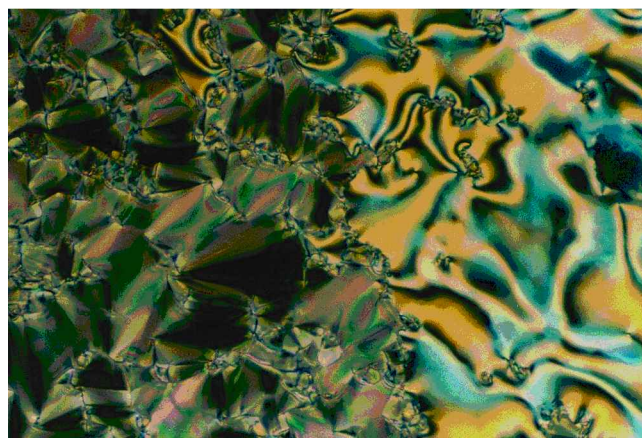
(c)

Figure 1. (a) Fan-shaped texture of the SmC phase of compound **4** (182°C). (b) Transition bars in the fan-shaped texture of the SmC phase of compound **4** (180.8°C). (c) Fan-shaped texture of the SmA phase of compound **4** (180°C).

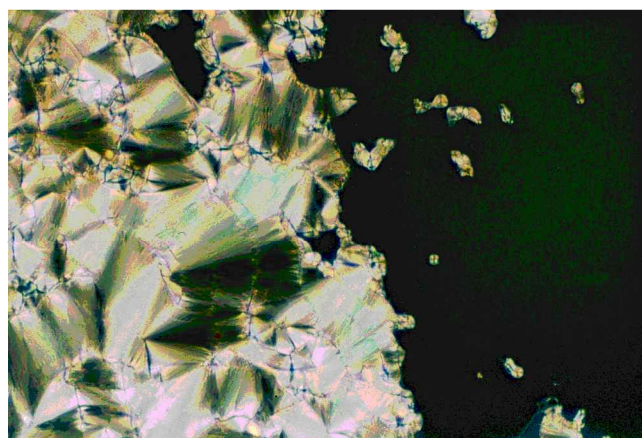
with a 2D detector (HI-Star, Siemens A6). The alignment of the samples was achieved by annealing a drop of liquid crystal placed on a glass plate immediately below the clearing temperature. For this sample preparation only the scattering intensity of the upper half of the reciprocal space could be recorded. The temperature gradient over the powder samples was estimated to be  $< 0.5^\circ\text{C}$  and about  $1^\circ\text{C}$  for the aligned samples.

#### 4. Results

The smectic A and smectic C phases of the homologous compounds could be clearly assigned by their characteristic textures. The SmA phase appears as typical fan-shaped texture or as a homeotropic texture. On cooling the isotropic liquid, the SmC phase forms a fan-shaped texture which is more reminiscent of a SmA phase than of a SmC phase (figure 1(a)); but a homeotropic texture could never be obtained. At the transition



(a)



(b)

Figure 2. (a) Fan-shaped texture and schlieren texture of the SmC phase of compound **5** (207°C). (b) Fan-shaped texture and homeotropic texture of the SmA phase of compound **5** (202°C).

from SmC to SmA, the focal-conic fans become crossed with bars which are transitory in nature, figure 1(b, c). Furthermore, this transition is accompanied by a clear increase of the birefringence. If the SmC phase forms a schlieren texture, the SmA phase appears as a homeotropic texture (figure 2). It is seen from figure 3 that the schlieren texture exhibits not only singularities with four brushes ( $s = \pm 1$ ) which are typical for a SmC texture, but in addition, singularities with two ( $s = \pm 1/2$ ) and six brushes ( $s = \pm 3/2$ ) occur which have also been observed in antiferroelectric SmC phases [8] or intercalated SmC phases of mesogenic twins [2, 3, 9]. The occurrence of such singularities is the result of an alternating tilt between adjacent layers and can be explained by a combination of a disclination and a screw dislocation (dispiration) [8–10].

On cooling the SmC phase of compounds 1–3 or the SmA phase of compounds 4–7, the crystal E phase shows characteristic textures. If the E phase arises from a SmA or SmC fan-shaped texture, concentric arcs develop within the original texture (see figure 4). If the phase arises from a homeotropic SmA texture or a schlieren texture of SmC, a ‘scale’-like mosaic texture occurs.

