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The binary system composed of a bent-core compound forming a B₇ phase and a nematogenic calamitic compound

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The isobaric phase diagram for a binary system of liquid crystals is presented. One mixing component is a bent-core mesogen forming a B₇ phase and the other one is a nematogenic calamitic compound. The occurring mesophases have been identified by their optical textures as well as by X-ray investigations. The B₇ phase exists down to about 60 mol% of the bent-core compound **A** / 40 mol% of the calamitic compound **B**. Two additional mesophases are induced in the mixed phase region. At medium concentrations (around 50 mol%) an oblique columnar phase appears which shows a similar X-ray pattern to the B₇ phase but an utterly different nucleation on cooling the isotropic liquid and a completely dissimilar texture. At concentrations below 35 mol% **A**, a further phase is induced which possesses an irregularly modulated layer structure. This phase can be regarded as an intermediate state between the regularly modulated Col_r (B₁) phase and the intercalated B₆ phase. It transforms on cooling into the phase with a regularly modulated structure.

Keywords: bent-core mesogen; binary system; B₇ phase; calamitic mesogen; columnar phases

1. Introduction

Bent-core mesogens have attracted much attention because they are able to form new mesophases with unusual physical properties. Owing to their bent shape, the molecules are packed within smectic layers in a polar fashion which leads to a long-range correlation of the lateral dipoles that means to a polar axis parallel to the layers [1]. Depending on the correlation of the polar order in adjacent layers ferroelectric or antiferroelectric smectic phases can occur [2–7]. In order to escape from macroscopic polarisation, the polar smectic phases (SmAP, SmCP) preferably form antiferroelectric structures (alternating polar axes in adjacent layers) which can be switched into the corresponding ferroelectric state after applying a sufficiently strong electric field [2–7]. Interestingly, a chirality of the smectic layers arises in tilted polar smectic phases (SmCP, SmGP) even when the constituent molecules are achiral; this means the combination of director tilt and polar order gives rise to the layer chirality [8, 9].

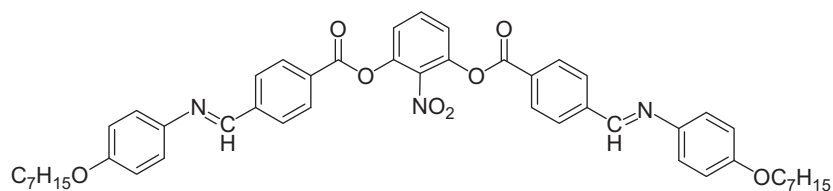
Another way to avoid (or minimise) the polarisation in a layer structure of bent molecules is to modify the layers, resulting in 2D ordered superstructures which can be regarded either as undulated smectic phases in case of wavy deformed layers or, in case of ‘broken layers’, as 2D modulated or columnar phases in which the columns are represented by the polar layer fragments [2–5].

Among the mesophases formed by bent-core compounds, the B₇ phase is of particular interest because

of its unusual nucleation as well as its beautiful optical textures. As first reported by Pelzl *et al.* [10], the B₇ phase forms screw-like and telephone-wire nuclei and beaded filaments on slowly cooling the isotropic liquid. These nuclei coalesce to a complex texture with striped focal conics, banana leaf-like and circular domains and checkerboard textural elements [2, 10–12]. The X-ray patterns of powder-like samples show a diffuse wide-angle scattering proving a liquid-like lateral order of the molecules. Several sharp reflections could be observed in the small-angle region which point to a 2D or even 3D superstructure. In addition, a slightly broadened reflection appears in the medium-angle region which seems to be characteristic of B₇ phases. Nearly simultaneously with the discovery of the B₇ phase another ‘banana phase’ was detected which possesses an undulated layer structure and exhibits a quite similar texture and nucleation from the isotropic liquid [13]. This phase, which was later designated as B₇' [3, 12], shows in most cases a polar switching in contrast to the B₇ phase [13]. Detailed experimental studies by Coleman *et al.* [14] provided evidence that one of the structural features of the B₇ as well as the B₇' phase is the splay of polarisation which prevents macroscopic polarisation and supports the undulation (B₇') or breaking of the layers (B₇). The splay of polarisation is also the origin of characteristic defect walls [14]. The present stage of research on the B₇ phase is reviewed by Pelzl *et al.* [12].

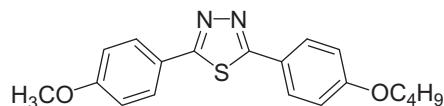
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Mixing component **A** exhibiting a B_7 phase



A Cr 85 B₇ 176 Is [2, 10]

Calamitic mixing component **B**



B Cr 96 N 195 Is [15]

Scheme 1.

