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## Liquid Crystals

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## Helical smectic A ( $S_A^*$ ) in polymorphic liquid crystalline systems with induced spiral structure

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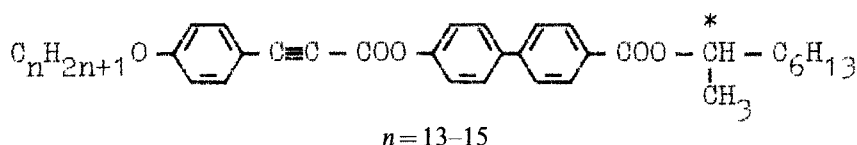
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The existence of the induced helical smectic A ( $S_A^*$ ) phase was proved by textural, optical and calorimetric studies and by small angle X-ray scattering using binary systems which consisted of achiral 4-*n*-hexyloxyphenyl 4-*n*-octyloxybenzoate ( $C \leftrightarrow S_C \leftrightarrow N \leftrightarrow I$ ) and chiral *N*-(4-*n*-nonylphenylbenzoyloxy)benzylidene-*S*-1-benzylethylamine ( $C \leftrightarrow S_A \leftrightarrow I$ ). The induced  $S_A^*$  and cholesteric ( $N^*$ ) phases appeared even at small concentrations of the chiral compound ( $\approx 1$  mol per cent) together with increases in the  $S_C^* \rightarrow S_A^*$  transition temperatures, compared those for the  $S_C \rightarrow N$  transitions, and decreases in the  $\theta_c$  tilt angle. Structural factors are discussed as possible causes of the formation of the induced  $S_A^*$ , blue phases I, II and III, and another polymorphic state in the systems studied.

### 1. Introduction

The observation of the new helical phase—chiral smectic A ( $S_A^*$ ) in the homologous series of *R*- and *S*-enantiomers



has been recently reported in the literature [1, 2]. The new phase appeared between the isotropic and chiral smectic C ( $S_C^*$ ) phases within a narrow temperature range; the mesophase type was proved by polarizing optical microscopy, small angle X-ray scattering and differential scanning calorimetry. A molecular model of the  $S_A^*$  phase was proposed by the authors on the basis of the results obtained. The appearance of the  $S_A^*$  phase has been explained by disordering of screw dislocations within the pre-transitional range in a way similar to that in which the Abrikosov flux lattice phase can occur between normal and superconducting phases.

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|| It is regrettable that revised copies of the manuscript of this paper were twice lost in the post, once during 1992 and later sometime after February 1993, leading to the long delays in final acceptance/publication of this paper (Editor).

The report of the observation of a helical phase was made earlier for certain polymeric liquid crystals (cholesterol-containing homopolymers) by Freidzon *et al.* [3]. Layer ordering in the disposition of the mesogenic groups was observed in the cholesteric mesophase. A scheme for the macromolecular packing in this phase was proposed which was similar to that proposed by Goodby *et al.*, for the  $S_A^*$  phase.

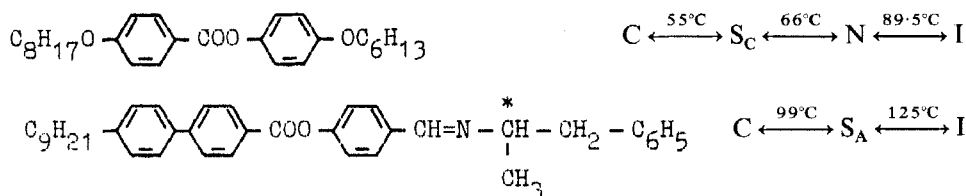
It was later revealed [4] that the new  $S_A^*$  phase appeared between the cholesteric and smectic phases in induced spiral systems which contained a high percentage of the chiral component (70 per cent of cholesteryl nonanoate and 30 per cent of 4-nonyloxybenzoic acid). Our previous research [5] allowed us to suppose that the new chiral  $S_A^*$  phase can occur in many induced systems, including low concentration systems.

