Journal of Research in Physics Vol. 33, No. 1, 29 - 35 (2009)

Phase Transition Temperature Shifts in Binary Cholesteric Liquid Crystalline Mixtures Doped with some Chiral Nonmesogenic Additives

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Received: *December 11, 2009*

Abstract

We have investigated the influence of three chiral nonmesogenic estradiol derivatives on the physical characteristics of the binary mixture of cholesteric liquid crystals cholesteryl myristate and cholesteryl enantate. We observed that the addition of the chiral additives induces a shift of the phase transition temperatures. The characterization of the mesophases has been made by X-ray diffraction. These data enabled the determination of some structural parameters of the mixtures: the thickness of smectic layers and the average distance between the long axes of neighbouring molecules.

Key words: X-ray diffraction, estradiol derivatives, cholesteric liquid crystals

1. Introduction

This work represents the continuation of our studies on binary and multicomponent mixtures of cholesteric liquid crystals, undertaken with the aim to obtain systems with stable mesophases and transition temperatures close to room temperature [1,2]. Estradiol derivatives have a steroidal configuration similar to that of the cholesteryl backbone, which makes them suitable as chiral additives in cholesteric mixtures even though they do not have mesophases. In natural biological systems, estradiol and estradiol derivatives play a significant physiological role [3].

In the present paper we investigate the influence of some estradiol derivatives on the mesophase behaviour of a binary mixture of cholesteryl laurate and cholesteryl enantate. Measurements have been carried out to identify the types and textures of mesophases and determine the phase transition temperatures by optical microscopy. X-ray measurements have also been performed to confirm the structure of mesophases and determine structural parameters.

2. Experimental

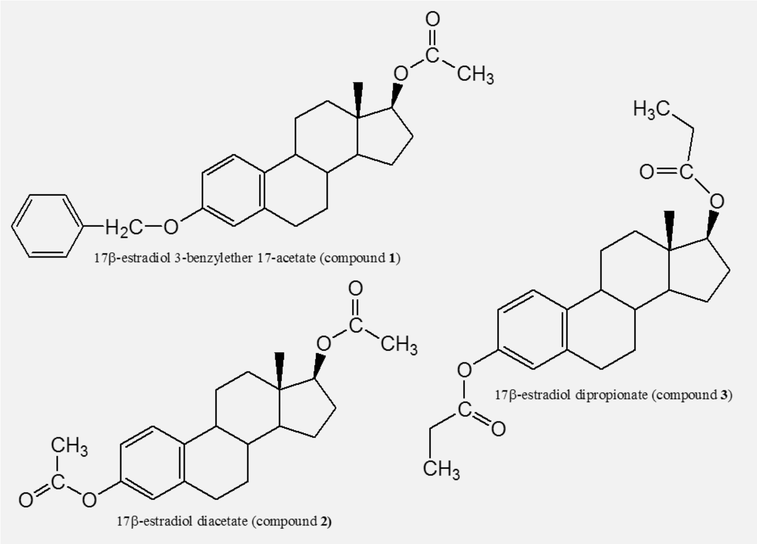
2.1. Methods and equipments

The optical studies were performed using a polarizing microscope (Carl Zeiss, Jena) in transparent light using crossed polarizers. A hot stage allowed controlled heating and cooling of the sample. Homeotropical alignment of the liquid crystal was obtained by evaporation of gold onto the glass plate using the vacuum evaporator JEOL JEE-4B.

Unoriented samples were investigated by X-ray diffraction in the transmission geometry on a conventional powder diffractometer (Seifert V-14) equipped with an automatic high temperature kit Paar HTK-10, using CuK$_\alpha$ radiation at 0.154 nm. The X-ray diffraction data allowed the determination of structural parameters characteristic for the molecules and the mesophase they form [4]. Namely, the layer spacing (d) in the smectic A* (SmA*) phase and the average intermolecular distance (D) (i.e. the mean distance between the long axes of the neighbouring parallel molecules) could be obtained using Braggs law: $\lambda = 2x \sin\theta$. Here, the distances x = (d and D) were calculated from the positions of the small angle and the large angle diffraction peaks, respectively.

