Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 29 June 2010

To cite this Article Sauer, Christiane , Diele, Siegmar and Tschierske, Carsten(1997) 'Formation of columnar mesophases by calamitic molecules: a modulated SmA phase in mixtures of amphiphilic and bolaamphiphilic biphenyl derivatives', Liquid Crystals, 23: 6, 911 — 917

To link to this Article: DOI: 10.1080/026782997207858

URL: http://dx.doi.org/10.1080/026782997207858

LIQUID CRYSTALS, 1997, VOL. 23, NO. 6, 911–917

Formation of columnar mesophases by calamitic molecules: a modulated SmA phase in mixtures of amphiphilic and bolaamphiphilic biphenyl derivatives

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(*Received 16 May 1997; in final form 8 August 1997; accepted 28 August 1997*)

Binary mixtures of bolaamphiphilic biphenyl derivatives with each other and with amphiphilic biphenyl derivatives were investigated by means of optical microscopy. The miscibility of the bolaamphiphiles is very sensitive to the molecular length of the components. The SmA phases of bolaamphiphiles with the same length are completely miscible. If the length difference between the two components of the binary system increases, a miscibility gap occurs. Due to their different phase structures (bilayer versus monolayer) no miscibility in the SmA phases was found for amphiphilic and bolaamphiphilic compounds with comparable molecular lengths. However, in some cases a novel mesophase was induced in the contact region. This mesophase was investigated by X-ray diffraction. It represents a two-dimensionally modulated (columnar) phase with a rectangular lattice (Col_r), but the local order is similar to that of disordered smectics. Its formation is explained in terms of ribbon structures resulting from the collapse of smectic bilayers, in strong analogy to the antiphases ($Sm\tilde{A}$) of terminally polar calamitic mesogens.

1. Introduction

The formation of columnar mesophases is usually associated with a disc-like or tapered shape molecular geometry. However the first thermotropic columnar mesophases were reported for metal soaps [1]. Some of them can be described as ribbon phases resulting from breaking up the layers of head group lattices into ribbon-like segments of definite breadth.

More recently, ribbon structures have been described for thermotropic phases of calamitic molecules. They can occur if attractive forces and the segregation of incompatible molecular segments into different regions strongly force the molecules to arrange in layers. If, additionally, the different space filling of incompatible parts of the molecules or dipolar interactions disturb the layer structure, the molecules can escape from this frustration by breaking up the smectic layers into ribbons and forming two-dimensionally modulated phases [2]. Such ribbon phases have been found for mesogens with fluorinated terminal chains [3–6], polycatenar compounds [7–9], rod-coil molecules [10, 11], amphiphilic diols incorporating rigid biphenyl units [12] and facial amphiphiles [13]. However, modulated phases were also detected for polymeric and oligomeric [14] mesogens [15–17], terminally connected dimesogens with odd spacer units [18–20] and other bent molecules [21, 22].

Another source of modulated phases results from a competition between different length scales. For polar calamitic molecules there can be an incompatibility between periodicities corresponding to the molecular length and the length of antiparallel molecular pairs. One possible compromise between these competing periodicities is to form two-dimensional modulated phases. The rectangular antiphase [23] $Sm\tilde{A}$ or the tilted antiphase [24] (ribbon phase, $Sm\tilde{C}$) has been found as an intermediate phase between smectic single-layer (SmA_1) and smectic double-layer phases (SmA_2) or bilayer phases (SmA_d) of some calamitic liquid crystal materials with polar terminal groups [2, 23–29]. They are two-dimensionally ordered like columnar mesophases, but the local order within the ribbons is similar to that of smectics (figure 1).