In this paper we present a binary system in which one mixing component is a bent-core compound forming a B_7 phase and the other one is a three-ring calamitic nematogenic compound. It will be shown that in the mixed-phase region interesting intermediate mesophases occur, the structure of which will be discussed in more detail.

2. Materials

The chemical formulae of both mixing components are shown in Scheme 1. Component **A** is the heptyloxy homologue of the original B_7 series [2, 10]. The thiadiazole component **B** exhibits a slightly bent molecular shape and is able to form a nematic phase in a broad temperature range [15].

3. Experimental details

The phase transition temperatures were determined with a differential scanning calorimeter (Pyris1, Perkin Elmer) and a polarising microscope (DMRXP, Leica) equipped with a hot stage HT80 and an automatic temperature controller (Mettler-Toledo). The assignment of the mesophases is mainly based on X-ray diffraction studies. Measurements were carried out on powder-like samples in glass capillaries kept in a temperature-controlled heating stage using a Guinier film camera (Huber Diffractionstechnik GmbH) and quartz-monochromatised $\text{CuK}\alpha$ radiation. In cases when surface-aligned fibre-like disordered samples could be obtained by slowly cooling a

drop of the isotropic liquid placed on a glass plate on a temperature-controlled heating stage, 2D diffraction patterns were recorded using Ni-filtered $\text{CuK}\alpha$ radiation and an area detector (HI-Star, Siemens/Bruker).

The isobaric phase diagram was determined by contact preparation as well as by the study of mixtures of a known concentration. From the contact preparations we obtained the temperatures of the three phase equilibria. Electro-optical measurements were done using commercial ITO cells (EHC Corp.) of 5 or 6 μm thickness.

4. Results

It is known that the addition of calamitic molecules to a sample forming a 'banana phase' such as SmCP or B_1 can cause not only structural modifications of these phases but also the induction of new intermediate phases [16–21]. For this reason we studied a binary system in which one mixing component is the bent-core compound **A** which forms the B_7 phase. The other mixing component is the calamitic compound **B** exhibiting a nematic phase in a relatively large temperature range. The clearing temperatures of the mixtures (if possible also the melting temperatures) were determined by differential scanning calorimetry and polarising microscopy. As the observed mesophases could be clearly distinguished by their characteristic textures, we were able to determine the temperatures of the three phase equilibria by the study of contact preparations. The isobaric phase diagram is presented in Figure 1.

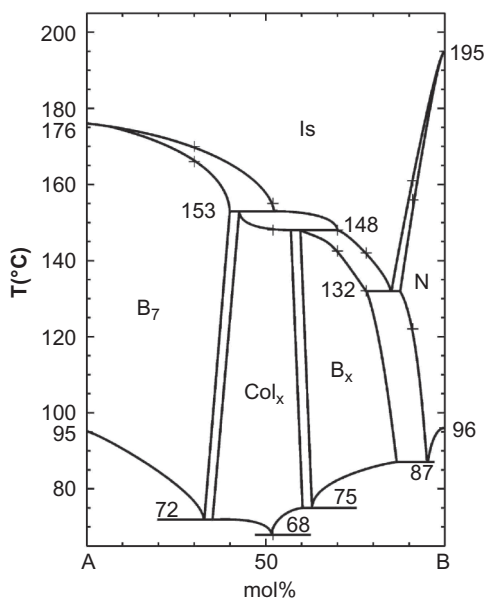


Figure 1. Isobaric phase diagram of the binary system A/B.

The B_7 phase exists down to about 60–67 mol% of the bent-core compound, indicated by the characteristic texture with screw-like nuclei and beaded filaments which appear on slow cooling of the isotropic liquid (see Figure 2).

At medium concentrations (around 50 mol% A, see Figure 1) another phase occurs which exhibits a multi-coloured texture with many circular domains in which the extinction crosses are parallel to the crossed polarisers (Figure 3). At relatively high electric fields (up to $40 \text{ V}/\mu\text{m}$) a slight texture change was observed but no polar response could be detected.

At lower concentrations (less than 40–35 mol% A) a further mesophase occurs. It forms dendritic nuclei on cooling the isotropic liquid which coalesce to a fan-like texture (see Figure 4).

When a moderate electric field is applied ($15\text{--}20 \text{ V}/\mu\text{m}$) during the cooling process mainly circular domains are visible with the extinction cross parallel to the crossed polarisers, see Figure 5. This phase also does not show a polar switching.