In this paper the study of polymorphic states is presented for induced spiral systems within a wide concentration range of the chiral dopant. The chiral  $S_A^*$  appears at very small concentrations ( $\approx 1$  mol%) and remains up to 32 mol% concentration.

The polymorphic states were studied by X-ray diffraction, differential scanning calorimetry, optical polarizing microscopy and temperature/helical pitch measurements.

## 2. Materials

In this work binary liquid crystalline systems were studied. Compound **I** (matrix) and compound **II** (chiral dopant) were used and their individual phase transition temperatures are presented below:



The compound **I** is a well-known achiral ester with no smectic A phase [6]. Compound **II** is a new chiral mesogen synthesized by the authors [7]. The peculiarities of this compound are its own mesomorphism (the formation only of an enantiotropic  $S_A$  phase) and its high degree of molecular chirality. The structural similarity between the achiral and chiral compounds and their miscibility in any proportion allowed us to study the phase states over all concentration ranges.

## 3. Experimental

The identification of phase textures was achieved using a Polam P-111 polarizing microscope [8]. The samples were sandwiched between two glass plates which were previously rubbed in one direction. The sample thickness was varied from 14 to 60  $\mu\text{m}$  by using teflon spacers. The mounted material was confined in a specially constructed cell which had a  $\pm 0.5^\circ$  temperature control accuracy.

As a result of the microscopic work, the phase diagram of the binary system is represented on cooling (see figure 1); only the  $\text{C} \rightarrow \text{S}_\text{C}^*$  (or  $\text{S}_\text{A}$ ) transition temperatures are for heating, because the mixtures undergo supercooling).

Temperatures and heats of transition were determined by differential scanning calorimetry using a Sateram DSC-111 calorimeter. The heating rates were  $0.5^\circ\text{C min}^{-1}$  and  $2^\circ\text{C min}^{-1}$ . The thermogram of the binary mixture with 25.3 mol% of the chiral

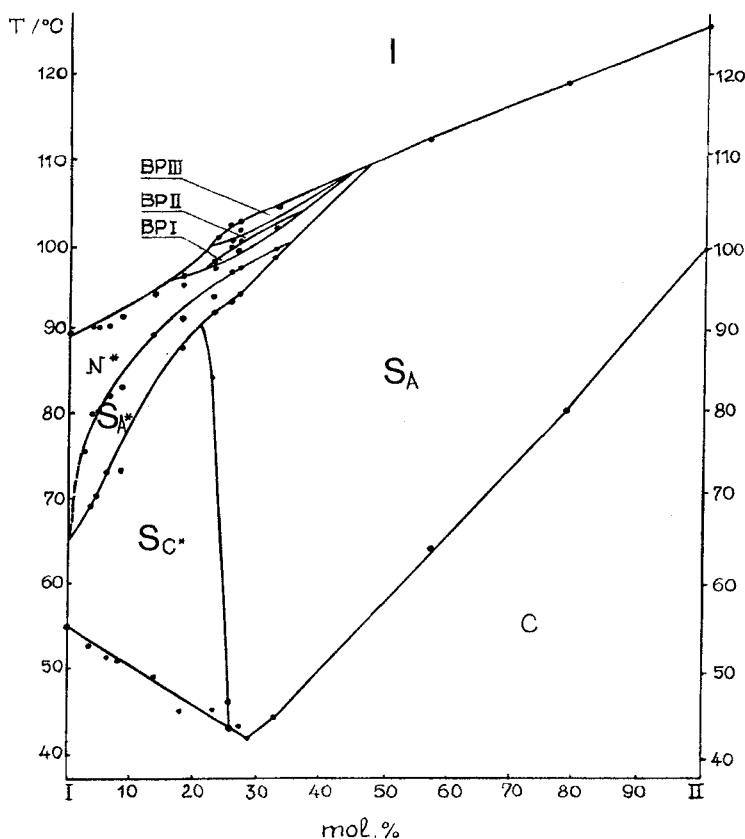


Figure 1. The phase diagram of the binary I-II system.

dopant is shown in figure 2, as an example. The thermogram of II (see figure 3) was determined using a Perkin-Elmer calorimeter at a heating rate of  $5^\circ\text{C min}^{-1}$ .