In order to prove the generality of this principle it

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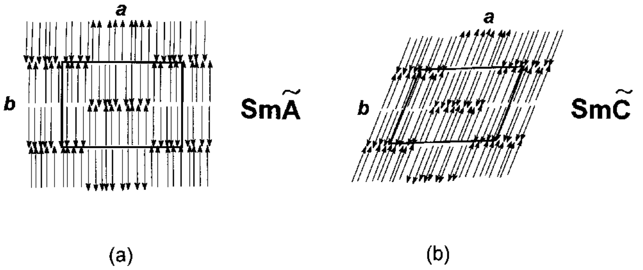


Figure 1. Schematic structure of modulated smectic phases: (*a*) centred rectangular SmÃ phase (antiphase) [23]; (*b*) the oblique SmC̃ phase (tilted antiphase, ribbon phase) [24].

was of interest to investigate whether ribbon structures can also be obtained as intermediate phases between the double layer structures of amphiphiles and the monolayered mesophases of bolaamphiphiles. Stable bilayers are usually found in mesophases of amphiphilic compounds with highly polar head groups such as ionic groups or polyhydroxyl groups [30–32]. Such highly polar substituents can also be fixed at both ends of a hydrophobic moiety to give bolaamphiphiles. These compounds form mesophases consisting of monolayers [33, 34].

There are two ways to achieve this aim. First, one can synthesize bolaamphiphiles with different polar groups at the ends; this has been done recently [35]. As is obvious from table 1, only the bolaamphiphiles **3** and **5** [35] and the amphiphile **1**[31] are liquid crystals.

The mesomorphic properties are lost if the CH_2OH end group of **3b** is replaced by the carboethoxy group (compound **2**) [35]. Also in other cases it has been found that smectic phases are suppressed by increasing the polarity of the hydrophobic part of amphiphiles [36]. However, a modulated mesophase has never been detected. Therefore we have investigated binary mixtures of amphiphilic diols with bolaamphiphiles and mixtures of different bolaamphiphiles with each other; these will be reported herein.

2. Materials

The compounds **1**, **3** and **5** used in these investigations, together with their transition temperatures, are summarized in table 1. All compounds represent racemic mixtures. The synthesis and details of their mesomorphic behaviour have been described recently [31, 35].

3. Techniques

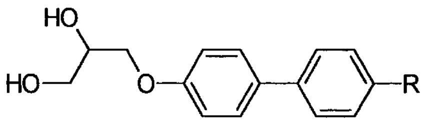
Texture observations involving the pure and mixed phases were performed using a polarizing light microscope. The determination of the principal types of binary phase diagrams was made using the contact preparation method. The final phase diagrams were obtained from microscopic and calorimetric studies of actual binary mixtures. X-ray patterns of powder-like samples were taken using Guinier equipment (computer controlled diffractometer or special film method).

4. Results

4.1. *Binary mixtures of bolaamphiphiles with each other*

Contrary to the miscibility behaviour of conventional non-amphiphilic liquid crystals, miscibility of the SmA phases of bolaamphiphiles strongly depends on the difference between the molecular lengths of the two compounds. Three types of phase diagram were obtained. In binary systems of two bolaamphiphiles with comparable molecular lengths [compounds **3a** and **5a**

Table 1. Phase transition temperatures (°C) of the compounds **1** [31] and **2–5** [35].



Compound	*R*	Cr		SmB		SmA		I
1[a]	$-C_6H_{13}$	•	167	—	—	•	196	•
2	$-O(CH_2)_5COOC_2H_5$	•	154	—	—	—	—	•
3a	$-O(CH_2)_3OH$	•	227	—	—	•	242	•
3b	$-O(CH_2)_6OH$	•	172	•	191	•	209	•
3c	$-O(CH_2)_{11}OH$	•	184	—	—	•	188	•
5a	$-OCH_2CH(CH_2OH)_2$	•	210	—	—	•	260	•
5b	$-O(CH_2)_{11}CH(CH_2OH)_2$	•	180	—	—	•	207	•

[a] Reported values: Cr 160 SmA 194 I[31].

in figure 2 (*a*)] complete miscibility in the SmA phase with approximately ideal behaviour was observed. Increasing the length difference results in mesophase destabilization [figure 2 (*b*)]. By further increasing the difference in the molecular length, the SmA phases do not show complete miscibility and over wide concentration regions mesomorphic properties disappear [figure 2 (*c*)].