Furthermore, we found that the corresponding phases of the homologous compounds (SmA, SmC) are completely miscible. Figure 5 shows the phase diagram of the binary system of the homologous compounds 3 and 7, which exhibit only a SmC and a SmA phase, respectively. It is not surprising that also in this binary system the SmC phase is the high temperature phase with respect to the SmA phase. In addition, an intermediate nematic phase occurs at intermediate concentrations.

Generally X-ray diffraction measurements could be performed up to 200°C. In the case of the C<sub>8</sub> homologue,

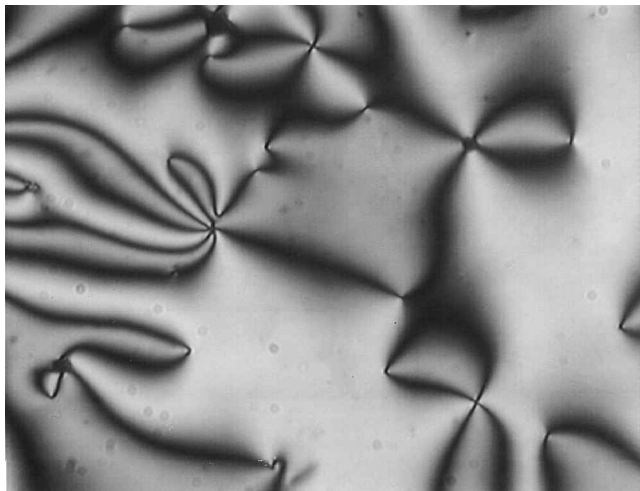


Figure 3. Schlieren texture of the SmC phase of compound 3 (208°C).

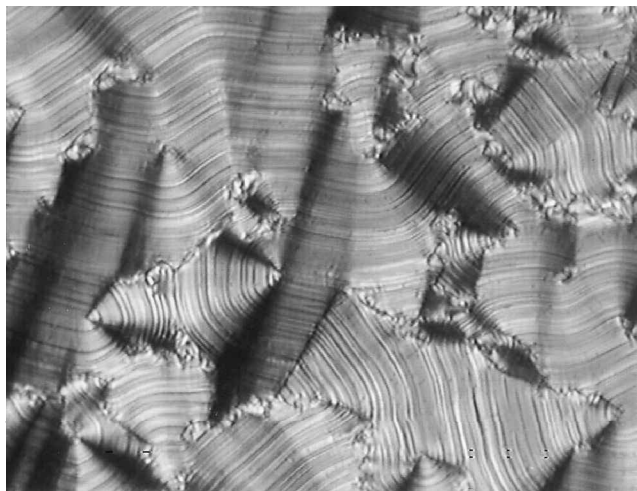


Figure 4. Fan-shaped texture with concentric arcs of the E phase of compound 5 (145°C).

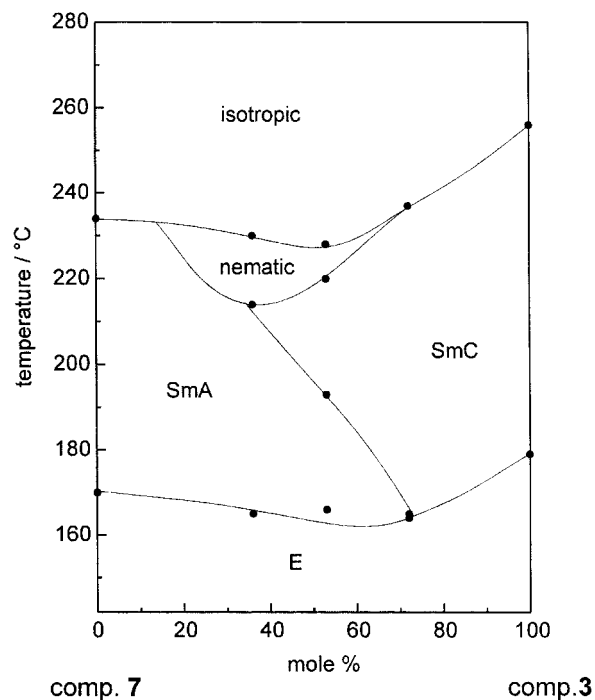


Figure 5. The composition–temperature phase diagram for the binary system with compounds 3 and 7.

measurements were done up to 210°C. In both smectic phases the X-ray patterns of non-aligned samples show a diffuse scattering in the wide angle region which clearly points to a liquid-like order within the smectic layers. From the Bragg reflections in the small angle region, the layer spacing  $d$  in the SmA and SmC phase could be determined. It was found that for both the SmA and SmC phases the layer spacing does not change markedly with temperature (see figure 6).