X-ray measurements give information about the structural features of the intermediate phases. A mixture with 75 mol% A was investigated to compare the B_7 phase in the mixed phase region with that of the pure compound A. The 2D X-ray diffraction patterns of both samples are shown in Figure 6. Both samples exhibit the X-ray patterns typical for B_7 phases as described in the introduction with a diffuse scattering at wide angles, several sharp reflections in the small-angle region and a slightly broadened one at $2\theta \approx 12^\circ$, $d \approx 7.4 \text{ \AA}$ (Figures 6(a) and 6(b)). As in

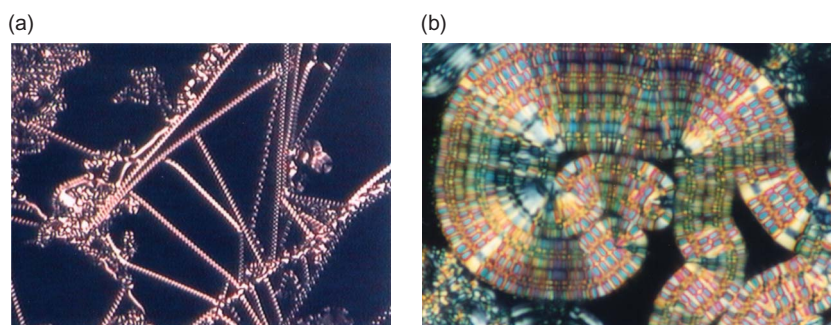


Figure 2. Compound A: (a) nucleation of the B_7 phase at 175°C ; (b) texture of the B_7 phase at 173°C , sample thickness $6 \mu\text{m}$ (colour version online).

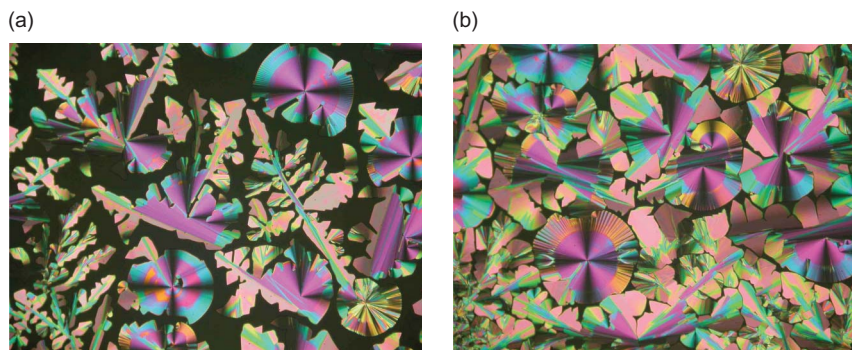


Figure 3. Mixture of 52.5 mol% A: (a) nucleation of the Col_x phase at 150°C ; (b) texture of the mesophase at 144°C , sample thickness $5 \mu\text{m}$ (colour version online).

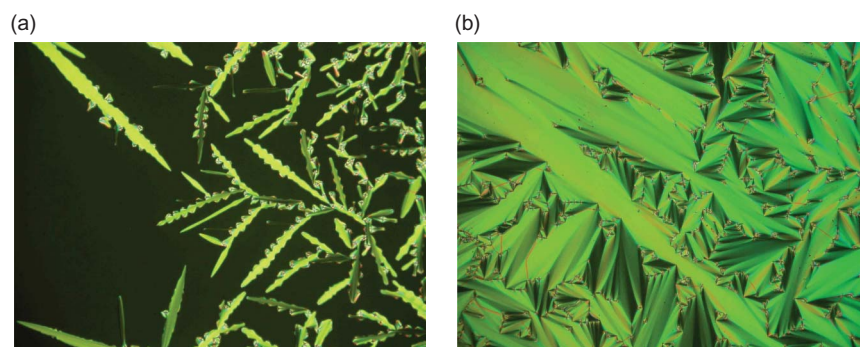


Figure 4. Mixture of 22 mol% **A**: (a) nucleation of dendritic nuclei at 138°C; (b) texture of the B_x phase at 116°C (colour version online).

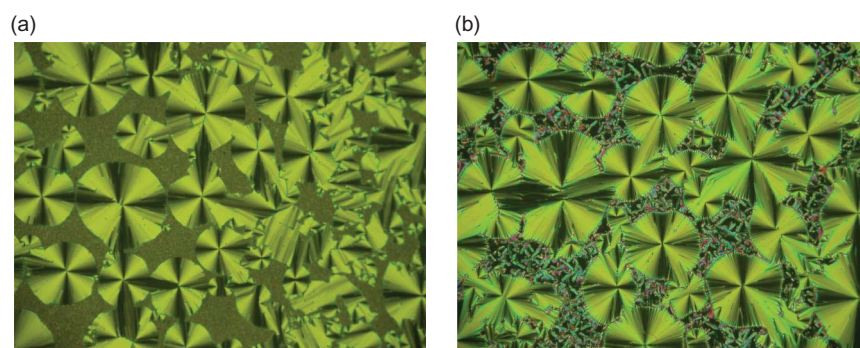


Figure 5. Mixture of 22 mol% **A**: (a) formation of the texture of the B_x phase in presence of an a.c. field (10 Hz; 160 Vpp) at 138°C; (b) texture after removing the a.c. field at 112°C; sample thickness 5 μm (colour version online).

