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Evidence for a polar biaxial SmA phase (C_{PA}) in the sequence SmA–C_{PA}–B_2

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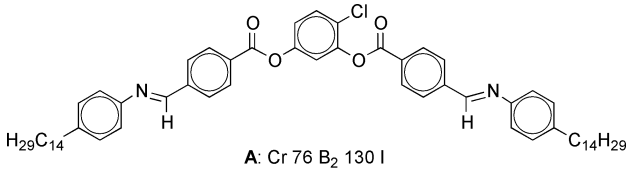
The isobaric phase diagram of a binary system is presented where one mixing component is an achiral five-ring bent-core mesogen and the other is the electron acceptor compound 2,4,7-trinitrofluorenone (TNF). In the mixed phase region a SmA phase as well as a polar (antiferroelectric) biaxial SmA phase (C_{PA}) are induced. Depending on the concentration the unusual phase sequences B_2–SmA, C_{PA}–SmA and B_2–C_{PA}–SmA could be observed. The mesophases occurring in this system have been characterised by their optical textures, by X-ray investigations and by electro-optical measurements.

Recently we have found transitions between the B_2 phase and conventional smectic phases (SmA, SmC) in selected banana-shaped compounds.[1–3] The question arises of whether it is also possible to induce such phase sequences in binary mixtures of bent-shaped mesogens with calamitic mesogens. According to preliminary studies of the phase diagrams of such binary systems the region of the B_2 phase was clearly separated from the regions of conventional smectic phases, indicating a pronounced incompatibility of these different types of mesophases. On the other hand, recently a binary system of a bent-core and a calamitic mesogen has been investigated in which a non-polar biaxial SmA phase could be detected in a limited concentration range.[4]

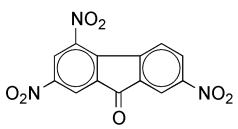
Now we are able to present a phase diagram where transitions between a SmA phase and "banana phases" could be realised. In this binary system a transition from an antiferroelectric biaxial SmA phase (C_{PA}) into a B_2 phase was observed for the first time.

Materials

The mixing components of the binary systems are the chlorine-substituted bent-core mesogen **A** and the nonmesogenic electron acceptor compound trinitrofluorenone (**TNF**). The synthesis and characterisation of the bent-core mesogen **A** have been described by Weissflog *et al.*[5] This compound exhibits a B_2 phase only, while trinitrofluorenone (**TNF**) has no mesomorphic properties.



A: Cr 76 B_2 130 I



TNF: Cr 175 I

Results

Fig. 1 shows the phase diagram of the binary system. It is seen that between 40 and 85 mol% of the banana-shaped compound a SmA phase is induced which is obviously the result of an electron donor–acceptor (EDA) interaction. The EDA interaction is indicated by the intense yellow–brown colour of the mixed phases whereas the pure compounds are colourless (compound **A**) or yellowish (**TNF**). The SmA phase can be recognised by its fan-shaped or homeotropic texture.

On cooling down the SmA phase of mixtures with concentrations between 72 and 85 mol% of compound **A** a phase transition can be observed. At this transition the fan-shaped texture is transformed into a grainy fan-shaped texture, whereas the homeotropic texture adopts a schlieren texture. These changes in the microscopic picture are comparable with the direct transition from (a) into (c) as shown in Fig. 2 for the mixture with 71.5 mol% A. The X-ray investigations on oriented samples give evidence that the low-temperature phase

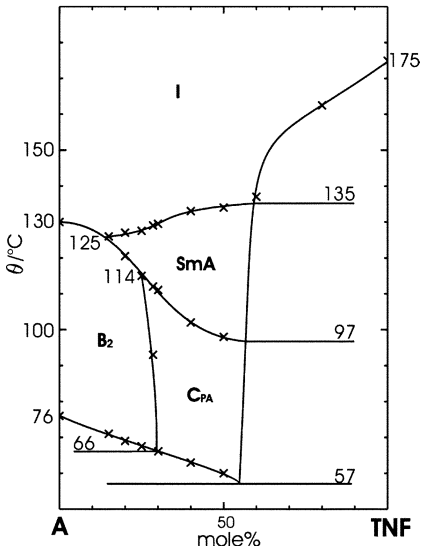


Fig. 1 The phase diagram for the binary system with the components **A** and **TNF**.

is a tilted smectic phase. Also the temperature dependence of the layer spacing for a concentration of 85 mol% **A**, shown in Fig. 3, points to a tilt angle. There is a small drop in the layer spacing at this transition by about 1 Å; within the range of the low-temperature phase the *d*-value is nearly temperature-independent. From the different *d*-values a tilt angle of about 13° can be estimated. On the other hand, the electro-optical behaviour is characteristic for a B_2 phase, which means that the ground state is an antiferroelectric one that can be switched into ferroelectric states.