Structural evidence of mesophase type for compounds I and II and their mixtures (involving 2.3, 3.75 and 26.8 mol% concentrations of II) were obtained by X-ray diffraction measurements on cooling from the isotropic liquid. For this study the unaligned samples were prepared in 1 mm glass capillaries. Small angle X-ray measurements were performed in the range  $2\theta = (0.1-5^\circ)$ . Monochromatic  $\text{CuK}_\alpha$  radiation was used as the X-ray source (30 kV, 30 mA, focus size  $0.4 \times 8 \text{ mm}^2$ , X-ray wavelength  $\lambda_x = 1.541 \text{ \AA}$ ). The instrumental resolution was  $0.02^\circ$  in the scan direction. The main X-ray results are presented in figures 4 and 5.

The helical pitch, which is a fundamental parameter of cholesteric ( $N^*$ ) and chiral smectic ( $S_A^*$ ,  $S_C^*$ ) phases was determined by the following methods:

- (1) Grandjean-Cano method; the helical axis was perpendicular to the glass plates in the wedge-shaped cell. Such an orientation of the helical axis was realized by aligning the molecular long axes such that they lay parallel to glass plates in the  $N^*$  and  $S_A^*$  phases and approximately perpendicular in the  $S_C^*$  phase. The helical pitch value was determined from the spacing between the dark strips.
- (2) Using the Bragg condition for diffraction from the focal-conic texture.
- (3) From the peak wavelength of the selective transmittance band in a cell where the helical axis was perpendicular to the glass plates

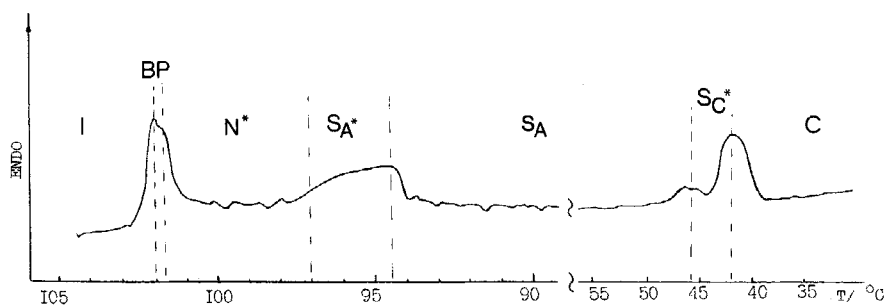


Figure 2. The DSC thermogram of the mixture containing 25.3 mol% of the chiral dopant II.

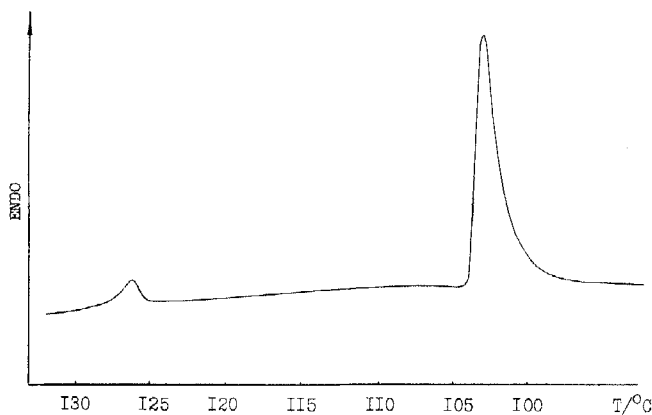


Figure 3. The DSC thermogram of compound II.