2.2. The chiral additives

The investigated chiral additives, 17β-estradiol 3-benzylether 17-acetate (**1**), 17β-estradiol diacetate (**2**) and 17β-estradiol dipropionate (**3**), are well known compounds [5]. We synthesized them, however, by modified methods. Compound **1** was synthesized by benzylation of estradiol in dry mixture of methanol and acetone in the presence of potassium carbonate, followed by acetylation of the resulting benzyl ether of estradiol by acetic anhydride in dry pyridine. Compounds **2** and **3** were synthesized from estradiol, by the reactions of esterification with acetic anhydride and propionic anhydride in dry pyridine, respectively. The chemical formulae of the prepared chiral additives are given in Figure 1. Compounds **1** to **3** are non-mesogenic, their melting points are listed in Table 1.


17β-estradiol 3-benzylether 17-acetate (compound **1**)

17β-estradiol diacetate (compound **2**)

17β-estradiol dipropionate (compound **3**)

Figure 1. Chemical structures of the chiral additives **1**, **2** and **3**

Table 1. The phase sequences and phase transition temperatures of the pure compounds.

Compound	Phases and transition temperatures (°C)
Cholesteryl myristate	I 84.6 Ch 79.1 SmA* 71 Cr
Cholesteryl enantate	I 114 Ch 99.5 Sm A* 92.5 Cr
1	Cr 101-107 I
2	Cr 121-124 I
3	Cr 101-104.5 I

2.3. The mixtures

In order to investigate the influence of the synthesized chiral additives on the mesophase behaviour we had to prepare first a binary mixture, **Mixbin**, which contained cholesteryl myristate and cholesteryl enantate in the 1 : 1 ratio by weight. **Mixbin** served as a reference mixture for our studies. Before preparing the reference mixture, its components have been checked by polarizing microscopy. The obtained phase sequences and phase transition temperatures are also listed in Table 1, and thy show a good agreement with the existing literature data [6].

The chiral additives were tested in threecomponent mixtures (**Mix1**, **Mix2** and **Mix3**), composed of **Mixbin** (90% by weight) and one of the chiral derivatives (10% by weight of **1**, **2** and **3**, respectively).

3. Results and discussion

Optical microscopic studies have been carried out on the reference mixture **Mixbin**, as well as on the three-component mixtures **Mix1** to **Mix3**. Observation of the textures allowed to determine the phase sequences and the phase transition temperatures. Results of the observations are summarized in Table 2. The layer structure in the SmC phase of compound **II** is characterized by one reflection at a small angle $2\theta = 3.1\,^{\circ}$. In mixtures **Mix1** and **Mix2**, similarly, one reflection peak could be found at small angles at the same position as for the rod-like molecule, indicating the presence of the SmC phase.

In all investigated mixtures, focal conic polygonal textures were observed. This texture is characteristic to such cholesteric liquid crystals where the cholesteric quasi-layers have an oblique orientation with respect to the substrates, i.e., the helical axis is strongly tilted. Such an orientation occurs if the surface area is occupied by the polygonal base of a focal conic domain. However, formation of such a domain, although it reduces the surface energy, is also accompanied by an increase of the “bulk” energy due to the director distortions. The energy balance dictates that the focal conic domains has to be larger than some critical size in order to become stable [7-10].

Figure 2a presents an example for this texture of the cholesteric (Ch) phase observed in a homeotropic cell. The observed colour is due to the selective reflection originating from a helical structure of the short pitch.

The focal conic texture of the SmA* phase in a homeotropic cell are shown in Figure 2b. The apparent optic axis is parallel to the layer normal direction in the SmA* phase. In many SmA* materials, the layer normal direction points to the centre of the focal conic, i.e. the layers orient tangentially in a circular focal conic domain.