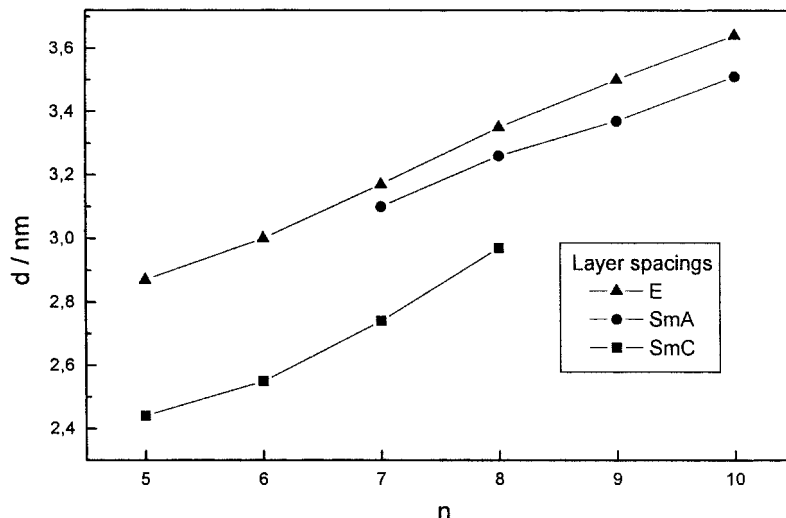


Figure 6. Layer spacings  $d$  in the SmA and SmC phases of the homologues 2–7.

For the homologues (4, 5) which exhibit smectic dimorphism, the layer spacing changes discontinuously at the phase transition SmA–SmC in contrast to usual calamitic compounds (figure 7). This jump is clearly indicated by the observation that in presence of a small temperature gradient both reflections with their characteristic scattering vectors appear (figure 8). The discontinuous change points to a phase transition of first order (figure 7). It is also remarkable that the layer spacing of the SmA and SmC phases is only about the half of the molecular length.

The unusual transition of the SmA low temperature phase into the SmC high temperature phase could be unambiguously proved by the X-ray pattern of oriented samples. Figure 9(a) displays the typical diffraction pattern of a SmA phase with the Bragg reflections on the meridian of the pattern and the diffuse wide angle scattering on the equator. At the transition into the high temperature phase, the diffuse outer maxima are shifted

out of the equator (figure 9(b)), indicating a tilt within the smectic layers. From the  $\chi$ -scan, a tilt angle of  $17.5^\circ$  for the SmC phase of the  $C_7$  homologue and of  $20^\circ$  for the  $C_8$  homologue can be determined. These are in satisfying agreement with those values obtained by the simple equation  $\cos \vartheta = d_c/d_\lambda$ . We explain the tilt by the transition of the molecules from a rod-like shape (SmA) to an angled shape (SmC).

As mentioned before, the ratio of the layer spacing  $d$  to the estimated molecular length  $L$ , obtained from molecular models is approximately 0.5. This result suggests that the molecules are forming an interleaved structure in which the mesogenic units are overlapped and the spacer and terminal chains are randomly mixed. Such smectic phases are designated as intercalated smectic phases which have also been described for twins with two-ring mesogenic units [1–3, 9].

Cooling the sample into the low temperature phase, an X-ray pattern has been obtained which is known for

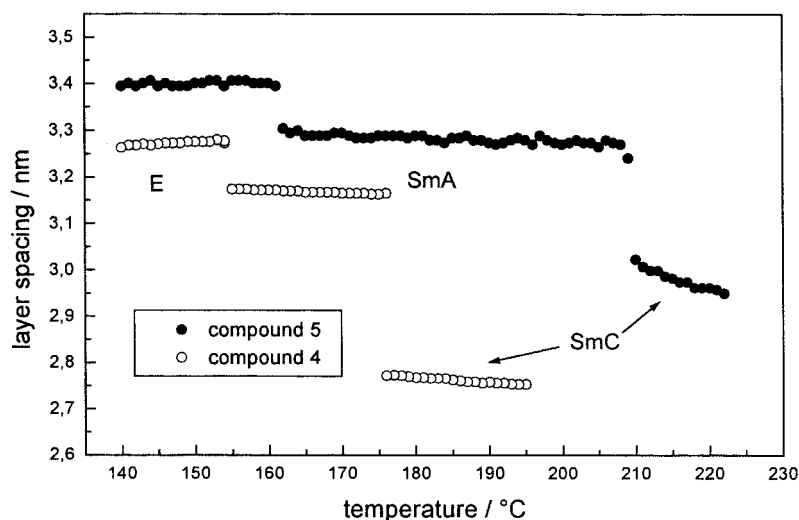


Figure 7. Change of the layer spacing  $d$  at the transition SmC→SmA of compounds 4 and 5.