most cases for this phase type we could not align the samples and obtained only powder-like X-ray patterns, therefore the determination of the 2D lattices is not unambiguous. A tentative indexing in analogy to the indexation on oblique 2D lattices for the small-angle patterns of the B_7 phases presented for new 2-nitroresorcinol esters by Pelzl *et al.* [22] gives best fits for a unit cell without systematic extinctions for the reflections and lattice parameters $a = 92.4 \text{ \AA}$, $b = 34.6 \text{ \AA}$ and $\gamma = 90^\circ$ for **A** at 160°C and $a = 89.9 \text{ \AA}$, $b = 35.0 \text{ \AA}$ and $\gamma = 90^\circ$ for its mixture with 75 mol% **A** at 150°C, which closely resemble each other and indicate the same phase type for both samples (Figures 6(d) and 6(e); Table 1). This means that the calamitic molecules of **B** just adapt to the molecular packing of **A**. The symmetry of the intensities cannot be determined from the powder X-ray patterns, therefore we cannot decide if the correct symmetry of the lattice is rectangular or oblique with γ equal to or near 90° . The molecules are significantly longer than the spacing of the undulated/modulated layers (this is b in case of a rectangular cell in the current setting) and should be tilted with respect to the layer normal, excluding plane groups with a mirror plane. Since no systematic extinctions are indicated, centred

cell types or such with glide lines are also excluded, hence the actual symmetry is most probably oblique as in case of the B_7 phases of new 2-nitroresorcinol esters presented by Pelzl *et al.* [22]. The shape of the outer diffuse scattering showing two maxima at $2\theta \approx 19.0^\circ$, $d \approx 4.7 \text{ \AA}$ and $2\theta \approx 22.3^\circ$, $d \approx 4.0 \text{ \AA}$ for both samples points to the phase type found for the low temperature B_{7L} phase of 2-nitroresorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate], which was reported by Pelzl *et al.* [22] (Figure 6(g)).

Figure 6(c) shows the X-ray pattern for a surface-aligned sample of the mixture with 52.5 mol% **A**. The diffuse outer scattering with one maximum at $2\theta = 18.8^\circ$ proves the liquid-like order of the lateral molecular distances. The small-angle reflections can be indexed on a 2D oblique lattice with parameters $a = 140 \text{ \AA}$, $b = 37.5 \text{ \AA}$ and $\gamma = 104^\circ$ (Figure 6(f); Table 1), which can be interpreted as follows: b is characteristic for the spacing of the modulated layers ($d = 36.4 \text{ \AA}$) and a for the width of the blocks, respectively. As in the B_7 phases reported above, the striking difference to the usual columnar phases of bent-core compounds is the sharp streak parallel to the meridian of the X-ray pattern with its maximum on the equator indicating an additional long-range order in the structure most