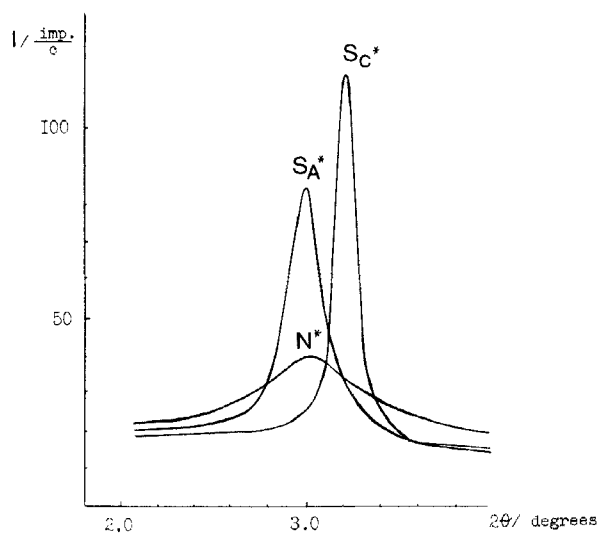


Figure 4. Peaks of small angle X-ray scattering for the mixture containing 3.75 mol% of the chiral dopant II at  $T = 60^\circ\text{C}$  within the  $S_C^*$ , at  $T = 74^\circ\text{C}$  within the  $S_A^*$  and at  $T = 85^\circ\text{C}$  within the  $N^*$  phase.

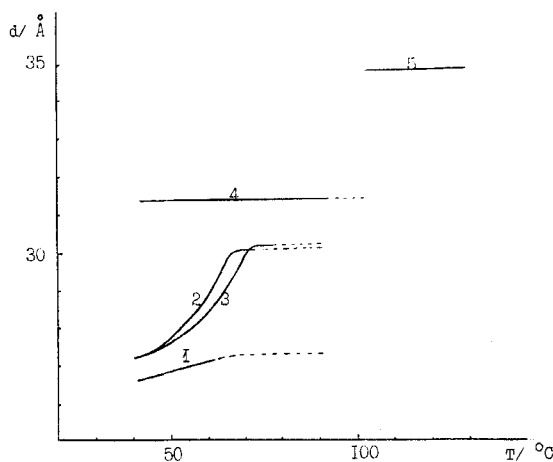


Figure 5. The temperature dependence of the layer spacing for compound I (curve 1), the mixtures containing 2.3 mol% of the chiral dopant (curve 2), 3.75 mol% of the chiral dopant II (curve 3) and 26.8 mol% of the chiral dopant II (curve 4) and compound II (curve 5). Dashed lines represent the temperature dependence of the layer spacing within the N\* phase or N phase.

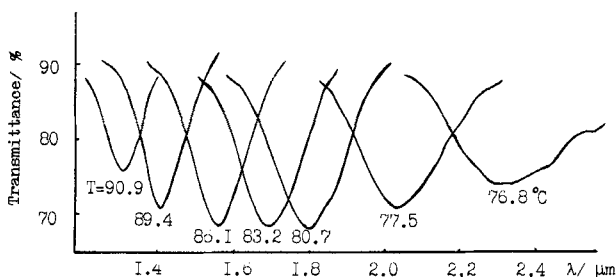


Figure 6. Spectra of the selective transmittance for the mixture containing 7.9 mol% of the chiral dopant II at the temperatures indicated.

To determine the helical pitch in the N\* and S<sub>A</sub>\* phases, all three methods were employed. The helical pitch for the S<sub>C</sub>\* phase was determined by the Grandjean–Cano method.

Using this method, the helical pitch was defined as

$$P = 2x \tan \alpha \quad (1)$$

where  $\alpha$  is the wedge angle and  $x$  is the period between Grandjean–Cano lines, in the case of the cholesteric and smectic A\* phases, and as

$$P = x \tan \alpha \quad (2)$$

in the case of the smectic C\* phase [9, 10].

It is noticed that the Grandjean–Cano disclination lines are distorted at the N\* → S<sub>A</sub>\* transition temperature and restored after the transition at any constant temperature within 15–20 min.

Selective transmittance spectra of the cholesteric and smectic A\* samples (planar oriented) were measured spectrophotometrically (Hitachi-330). The samples were contained between glass plates coated with polyvinyl alcohol and rubbed in one

Helical twisting power of the chiral dopant **II** in the liquid crystalline solvent **I**.