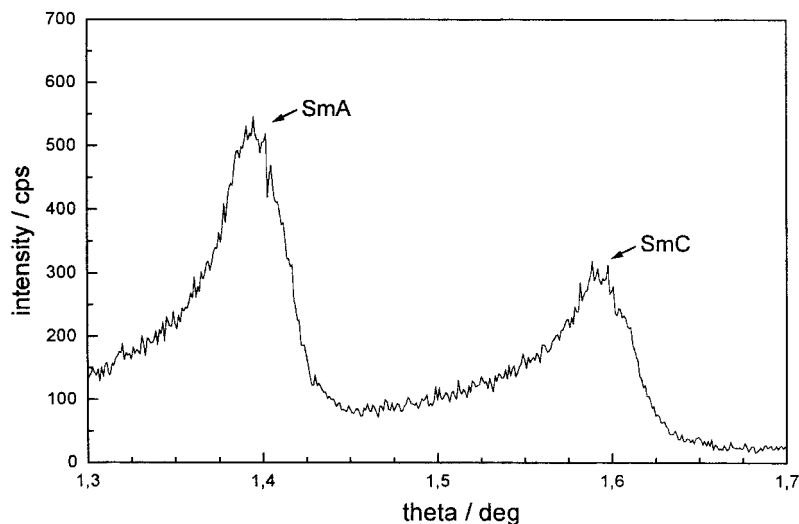


Figure 8. Small angle reflections at the transition SmC  $\rightarrow$  SmA of compound **4** (temperature gradient  $\sim 1^\circ\text{C}$ ).

a phase denoted in the past as SmE [11] and according to international convention is now called a crystal E phase (E) [12]. It is seen in figure 9(c) that besides the reflections at small angles (layer reflections) several outer reflections can be observed indicating the order in the layers. The pattern proves the perpendicular alignment of the molecules within the layers. But in most cases, additional weak reflections appear in the pattern, obviously resulting from partial crystallization. The thermal behaviour as well as the structure of this E phase will be discussed in a forthcoming paper.

## 5. Discussion

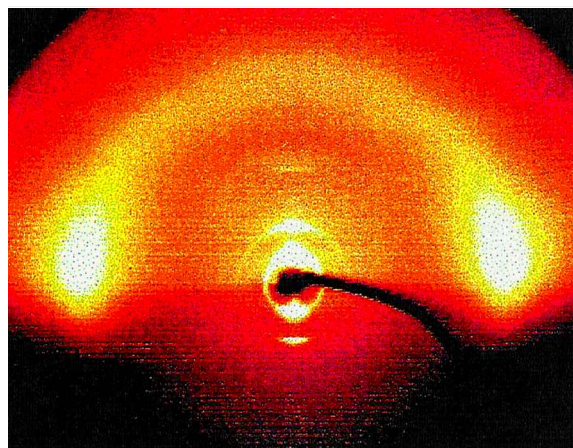
The molecular structure of the liquid crystalline dimers studied in this paper is similar to that of dimers described by Watanabe *et al.* [1, 2]. The main difference is that the mesogenic units contain three aromatic rings. Similar to twins with two-ring mesogenic units, intercalated smectic structures are observed. It is also plausible that the short chained homologues **1–3** exhibit an intercalated SmC phase because the spacer has an odd parity and because the length of the spacer and the length of the terminal chains are not so different, so that a randomized arrangement of spacers and terminal chains results. Not so clear is the occurrence of the SmA phase in spite of the odd-numbered spacer which favours, in general, a bent molecular structure.

The most interesting result is the inverse phase sequence SmA  $\rightarrow$  SmC with increasing temperature. The occurrence of a SmA phase as the low temperature phase with respect to the SmC phase is not completely unknown. There are binary systems where a phase sequence SmA–SmC–SmA was reported [13–16]. In these cases the tilt angle of the intermediate SmC phase