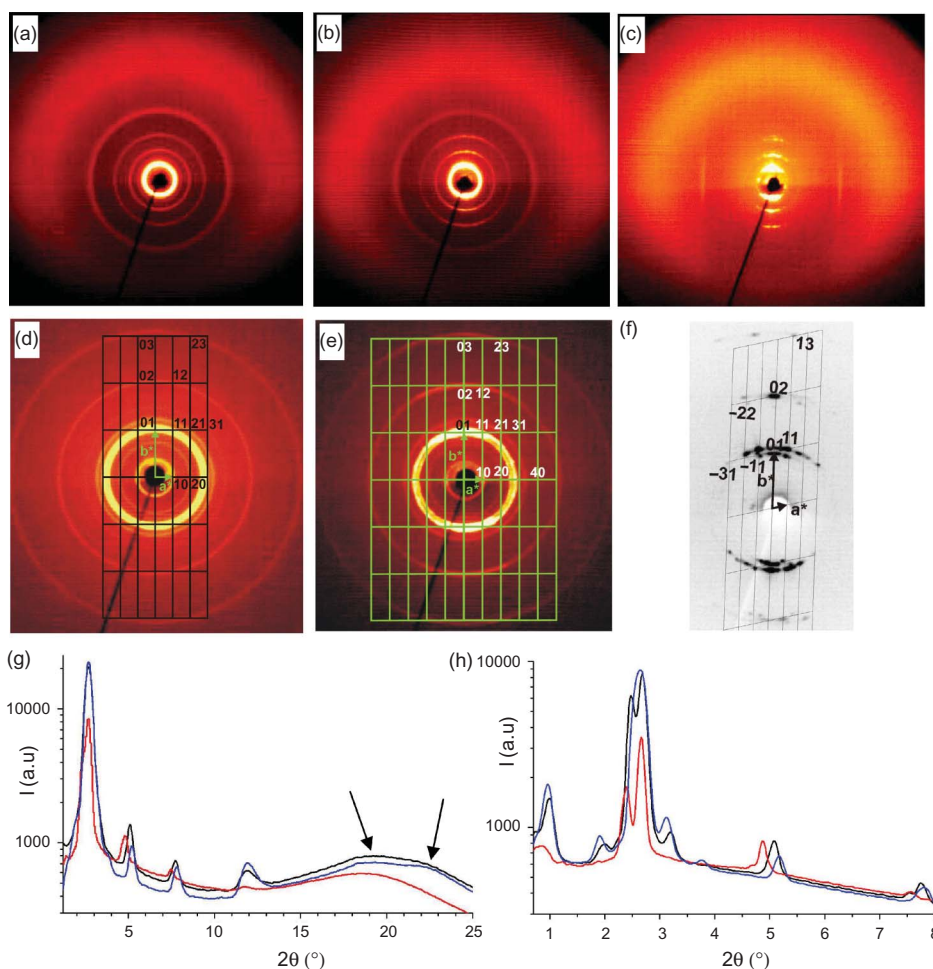


Figure 6. X-ray patterns for compound **A** at 160°C (a, d) and mixtures of 75 mol% **A** and 25 mol% **B** at 150°C (b, e) and of 52.5 mol% **A** and 47.5 mol% **B** at 146°C (c, f), all on cooling: (a–c) wide-angle patterns, (d–f) small-angle region showing axes and indexing for the reciprocal 2D lattices; (g, h) theta scans for the wide angle (g) and small-angle patterns for the three samples (blue curve: compound **A**, black curve: mixture with 75 mol% **A**, red curve: mixture with 52.5 mol% **A**, arrows pointing to the two maxima of the outer diffuse scattering for **A** and the mixture with 75 mol% **A**).

probably normal to the 2D lattice. For the modulated structure this is a stacking of the layer fragments with a period of about 7.6 Å. This reflection is smeared out parallel to the meridian of the pattern, which means there are no correlations in the position of the fragments along the columnar axis between neighbouring columns. Hence, the phase structure could be dominated by the bent-core molecules as in the case of the B_7 phases, the calamitic molecules of **B** adapting to their packing, two of them replacing one bent-core molecule (c.f. dimensions of the molecules in Figure 8 later).

For concentrations less than about 35 mol% **A**, another mesophase is indicated not only by a dramatic change of texture (compare Figures 3 and 4) but also by that of the X-ray patterns of surface-aligned samples (see Figure 7). The latter show (e.g. at 110°C on cooling, Figure 7(a), 7(d), and on heating Figure

7(f)) sharp reflections of only one order on the meridian of the pattern at $d_1 = 19.6$ Å and another pair of reflections smeared out along the equator crossing the meridian at $d_2 = 2d_1$. The outer diffuse scattering has one maximum in 2θ (see further data in Table 2). These patterns are well comparable with those caused by short-range ordered frustrated or irregularly modulated layer phases reported by Watanabe *et al.* [23] and recently for a mixture of a chlorinated five-ring bent-core compound with a calamitic thiadiazole derivative [21]. This phase corresponds to an intermediate type between the regularly modulated B_1 and the intercalated layer B_6 phases, and is here designated as B_x . The bent-core molecules are fully intercalated in these models, i.e. one molecule stretches over two layers formed by the shorter calamitic molecules, which is in line with the dimensions of the molecules measured by molecular models (Figure 8). The tilt, τ , of the

Table 1. Data for the small-angle X-ray reflections in the B_7 and Col_x phases on cooling: Indexing on 2D lattices with parameters $a = 92.4 \text{ \AA}$, $b = 34.6 \text{ \AA}$ and $\gamma = 90^\circ$ (compound **A** at 160°C), $a = 89.9 \text{ \AA}$, $b = 35.0 \text{ \AA}$ and $\gamma = 90^\circ$ (Mixture of 75 mol% **A** and 25 mol% **B** at 150°C), and $a = 140 \text{ \AA}$, $b = 37.5 \text{ \AA}$ and $\gamma = 104^\circ$ (Mixture of 52.5 mol% **A** and 47.5 mol% **B** at 146°C). hk : Miller indices, $2\theta_{\text{obs}}$: observed diffraction angle ($^\circ$), d_{obs} : d value (\AA) calculated from the observed Bragg angle, d_{calc} : d value (\AA) calculated from the lattice parameters.