$T/^\circ\text{C}$	Mesophase	$ \beta /\mu\text{m}^{-1}\text{ mol fr}^{-1}$
85	N*	$15.4 \pm 2.3$
75	S <sub>A</sub> *	$12.4 \pm 1.6$
63	S <sub>C</sub> *	$5.7 \pm 0.3$
55	S <sub>C</sub> *	$6.9 \pm 0.6$
45	S <sub>C</sub> *	$8.4 \pm 0.7$

direction. Homogeneous samples of high quality were obtained by slow cooling from the isotropic liquid. Selective transmittance spectra within the temperature ranges of the N\* and S<sub>A</sub>\* phases are shown in figure 6.

The twisting power  $\beta$  of the chiral compound **II** dissolved in compound **I** was determined for the N\*, S<sub>A</sub>\* and S<sub>C</sub>\* phases (see the table) using

$$\beta = 1/Pc, \quad (3)$$

where  $c$  is mol fraction of the chiral dopant.

#### 4. Results and discussion

The nematic and smectic C phases of compound **I** are transformed into cholesteric and smectic C\* phases by doping with a very small percentage of compound **II**. The temperature dependencies of the induced helical pitch for three mixtures (1.5, 4.4 and 7.9 mol % of **II**) are shown in figure 7. The helical pitch grows smoothly up to the S<sub>C</sub>\* phase transition upon cooling from the isotropic liquid. Such a temperature dependence is typical for induced cholesteric phases which precede a smectic phase [11]. As the sample was being cooled, regular stripes appeared in the cholesteric plane texture at 79, 81.5, 83°C, respectively for the three above-mentioned concentrations. This 'striped' texture changes into a 'finger-print' texture which differs from normal cholesterics in that the lines are blurred. The 'blurred finger-print' texture transforms into the focal-conic texture of the S<sub>C</sub>\* on subsequent cooling.

The observed 'blurred finger-print' texture was identified as relating to a new liquid crystalline phase which appeared between the induced cholesteric and smectic C\* phases. Such a mesophase type was observed for binary mixtures over the concentration range 1–17 mol % of **II**. The appearance of the 'blurred finger-print' texture for the 12.3 mol % mixture is shown in figure 8.

As the chiral dopant concentration increases the helical pitch decreases and the new phase texture picture is essentially modified. At the N\*→S<sub>A</sub>\* phase transition, the 'platelet' texture grows in the cholesteric plane texture filling all the sample volume. Such a texture was named 'platelet' because its domains had polygonal shapes (see figure 9).

As follows from our calculations, the twisting power of the chiral dopant is higher than that of some known chiral esters [12]. Due to this, visible selective light reflection is observed for the induced cholesteric and the new S<sub>A</sub>\* phases within the 23–32 mol % concentration range of compound **II**. It is noticed that the Grandjean plane texture of the S<sub>A</sub>\* appears iridescent and similar in nature to that of the cholesteric phase, but the colours of the selective reflection are more brilliant.

As shown in figure 7, the values of the S<sub>A</sub>\* helical pitch are close to those of the cholesteric pitch. On the basis of measurements of the helical pitch temperature

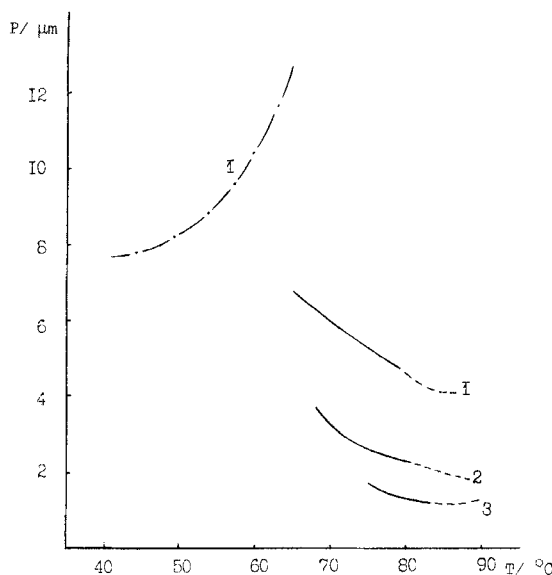


Figure 7. The temperature dependence of the helical pitch for the mixtures containing 1.5 mol% of the chiral dopant **II** (curve 1), 4.4 mol% of the chiral dopant **II** (curve 2) and 7.9 mol% of the chiral dopant **II** (curve 3). Dashed lines represent the pitch/temperature dependence within the  $N^*$  phase, continuous lines that within the  $S_A^*$  phase and dot and dash lines that within the  $S_C^*$  phase.