In the concentration range between 47 and 70 mol% of component **A** a phase transition also takes place on cooling the SmA phase. But in this case the fan-shaped texture of the SmA phase remains nearly unchanged, and only some irregular fine stripes parallel to the smectic layers arise. On the other hand, if the homeotropic texture is cooled down a transition into a weakly birefringent, strongly fluctuating schlieren texture appears indicating a biaxial smectic phase. It corresponds to a transition from (a) into (b) in Fig. 2. From the X-ray pattern of an oriented sample it follows that in this biaxial smectic phase the molecular long axes are, on average, perpendicular to the layer planes. This is indicated by the maximum of the diffuse outer scattering which is located on the equator as in the SmA phase .We confirmed this finding by a detailed analysis of the intensity of the diffuse scattering using a special procedure which is described by Eremin *et al.*[6] It is seen in Fig. 3 that for a mixture of 70 mol% **A** the *d*-value of the SmA phase slightly increases with decreasing temperature. At the transition of the SmA phase into the low-temperature phase a further continuous increase of the *d*-value is observed. This behaviour is obviously due to an increasing stretching of the terminal chains. In contrast to the SmA phase this orthogonal biaxial smectic phase shows a field-induced switching. Applying an electric field to the fan-shaped texture of the biaxial smectic phase the birefringence (and therefore the interference colour) is changed and the stripes within the fans disappear. It was found that the texture of the switched state is independent of the polarity of the applied field. Two current peaks could be recorded per half period of a triangular voltage indicating the switching from an antiferroelectric ground state into ferroelectric states. We can conclude from the experimental findings that the low-temperature phase is an antiferroelectric variant of a polar biaxial SmA phase which was theoretically predicted by Brand *et al.*[7,8] and was designated C_{PA}. In this phase the smectic layers have C_{2v} symmetry whereas in the B_2 phase a C_2 symmetry exists. Recently a C_{PA} phase was experimentally proved in a banana-shaped 4-cyanoresorcinol derivative for the first time.[6]

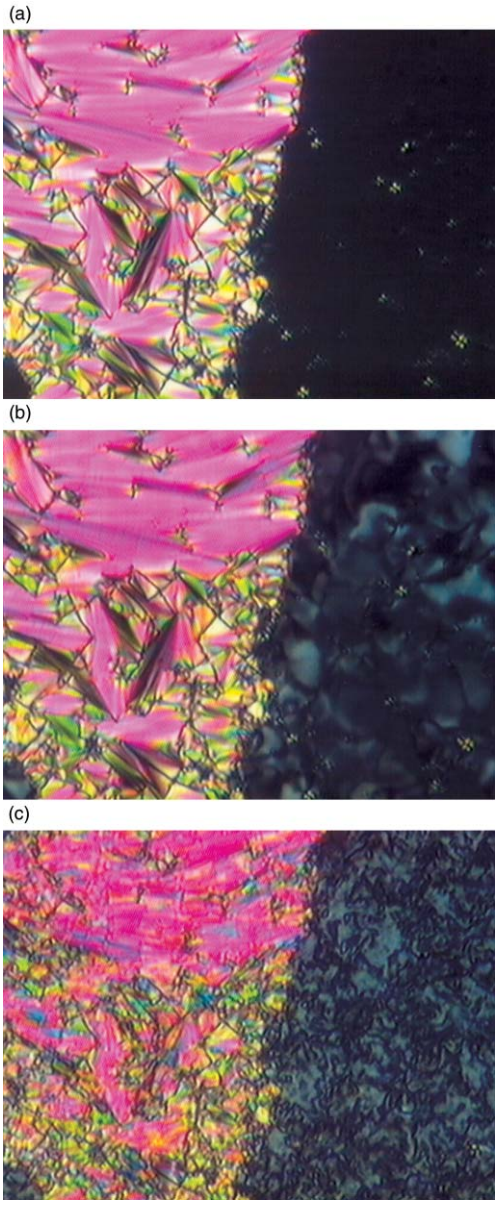


Fig. 2 Textures of the smectic phases for a sample with 71.5 mol% **A**. (a) Fan-shaped and homeotropic texture of the SmA phase (115 °C); (b) fan-shaped and fluctuating schlieren texture of the C_{PA} phase (96 °C); (c) grainy fan-shaped and schlieren texture of the B_2 phase (75 °C).