| Compound A at 160°C | | | | | Mixture of 75 mol% A and 25 mol% B at 150°C | | | |
|------------------------------------------|------------------------|------------------|-------------------|------------------------------------|-------------------------------------------------------------------------|------------------|-------------------|------------------------------------|
| hk | $2\theta_{\text{obs}}$ | d_{obs} | d_{calc} | $d_{\text{obs}} - d_{\text{calc}}$ | $2\theta_{\text{obs}}$ | d_{obs} | d_{calc} | $d_{\text{obs}} - d_{\text{calc}}$ |
| 10 | 0.956 | 92.4 | 92.4 | 0.0 | 0.987 | 89.5 | 89.7 | -0.2 |
| 20 | 1.906 | 46.3 | 46.2 | 0.1 | 1.968 | 44.9 | 44.8 | 0.1 |
| 01 | 2.552 | 34.6 | 34.6 | 0.0 | 2.478 | 35.6 | 35.0 | 0.6 |
| 11 | 2.687 | 32.9 | 32.4 | 0.5 | 2.684 | 32.9 | 32.6 | 0.3 |
| 21 | 3.135 | 28.2 | 27.7 | 0.5 | 3.203 | 27.6 | 27.6 | 0.0 |
| 31 | 3.775 | 23.4 | 23.0 | 0.4 | 3.885 | 22.7 | 22.7 | 0.0 |
| 40 | | | | | | | 22.4 | 0.3 |
| 02 | 5.172 | 17.1 | 17.3 | -0.2 | 5.076 | 17.4 | 17.5 | -0.1 |
| 12 | | | | | | | 17.2 | 0.2 |
| 03 | | | | | 7.536 | 11.7 | 11.7 | 0.0 |
| 23 | 7.805 | 11.3 | 11.2 | 0.1 | 7.761 | 11.4 | 11.3 | 0.1 |

| Mixture of 52.5 mol% A and 47.5 mol% B at 146°C | | | | |
|-----------------------------------------------------------------------------|------------------------|------------------|-------------------|------------------------------------|
| hk | $2\theta_{\text{obs}}$ | d_{obs} | d_{calc} | $d_{\text{obs}} - d_{\text{calc}}$ |
| -11 | 2.362 | 37.4 | 37.5 | -0.1 |
| 01 | 2.403 | 36.8 | 36.4 | 0.4 |
| 11 | 2.650 | 33.3 | 33.2 | 0.1 |
| -31 | 2.684 | 32.9 | 32.5 | 0.4 |
| -22 | 4.679 | 18.9 | 18.7 | 0.2 |
| 02 | 4.857 | 18.2 | 18.2 | 0.0 |
| 13 | 7.582 | 11.7 | 11.8 | -0.1 |

molecules with respect to the normal of the broken layers can be estimated at 23° from the direction of the maxima of the outer diffuse scattering (Figure 7(g)). A formal calculation of an effective molecular length for the calamitic molecules with these parameters gives $L_{\text{eff}} = d / \cos \tau = 21.3 \text{ \AA}$, a value which is a little shorter than the length of the fully stretched calamitic molecules of 24 \AA but significantly longer than half that measured for the strongly bent model conformation for **A** molecules of about $36 \text{ \AA} / 2 = 18 \text{ \AA}$. It is in the range between this and half the value for the fully stretched shape of about $50 \text{ \AA} / 2 = 25 \text{ \AA}$ (Figures 8(a) and 8(b)), which seems plausible for a mixture. On cooling down to 65°C each diffuse streak condenses to two sharp spots (Figures 7(b) and 7(c)), which can now be indexed as 11 reflections of a centred rectangular 2D lattice. The parameter a interpreted as an estimate for the average block width amounts to 47.8 \AA , b corresponding to the length of the bent-core molecule in our model amounts to 38.9 \AA , the tilt angle with respect to b decreases to 18° (Figure 7(h)), $L_{\text{eff}} = b / 2 \cos \tau = 20.5 \text{ \AA}$ for the calamitic molecules being in the same range as in the high-temperature

structure. Figure 8(d) shows a scheme of the possible packing in this regularly modulated layer structure. The same lattice can be assigned to the pattern recorded at 90°C on heating (Figure 7(e)). It should be emphasised that this structural change within the B_x phase is neither accompanied by a visible change of the texture nor by a calorimetric signal.