dependence for the plane oriented cholesteric and  $S_A^*$  samples and the optical microscopic work, it was established that the helical axis was orthogonal to the molecular long axes and parallel to the smectic layers in both phases. Such a model corresponds to the helical  $S_A^*$  which has been proposed for individual chiral mesogens [1, 2].

The smectic A ordering of the new induced helical phase was proved by small angle X-ray scattering. As shown in figure 4, the layer peak scan taken within the 88–79°C temperature range is typical for the cholesteric phase [13] (the peak position  $2\theta_{\max}$  is 3.00° and the peak half-width,  $\Delta 2\theta$ , is 0.70° at 85°C). As the temperature decreases, the peak intensity grows abruptly, without essential change in the peak position ( $2\theta_{\max} = 2.92^\circ$ ,  $\Delta 2\theta = 0.24^\circ$  at 74°C). Such a peak shape is typical for smectic molecular ordering [14, 15]. It is important that the peak position angle is constant within the 78–68°C temperature range. There is a shift of the small angle scattering peak towards greater angle values, the peak narrowing ( $2\theta_{\max} = 3.10^\circ$ ,  $\Delta 2\theta = 0.16^\circ$  at 60°C and  $2\theta_{\max} = 3.22^\circ$ ,  $\Delta 2\theta = 0.10^\circ$  at 40°C) and its intensity increasing on subsequent cooling. These facts prove the existence of two different smectic states in the system. The temperature dependence of the layer spacing has been found by using the temperature dependence of the peak position (figure 5). Similar dependencies were obtained for the individual compounds **I** and **II** and their mixtures.

As the temperature rises, the layer spacing increases continuously for the individual matrix of compound **I** (curve 1, figure 5) and the low concentration mixtures with **II** (curves 2 and 3, figure 5); this is typical for the  $S_C$  and  $S_C^*$  phases. The layer spacing of the chiral mixture is constant ( $d \approx 30 \text{ \AA}$ ) within the temperature range of the second smectic state (horizontal line on curves 2, 3 in figure 5) and corresponds to the length of the matrix molecules in their most elongated conformation ( $l = 30.2 \text{ \AA}$ ). Using X-ray





Figure 8. The 'blurred finger-print' texture of the  $S_A^*$  phase for the 12.3 mol% mixture.



Figure 9. The 'platelet' texture of the  $S_A^*$  phase for the 25.3 mol% mixture.

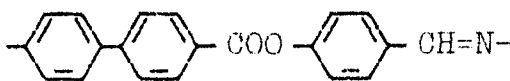
scattering, textural and helical pitch data we can conclude that the smectic state between the  $S_C^*$  and cholesteric phases is the  $S_A^*$  phase.

The correlation length  $\xi_{||}$  of smectic ordering within the  $S_A$  temperature range was estimated by using the Sherrer formula  $\xi_{||} = \lambda_x / \Delta(2\theta) \cos(2\theta/2)$  for the 3.75 mol% mixture. The estimation yields  $\xi_{||} = (200 \div 500) \text{ \AA}$  which implies that layer correlations extend over a distance of 7–15 molecular layers.

Structural elements of the new helical state are blocks of a few molecular layers which possess local  $S_A$  ordering. Due to such a build-up, the  $S_A^*$  phase shows more brilliant colours of selective reflection than does the  $N^*$  phase. It is important that a very small quantity of the chiral dopant leads to an increase in the layer spacing in the  $S_C$  phase of compound **I** (up to 0.7  $\text{\AA}$ ) and to a decrease in the  $\theta_c$  smectic tilt angle. The calculated value  $\theta_c$  is 28° for compound **I** and 25° for the 2.3 mol% mixture at 45°C.