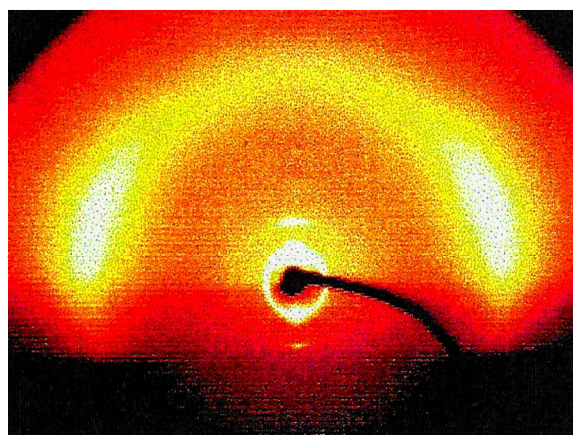
is rather low ( $\sim 10^\circ$ ) and the unusual phase sequence is only observed in a limited concentration range. The reason for this re-entrant behaviour is not clear but it seems that the occurrence of the re-entrant SmA phase is caused by the special steric situation.

In the case under consideration however, it is assumed that the transition from a SmA into a SmC phase is connected with a change of the molecular conformation from a 'rod-like' molecule in the SmA into an angled molecule in the SmC phase (figure 10). The latter situation is indicated by the defects in the textures, whereas the former is proved by the X-ray studies. The question arises what is the molecular origin of the stabilization of the SmA phase with increasing length of the terminal chains and of the inverse sequence of the SmA phase and SmC phase?

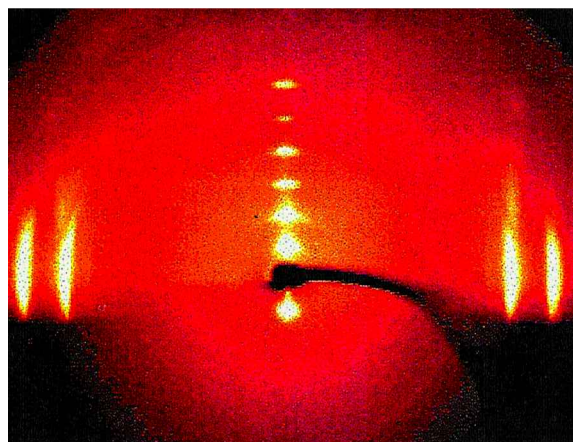
With respect to the first question, it can be assumed that for homologues with relatively short aliphatic chains (**1, 2, 3**), the length of the flexible spacer is not so different from that of the terminal chains so that a random mixing of both can occur. In this case also, an angling of the spacer is possible giving rise to an alternating tilt of the mesogenic units as indicated by the X-ray studies and by the characteristic disclinations. On the other hand, if the terminal chains are clearly longer than the spacer, a stretching of the spacer should be favoured because of space filling conditions. In this way the mesogenic units are aligned perpendicular to the layer planes so that a SmA structure results (figure 10). This effect—the stretching of the spacer—is reinforced with decreasing temperature. It explains why for homologues with an intermediate length of the terminal chains, on cooling the SmC phase, the angled spacer becomes stretched and a transition from SmC to SmA occurs. Probably also the stronger lateral cohesion of the relatively long



(a)



(b)



(c)

Figure 9. X-ray pattern of oriented samples. (a) SmA phase of compound **5** (202°C); (b) SmC phase of compound **5** (213°C); (c) E phase of compound **3** (148°C).

mesogenic units plays a role which could be enhanced by the antiparallel aligned dipoles of the linkage groups of neighbouring mesogenic units.

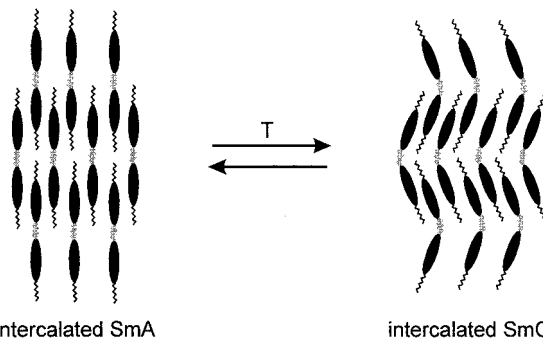


Figure 10. Structural models of the intercalated SmC phase and intercalated SmA phase of the mesogenic twins.

There are a number of microscopic models to describe the transition of the SmA into the SmC phase [17–20] where electrostatic or steric interactions are taken into consideration. According to recent theoretical models [21–23], the molecular tilt is an intrinsic property of any layered quadrupolar structure. In this connection, strong quadrupolar moments due to acentral transversal dipoles (“outboard” dipoles) play an important role. But in all theories, the molecular structure must be approximated by simplified models so that it cannot be expected that these theories are able to describe the unusual phase sequence for the compounds under discussion.

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