Another interesting observation is the induction of an E phase [figure 2 (*b*)] in the middle concentration range

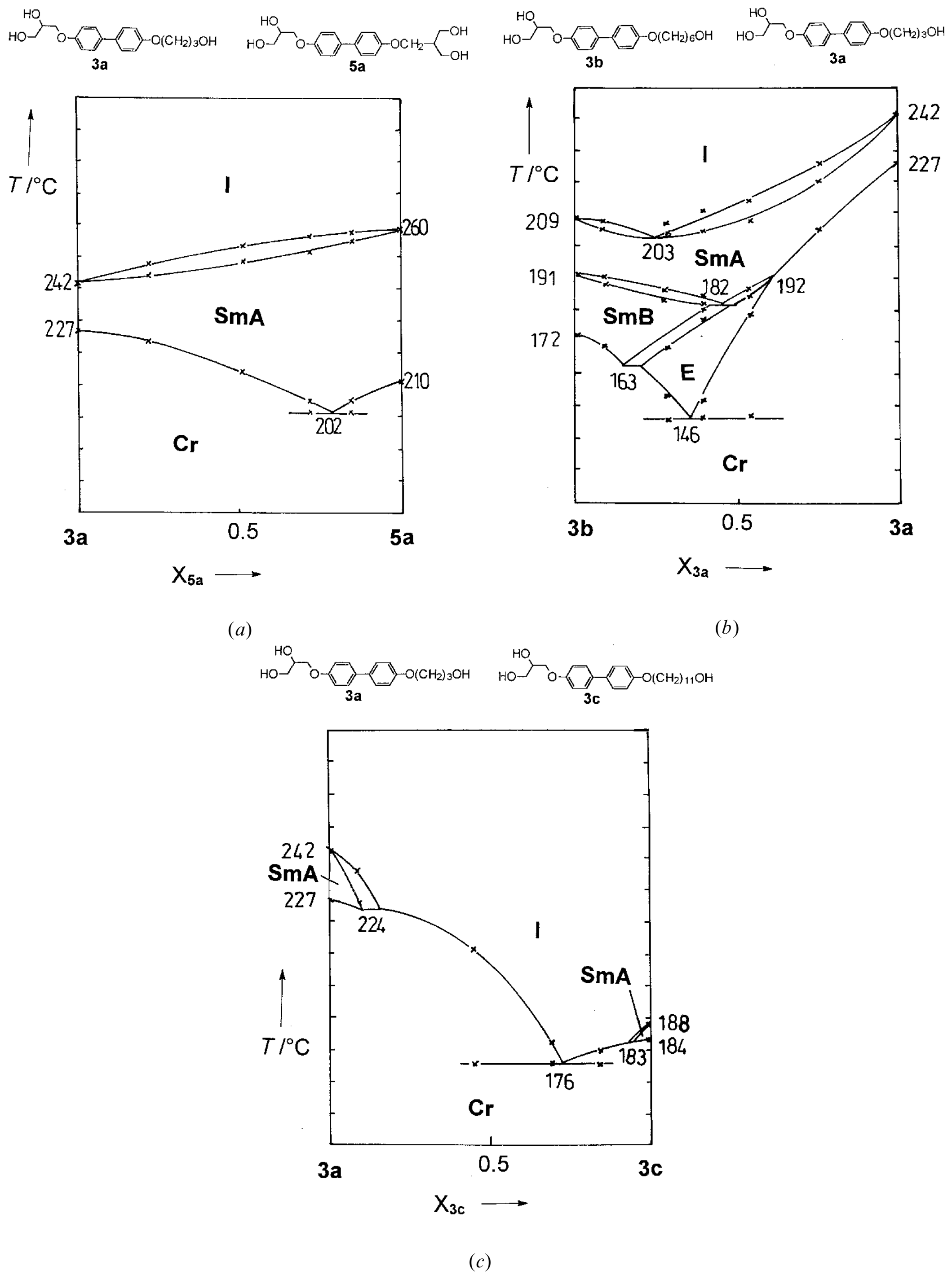


Figure 2. Binary phase diagrams of the systems **3a/5a** (*a*), **3b/3a** (*b*) and **3a/3c** (*c*).

of the contact region between **3a** and **3b**†. The texture of the E phase is shown in figure 3.