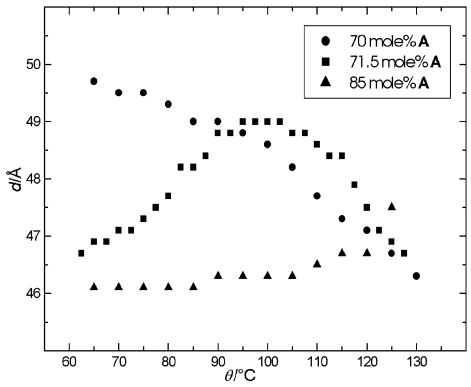


Fig. 3 Layer spacing *d* of the smectic phases as a function of temperature θ for three samples with different concentrations.

Over a limited concentration range (70.5–72 mol% **A**) a novel phase sequence could be clearly detected: Cr 66 B_2 89–93 C_{PA} 108–112 SmA 127.2–128.7 I (71.5 mol% **A**).

The phase transitions SmA → C_{PA} and C_{PA} → B_2 are accompanied by clear changes of the optical textures. The transition SmA → C_{PA} is indicated by a transition of a homeotropic into a strongly fluctuating schlieren texture whereas the fan-shaped texture remains unchanged [Fig. 2(a) and (b)]. This transition was also detected by a small calorimetric peak. At the transition C_{PA} → B_2 the smooth fan-shaped texture is transformed into a grainy one [Fig. 2(b) and (c)]. The schlieren texture becomes more birefringent while the fluctuations completely disappear. The unusual phase sequence has been confirmed by X-ray and electro-optical measurements. The X-ray pattern of the SmA and C_{PA} phase are nearly identical [Fig. 4(a) and (b)]. In the pattern of the B_2 phase the outer diffuse scattering [Fig. 4(c)] is a little shifted out of the equator. In Fig. 3 the *d*-values of this mixture (71.5 mol% **A**) are presented as a function of temperature. In the SmA phase the *d*-value continuously increases with decreasing temperature. In the range of the C_{PA} phase *d* is nearly constant. At the transition into the B_2 phase a continuous decrease of *d* occurs which is obviously the result of the tilt of the bent molecules within the smectic layers. At a temperature of 60 °C a tilt angle of 16° can be estimated *via* $\cos\alpha = d^{C_{PA}}/d^{B_2}$.

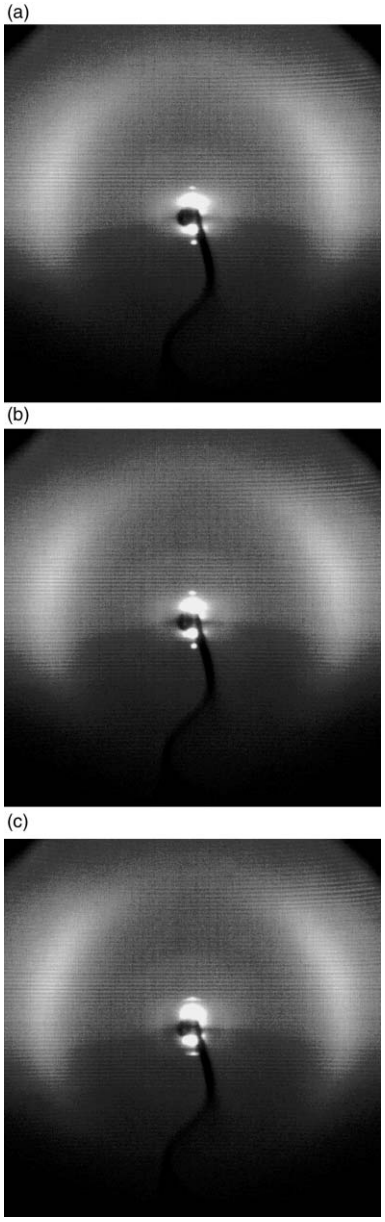


Fig. 4 X-Ray pattern of monodomains (71.5 mol% **A**) (a) of the SmA phase (120 °C); (b) of the C_{PA} phase (100 °C); and (c) of the B_2 phase (65 °C).

In the B_2 phase the textures of the switched state are different for an opposite sign of the electric field indicating homogeneous chiral domains (see Fig. 5). From the field-induced rotation of the extinction direction between crossed polarizers a tilt angle of 15° could be determined which is in good agreement with the value obtained by X-ray measurements. In contrast, in the C_{PA} phase the switched states are independent of the sign of the applied field (see Fig. 6). In both the C_{PA} and B_2 phases the current response clearly points to an antiferroelectric ground state which is indicated by two current peaks per half period of the applied triangular voltage [see Fig. 7(a) and (b)]. It is also interesting that the spontaneous polarization P_S obtained from the current response continuously increases at the transition $C_{PA} \rightarrow B_2$ (see Fig. 8).