5. Discussion

It is generally known that the occurrence of mesophases and their structural features strongly depend on the shape of the molecules. Therefore binary mixtures composed of molecules with quite different shapes can form the mesophases of the pure mixing components with structural modifications as well as additional mesophases. For example, this behaviour is observed in binary systems of bent-core and calamitic mesogens [16–21, 23], in which the bent-core compounds exhibit either a SmCP_A phase or a Col phase. The open question was: what are the consequences of a ‘dilution’ of the complex B_7 structure by mixing the bent-core compound with a calamitic one

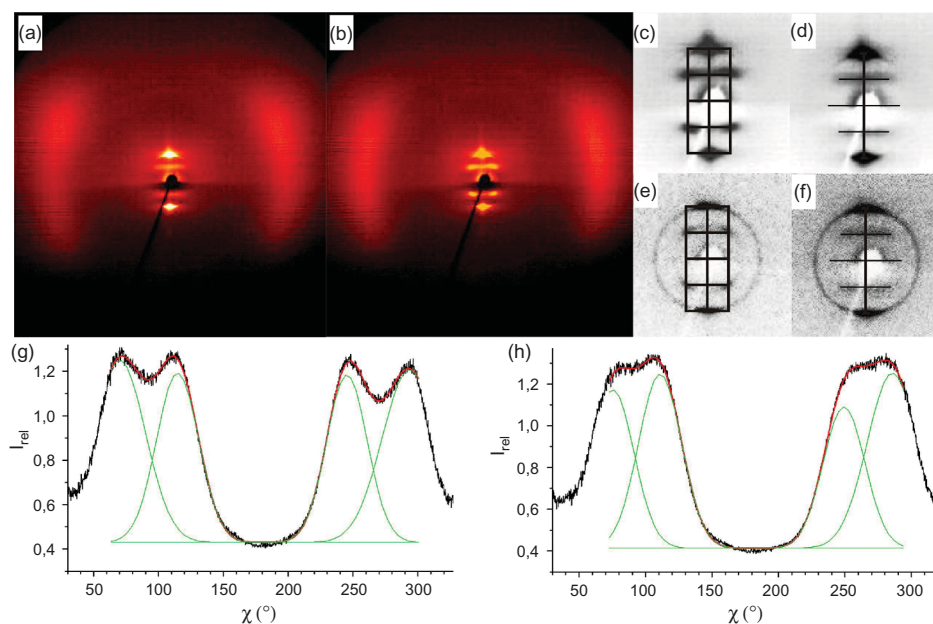


Figure 7. 2D X-ray patterns for a surface-aligned sample of a mixture with 22 mol% **A** and 78 mol% **B** in the B_x phase: wide-angle patterns on cooling (a) at 110°C, (b) at 65°C, (c–f) small-angle region showing the reciprocal lattices (a^* along the equator, b^* along the meridian of the pattern) and the positions of the diffuse reflections (black lines above and below the equator), respectively, at 65°C (c) and at 110°C (d) on cooling and at 90°C (e) and at 110°C (f) on heating and (g, h) χ scans for the outer diffuse scattering (black lines) with Gaussian fits for four maxima (green and red lines) for the patterns (g) at 110°C (maxima at 70, 115, 245, and 294°) and (h) at 65°C (maxima at 75, 111, 249, and 286°).

consisting of relatively short molecules which form a nematic phase?

As seen in Figure 1, the B_7 phase of compound **A** is preserved down to about 60–67 mol% of the bent-core compound **A**. This is indicated by the same optical textures but also by very similar X-ray patterns recorded for the pure compound **A** and the

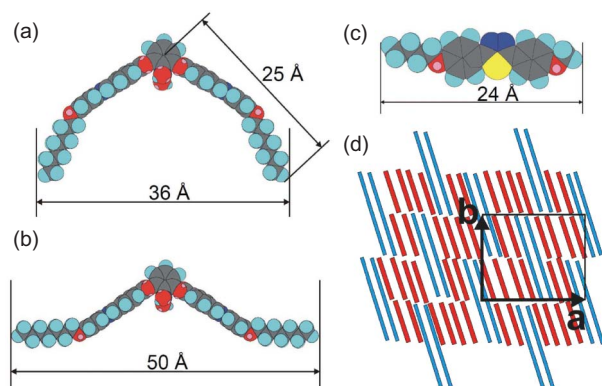


Figure 8. (a–c) Molecular models (Chem3D) for **A** in a strongly bent (a) and in a stretched shape (b) and for **B** (c) with overall molecular length which is comparable to the length of one wing of **A** also shown in (a), (d) packing scheme for the regularly modulated low-temperature structure (red: calamitic molecules of **B**, blue: bent-core molecules of **A**, bend direction normal to the 2D lattice).