The X-ray pattern displayed in figure 4 shows, besides the inner layer reflection, several sharp outer reflections indicating a higher structural order, which confirms an orthorhombic lattice for the E phase.

Indexing gave the lattice constants of the E phase as $a=0{\cdot}86$ nm; $b=0{\cdot}54$ nm; $c=2{\cdot}20$ nm. The c-parameter agrees very well with the averaged molecular length in the mixed phase which can be calculated by the relation $d=x_{3b}L_{3b}+x_{3a}L_{3a}=2{\cdot}19$ nm ($x_{3a,\ 3b}$=molar fraction of compounds **3a** and **3b**; $L_{3a,\ 3b}$=length of the molecules of compounds **3a** and **3b** obtained from CPK models in the most extended conformation).

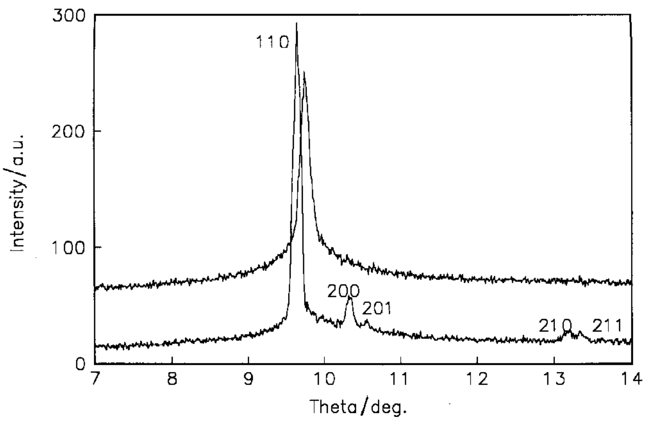


Figure 4. Wide angle region of the X-ray diffraction pattern of the mixture **3b/3a** ($x_{3b}=0{\cdot}70$) in the SmB phase at 180°C) and in the E phase at 160°C.

Table 2. Observed reflections of the induced E phase of the binary system **3b/3a** ($x_{3b}=0{\cdot}7$) at 160°C.

$\Theta_{exp.}$/°	$\Theta_{cal.}$/°	$\Delta\Theta$/°	h k l
2·01	—	—	0 0 1
9·61	—	—	1 1 0
10·24	—	—	2 0 0
10·47	10·45	0·02	2 0 1
13·11	13·14	0·03	2 1 0
13·27	13·30	0·03	2 1 1

† Probably the E phase is latently present as a monotropic mesophase of compound **3a**. This seems probable, because there is no maximum in the SmA–E transition temperature curve. Because the SmA phase of compound **3a** can only be supercooled to 215°C, this additional phase transition cannot be detected in the pure compound **3a**.

4.2. *Binary mixtures of bolaamphiphiles with amphiphilic compounds*

Mixtures of bolaamphiphiles with amphiphilic diols generally exhibit broad miscibility gaps between the SmA phases, due to the incompatibility of the different structures of their smectic A phases (monolayer versus bilayer). These miscibility gaps are especially broad if the amphiphile and the bolaamphiphile have a different molecular length. In these cases liquid crystalline properties are often lost in the medium concentration range [see figures 5 (*a*) and 5 (*c*)].

Even compounds with nearly the same molecular length, as for example **1** and **3b** [figure 5 (*b*)], have deep miscibility gaps accompanied by extremely broad heterogeneous regions. Surprisingly, in the binary systems of the diol **1** and the bolaamphiphiles **3b**, **3c** and **5b** [figures 5 (*b*), (*c*) and (*d*), respectively], the formation of a new mesophase in a small range at low concentrations of bolaamphiphile (e.g. 10–5·6 mols of diol **1** per mol of **3b**) was found. This phase is characterized by a spherulitic texture (figure 6) as often observed for columnar phases.