Discussion

Several aspects should be discussed with respect to the binary system presented here. The induction of the SmA phase at middle concentrations is obviously the result of an electron donor–acceptor (EDA) interaction which is mainly due to the strong acceptor properties of the TNF molecules. As is known

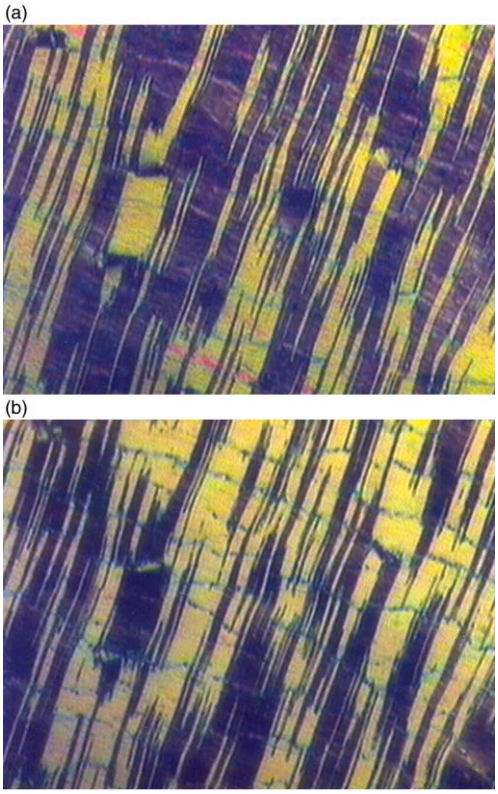


Fig. 5 The texture of the B_2 phase depending on the polarity of the applied electric field for the mixture with 71.5 mol% **A**: (a) +50 V; (b) −50 V (65 °C, cell thickness: 6 μm).

from binary systems of calamitic compounds the EDA interaction stabilizes the smectic A phase.[9] Because of the uniaxial character of the SmA phase we can assume that the molecules can rotate more or less freely around the long molecular axes. Obviously the mobility at higher temperatures

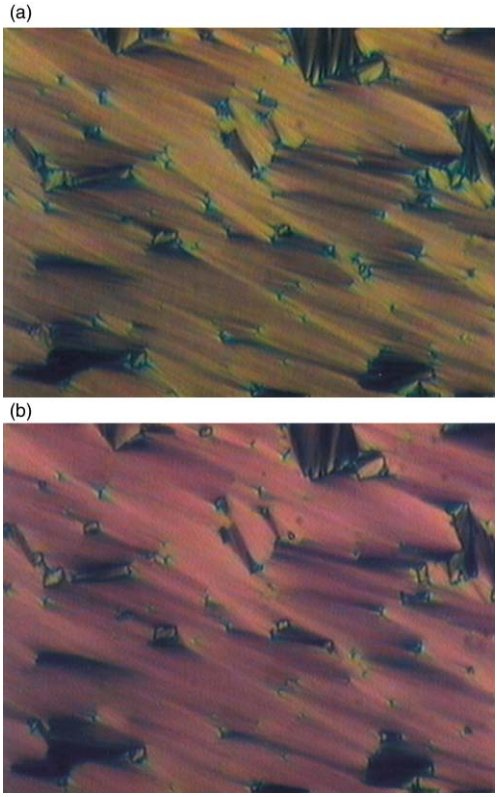


Fig. 6 Texture of the C_{PA} phase for the mixture with 71.5 mol% **A**: (a) 0 V; (b) ±40 V (100 °C, cell thickness: 6 μm).