The chiral compound **II** forms the  $S_A$  phase which has been proved by small angle X-ray scattering and optical polarizing microscopy. The X-ray pattern is typical for a smectic phase. The constant layer spacing over the entire smectic range ( $d = 34.8 \text{ \AA}$ ) corresponds to the molecular length of compound **II** in its most elongated conformation ( $l = 35.4 \text{ \AA}$ ). A similar situation is also observed for the high concentration mixture (26.8 mol% of the chiral dopant, line 4 in figure 5). The layer spacing has an intermediate value between the lengths of the matrix molecules (**I**) and those of compound **II** ( $d = 31.4 \text{ \AA}$ ). On the basis of the textural and optical studies, it is clear that this mixture exhibits both the  $S_A^*$  phase over a narrow temperature range and the  $S_{mA}$  phase, but the phases are indistinguishable by small angle X-ray scattering.

As the concentration of the chiral dopant increases (up to 23 mol%) the  $S_C^*$  temperature range broadens (by increase in the  $S_C^* \rightarrow S_A^*$  transition temperature) but the  $N^*$  and  $S_A^*$  phase ranges narrow (see figures 1 and 5). The increase in the  $S_C^*$  and  $S_A^*$  phase thermal stabilities is explained by the strongly smectic characteristics of compound **II** which are conditioned by its molecular structure, in particular, an anisometric molecular form and a high polarizability of the extended  $\pi$ -molecular skeleton



coupled with the presence of the long alkyl chain and the conformationally mobile benzyl group. The smectogenicity of compound **II** and its high degree of molecular chirality lead to the formation of the induced  $S_A^*$  phase.

Doping of the achiral compound **I** by the chiral dopant with a high  $\pi$ -polarizability promotes the formation of the smectic A ordering even at low concentrations of the chiral dopant. The analysis of the DSC data shows that the transition from  $N^*$  to  $S_A^*$  occurs through the  $S_A^*$  state for the 25.3 mol% concentration mixture (see figure 2). The high chirality of compound **II** and its molecular incommensurability with the achiral compound **I** promote the spiral deformation of the  $S_A$  phase.

Three blue phases—BPI, BPII and BPIII—appear over the temperature range from 1°C to 2.5°C between the isotropic and cholesteric phases for the 17–43 mol% concentrations (see figure 1). As the concentration of the chiral dopant grows, the blue, cholesteric,  $S_A^*$  and  $S_C^*$  phases gradually disappear and the binary system gains the mesomorphic properties which are typical of compound **II**, having only smectic A ordering.

### 5. Conclusion

Textural, optical, calorimetric and small angle X-ray diffraction data confirm the existence of the new  $S_A^*$  phase as the intermediate state between the induced cholesteric and  $S_C^*$  phases for mixtures of the achiral 4-*n*-hexyloxyphenyl of 4-*n*-octyloxybenzoate, which has N and  $S_C$  phases and the structurally similar chiral *N*-[4-(4-*n*-nonylphenylbenzoyloxy)benzylidene-*S*-1-benzylethylamine. The  $S_A^*$  and N\* phases are induced even by a small concentration of the chiral dopant ( $\approx 1$  mol %), together with an increase in the  $S_C^*$  thermal stability and a decrease in  $\theta_c$ , the tilt angle in the systems studied. The helical axis is oriented in the  $S_A^*$  phase as in the N\* phase and is orthogonal to the helical  $S_C^*$  axis. The helical  $S_A^*$  phase possesses visible selective light reflection with very brilliant colours (23–32 mol % concentrations of the chiral dopant II).

It can be supposed that the induced  $S_A^*$  state is conditioned by the smectogenicity and the high twisting power of the chiral dopant. The smectogenicity of the matrix and the molecular incommensurability of the chiral and achiral compounds are the important conditions for the formation of the  $S_A^*$  phase.

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