To characterize this induced phase, X-ray investigations of non-oriented samples of mixtures consisting of **1/3b** and **1/3c** were carried out. The diffraction patterns of both mixtures in the high temperature SmA phase exhibit the typical characteristics of smectic phases without order in the layers. The experimental thickness of the layer in the mixed SmA phases amounts to 4·01 nm and thus corresponds to that found in the SmA phase of the diol **1** (4·03 nm). This proves that the bilayer structure remains after addition of a small amount of bolaamphiphile **3**.

On cooling the mixtures into the induced phase, the amorphous halo at about 10° is maintained, but in the small angle region an additional interference appears [see figure 7 (*a*)]. The phase transition is accompanied by a very small shift of the inner reflection ($\Delta d \sim 0{\cdot}08$ nm).

The pattern [see figure 7 (*b*)] is of a well oriented sample and indexing of the reflections with 1 1, 3 1 and 0 2 (see table 3) corresponds to a rectangular two-dimensional cell ($a=24{\cdot}5$ nm, $b=4{\cdot}1$ nm). That means that the layers break with a period of about 24·5 nm.

5. Discussion

The miscibility of bolaamphiphilic compounds with each other is very sensitive to the molecular length of the components. This is contrary to the behaviour of most conventional non-amphiphilic calamitic compounds. Due to the strong segregation of the layers consisting of hydrogen bonding networks from the lipophilic layers of the central parts of the molecules, the guest molecules must fit into the given layer distances. The SmA phases of bolaamphiphiles with the same length are completely miscible. If the length difference of the two