mixture with 75 mol% **A**. The X-ray patterns display several sharp reflections in the small-angle region which can be indexed on 2D lattices as typical for modulated layer phases, b corresponding to the spacing of the layer fragments and a to the width of the blocks. The strong, slightly broadened reflection at about 7.5 Å is obviously caused by an additional long-range order most probably normal to the 2D lattice, i.e. by a stacking of the layer fragments with a period of 7.5 Å. A further feature of the X-ray patterns is the splitting of the outer diffuse scattering resulting in two maxima, the origin of which is not yet clear but is probably connected with the average lateral distance of the fluid alkyl chains on one side and the closer packing of the central bent core (perpendicular to the bent direction) of the molecules. Such X-ray patterns have been recently observed for the low-temperature B_7 phase of 2-nitroresorcinol bis[4-(4-*n*-dodecyloxybenzoyloxy)benzoate] [22]. Therefore this phase can be designated as B_{7L} .

Two further mesophases appear in the mixed-phase region which clearly differ from the B_7 phase by their optical textures. The mesophase formed at medium concentration (around 50 mol% **A**) is distinguished from the adjacent B_{7L} phase by the formation of distinct phase boundaries in the contact preparations which change reversibly with temperature. It shows a multi-coloured texture with circular

Table 2. Data for the small-angle X-ray reflections of the mixture with 22 mol% **A** and 78 mol% **B**: Indexing on a centred rectangular 2D lattice. *T*: temperature (°C), 2θ : observed diffraction angle (°), *d*: *d* value (Å) calculated from the observed Bragg angle.

| <i>T</i> | On cooling | | | | On heating | | | |
|----------|---------------------|----------|---------------|----------|---------------------|----------|---------------|----------|
| | Layer/02 reflection | | 11 reflection | | Layer/02 reflection | | 11 reflection | |
| | 2θ | <i>d</i> | 2θ | <i>d</i> | 2θ | <i>d</i> | 2θ | <i>d</i> |
| 125 | 4.506 | 19.6 | | | | | | |
| 120 | 4.503 | 19.6 | | | | | | |
| 110 | 4.514 | 19.6 | | | 4.529 | 19.5 | | |
| 90 | 4.532 | 19.5 | | | 4.543 | 19.4 | 2.933 | 30.1 |
| 80 | 4.541 | 19.5 | | | | | | |
| 70 | 4.547 | 19.4 | 2.802 | 31.5 | | | | |
| 65 | 4.549 | 19.4 | 2.928 | 30.2 | | | | |

and dendritic domains, whereas the textural elements of a B_7 phase are completely missing. Also, the nucleation of this phase on cooling the isotropic liquid shows no similarities with that of a B_7 phase. However, the X-ray pattern of this intermediate phase is quite similar to that of the B_{7L} phase of the **A**-rich mixtures (sharp reflections in the small-angle region indicating an oblique 2D lattice, a streak parallel to the meridian of the pattern at 7.5 Å). The only significant difference is the shape of the outer diffuse scattering showing one maximum instead of two. All these features of the X-ray pattern for the induced phase are nearly identical with that of 2-nitroresorcinol bis[4-(4-n-dodecyloxybenzoyloxy)benzoate] obtained on slow cooling at higher temperatures (B_{7H}) [22]. Interestingly, samples of both the latter and the induced phase of the current system could be surface aligned in contrast to the B_7 phase of **A** and its homologues. In spite of the obviously similar X-ray pattern we hesitate to assign this phase as a B_7 phase. Nearly all hitherto described B_7 phases show a typical nucleation with spiral nuclei as well as characteristic textures. The occurrence of such textural features, which are based on special defects [14], seems to be characteristic of B_7 phases. Therefore we think that this oblique columnar phase does not belong to the 'B₇ family'. It can be assumed that the higher concentration of the short calamitic molecules changes the intermolecular interactions in a way that the formation of B_7 -typical defects, and hence that of B_7 -typical textures, becomes impossible.

For samples with higher concentrations of the calamitic mixing component **B** (more than 65 mol% **B**), a further mesophase occurs which exhibits a smooth fan-shaped texture like SmA and a schlieren-like texture. The X-ray pattern of a surface-aligned sample corresponds to an irregularly modulated layer

structure. This structure can be regarded as an intermediate state between a regularly modulated Col_r (B_1) phase and the intercalated B_6 phase for the bent-core molecules in the mixture, two calamitic molecules replacing one bent-core molecule in the packing. The same phase type was recently reported in a binary system with a bent-core compound forming a SmCP phase and a calamitic compound [21, 23]. Furthermore, it should be reminiscent of similar sequences of smectic A_d and A_2 phases in frustrated phases of calamitic polar compounds [24]. At lower temperatures this structure transforms into a regularly modulated layer structure. This transition is not accompanied by a calorimetric signal or by a clear change of the texture. The structure model based on the results of the X-ray investigations is presented in Figure 8(d).

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