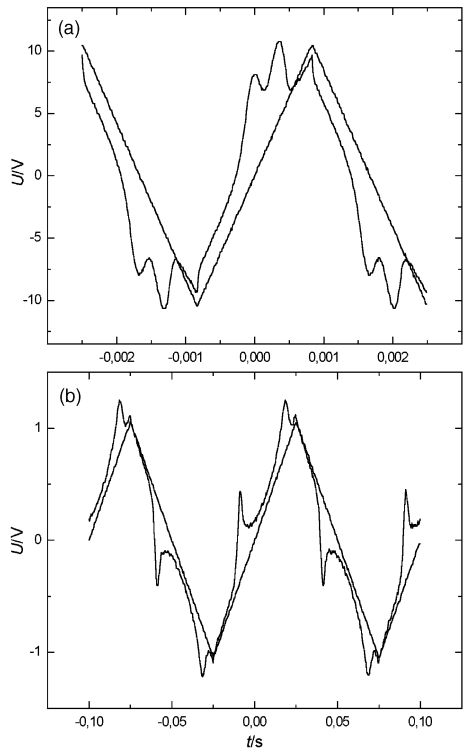


Fig. 7 Switching current response on applying a triangular voltage (mixture with 71.5 mol% **A**): (a) C_{PA} phase (101 °C, 210 V_{pp}, 300 Hz, cell thickness: 10 μm); (b) B_2 phase (65 °C, 210 V_{pp}, 10 Hz, cell thickness: 10 μm).

as well as the disturbing influence of the guest molecules prevent the polar packing. On cooling the mobility is reduced, which means that rotation around the long molecular axes is hindered as is also known for the B_2 phase.[10] Therefore, a polar packing can be assumed and the biaxial SmA phase appears, in which, on average, the molecules maintain an orthogonal alignment with respect to the layer planes. The polar character is proved by their electro-optical behaviour.

The phase region of the B_2 phase is restricted to about 70 mol% **A**. It is interesting that the tilt angle α decreases with an increasing concentration of **TNF** [α(**A**): 39°, α (71.2% **A**): 16°]. On the other hand, the spontaneous polarisation P_S of the B_2 phase does not change significantly by adding the mixing component, although the tilt angle is clearly reduced. This finding seems to be plausible because the direction of the polar axis does not change when the tilt angle changes. This behaviour differs from that in the chiral SmC* phase where the polarization P_S depends on the tilt angle α.[11]

Until now in the B_2 phase a relation between α and P_S could not be discussed since α as well as P_S was found to be nearly

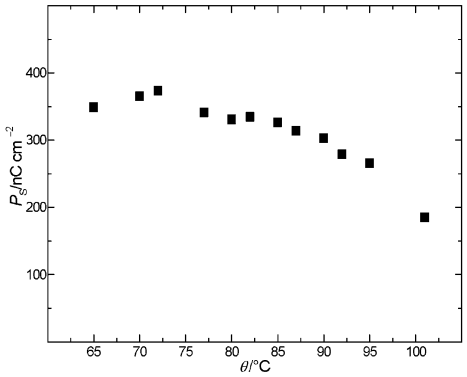


Fig. 8 Spontaneous polarisation P_S as a function of temperature θ for the mixture with 71.5 mol% **A**.

temperature-independent.[12] Binary mixtures of bent-core mesogens, however, where the tilt angle can be varied with the concentration, are suitable objects for studying this question more in detail.

To our knowledge, this is the first case where a phase sequence SmA → C_{PA} → B_2 has been observed. A C_{PA} phase in the sequence SmA–C_{PA} has already been found in a pure banana-shaped compound.[6] This transition was found to be first order. This is also the case for the binary mixtures studied in this paper. The transition enthalpy C_{PA}–SmA for a mixture of 71.5 mol% A (0.43 kJ mol^{-1}) was clearly lower than the transition enthalpy SmA–I (5.3 kJ mol^{-1}). In contrast, at the transition of the C_{PA} into the B_2 phase no calorimetric signal could be detected. The reason could be that the transition enthalpy is rather small and due to the transition interval of several degrees the peak is smeared and therefore not detectable. The more probable explanation seems to be that this transition is second order (similar to the transition SmA → SmC).

Experimental

To study the phase diagram of the binary systems the phase transition temperatures of mixtures of known concentrations were determined by polarising microscopy (Leitz Orthoplan). For selected mixtures the transition temperatures were measured using differential scanning calorimetry (Pyris 1, Perkin-Elmer). Three-phase reactions were studied by means of the contact method. X-Ray diffraction measurements on non-oriented samples were carried out using a Guinier film camera or a Guinier goniometer (Huber Diffraktionstechnik GmbH). Oriented samples were obtained by slowly cooling a drop of a liquid crystal placed on a glass plate. Under these conditions the smectic layers could be oriented parallel to the glass substrate. The scattered radiation has been recorded using a 2 D area detector (HI-Star, Siemens AG). The incident beam was parallel to the substrate which shadowed the lower part of the reciprocal space. Therefore, an additional analysis was required to obtain the full picture. Electro-optical measurements were performed using commercial ITO cells (EHC Corp.). The spontaneous polarisation was measured using the triangular wave voltage method.

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