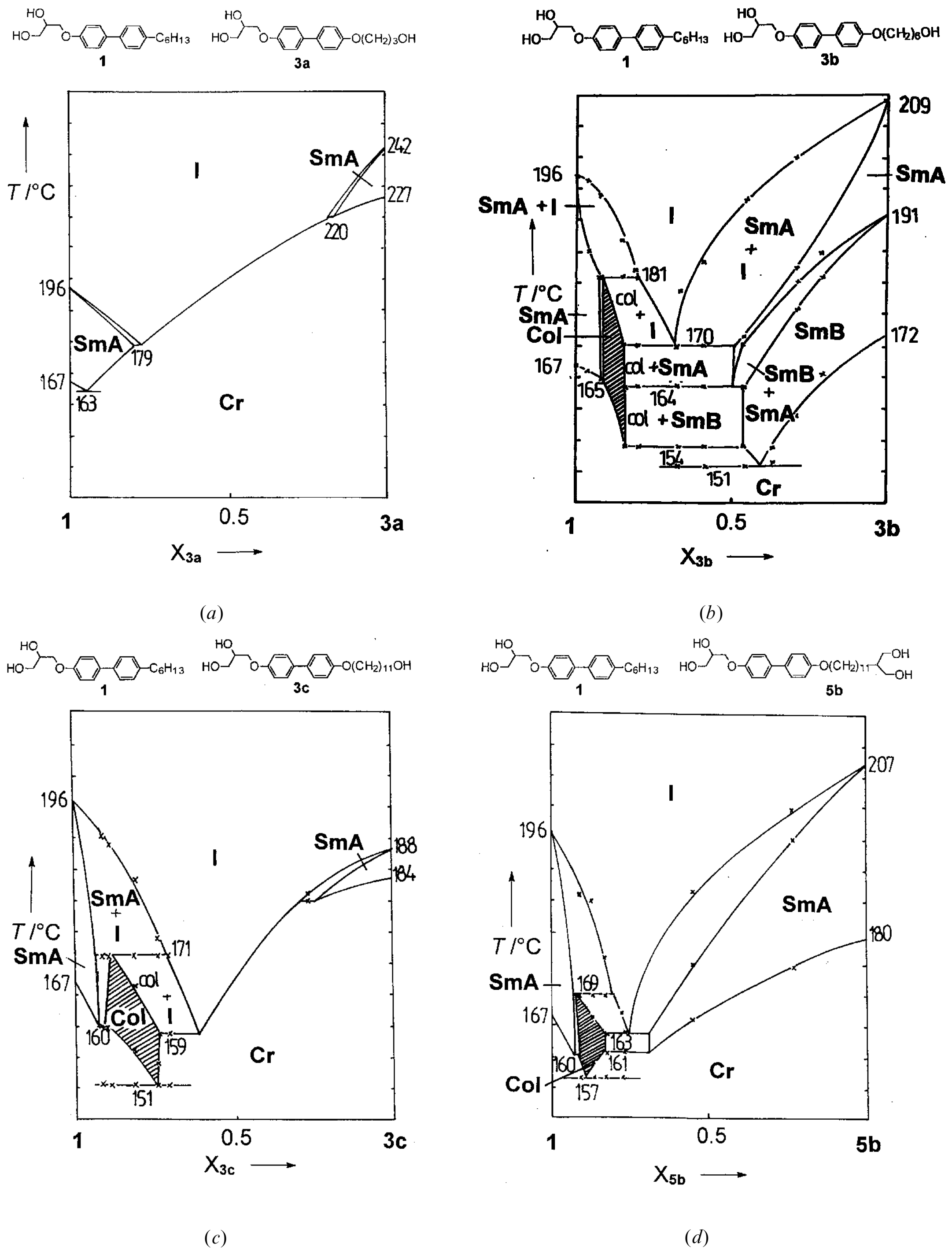


Figure 5. Binary phase diagrams of the systems **1/3a** (*a*), **1/3b** (*b*), **1/3c** (*c*) and **1/5b** (*d*).

components of the binary system increases, a miscibility gap occurs. Due to their different phase structures (bilayer versus monolayer) no miscibility in the SmA phases could be expected for amphiphilic and bolaamphiphilic compounds with comparable molecular lengths. However in some cases a novel mesophase is induced in the contact region. This phase represents a two-dimensionally modulated (columnar) phase with a rectangular lattice (Col_r) and can be regarded as a ribbon phase. One of the lattice parameters ($b=4{\cdot}1$ nm) corresponds to the layer spacing of the double layered SmA phase of the amphiphilic component. This means that the ribbons consist of smectic bilayers. The other periodicity ($a=24{\cdot}5$ nm) represents the distance between the centres of the ribbons and indicates

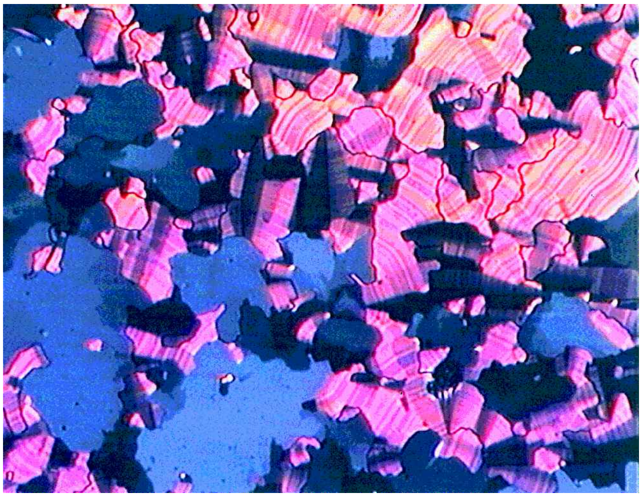
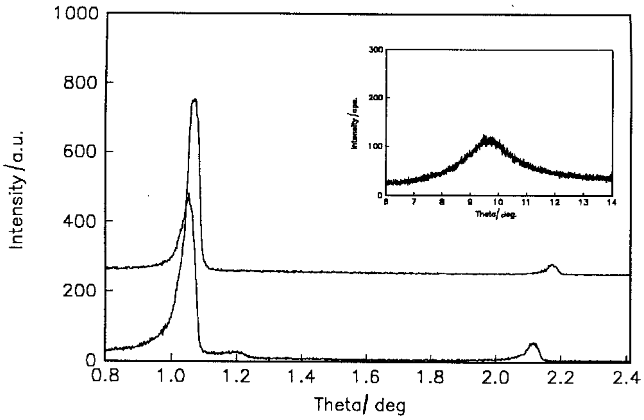
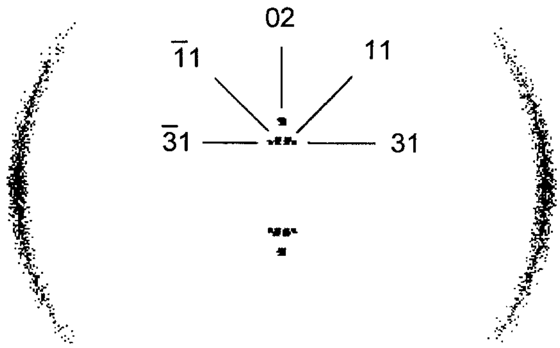


Figure 3. Polarized optical microscopic texture of the induced E phase of the mixture **3b/3a** ($x_{3b}=0{\cdot}7$) at 158°C.

Figure 6. Polarized optical microscopic texture of the induced columnar phase of the binary system **1/3b** ($x_1=0{\cdot}9$) at 165°C.



(*a*)



(*b*)

Figure 7. X-ray diffraction pattern of the mixture **1/3b** ($x_1=0{\cdot}9$): (*a*) non-oriented sample in the SmA mixture at 183°C and in the induced columnar phase at 165°C: (*b*) oriented sample of the induced columnar phase at 165°C.

that the breadth of the individual ribbons corresponds to approximately 25 molecules. Furthermore, it is remarkable that the modulated phases occur at low concentrations of the bolaamphiphile (5–10 mol%). These experimental findings suggest that this ribbon phase can be discussed by analogy with the antiphases (Sm$\tilde{A}$) [23]. The incompatibility between the two different molecular lengths of the two components of the mixture causes an interruption of the layers and gives rise to a ribbon-like structure. A possible model of this ribbon phase is displayed in figure 8.

The model consists of fragments of smectic bilayers with the bolaamphiphiles located at the boundaries of the ribbons. Thus two smectic 'phase types' are realized in this arrangement: the ribbons represent bilayers, whereas at the interfaces between the ribbons, smectic monolayer structures are realized.

Table 3. Observed reflections of the induced ribbon-phase of the binary system **1/3b** ($x_1=0{\cdot}9$) at 165°C.

$\Theta_{exp.}$/°	$\Theta_{cal.}$/°	h k
1·075	—	1 1
1·21	1·19	3 1
2·12	—	0 2

In summary the formation of columnar mesophases in binary mixtures of amphiphilic and bolaamphiphilic compounds has been observed for the first time. Their formation is explained in terms of ribbon structures resulting from the collapse of frustrated bilayers. Considering their two-dimensionally modulated structure, these ribbon phases represent rectangular columnar mesophases (Col$_r$), but with respect to the local order

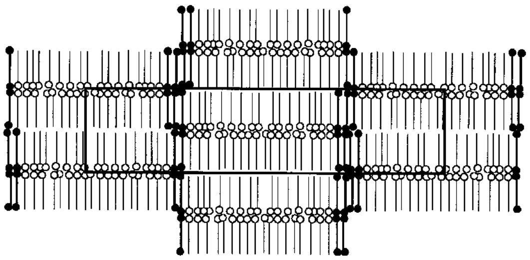


Figure 8. Schematic presentation of the arrangement of the molecules in the mesophase of the mixture **1/3b** ($x_1 = 0{\cdot}9$). Bolaamphiphiles are presented by bold lines with black heads.

within the ribbons and the size of these ribbons they are similar to fluid smectic phases (Sm$\tilde{\mathrm{A}}$).

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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