Table 2. Phase transition temperatures, width of the phase temperature ranges and the shift of the phase transition temperatures in the investigated mixtures. All temperatures are given in °C.

		Mixture			
		Mixbin	**Mix1**	**Mix2**	**Mix3**
Transition temperature	I→ Ch	67.6	65.6	54.1	62.4
Transition temperature	Ch → SmA*	65.0	57.0	44.1	57.0
Transition temperature	SmA* → Cr	55.0	43.7	38.0	41.0
Phase temperature range	Ch	2.6	8.6	10.0	5.4
Phase temperature range	SmA*	10.0	9.3	6.1	16.0
Temperature shift	I→ Ch		2.0	13.5	5.2
Temperature shift	Ch→ SmA*		8.0	20.9	8.0
Temperature shift	SmA* → Cr		7.3	17.0	14.0

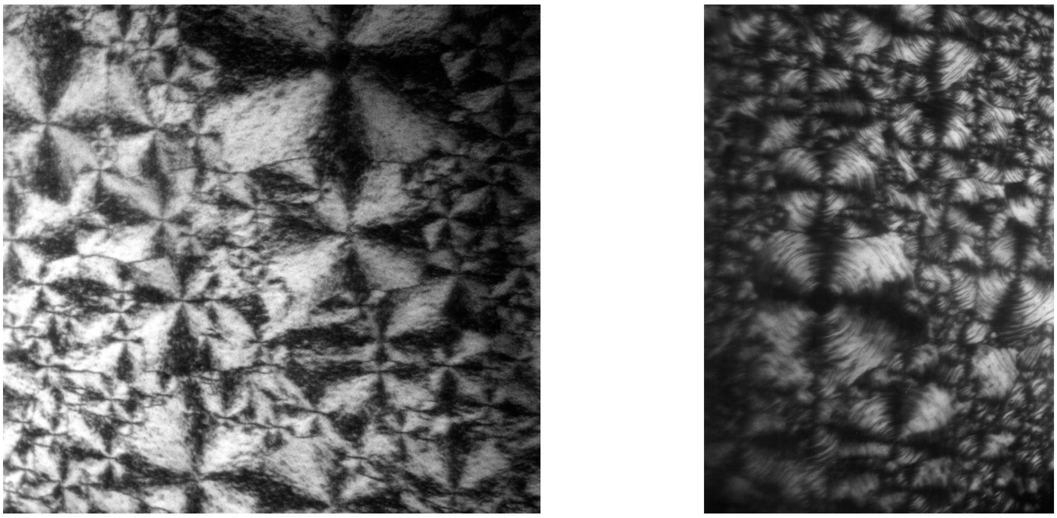


Figure 2a

Figure 2b

Figure 2. Textures of **Mixbin**: a) Focal conic polygonal texture observed in the Ch phase.
b) Texture with circular focal conic domains in the SmA* phase.

The optical observations have shown that the phase sequence of the mixtures (Table 2) is not affected by the chiral additives: in all mixtures a sequence of isotropic (I) - cholesteric (Ch) - smectic A* (SmA*) - crystal (Cr) was found. The phase transition temperatures are, however, shifted toward lower values in the three-component mixtures **Mix1** to **Mix3** compared to the binary mixture Mixbin. The largest temperature shifts have been recorded after the addition of the chiral non-mesogenic additive **2**. The phase transition temperatures did not shift uniformly, hence the width of the temperature range of the mesophases is also affected by the additives. Interestingly, all three additives induced a broadening of the Ch phase range, compound **2** being the most effective (**Mix2** exhibited a 10 °C wide cholesteric phase. The widest SmA* phase (~ 16 °C) was registered in the case of **Mix3** (Table 2).

Having determined the phase sequences by microscopy we also performed X-ray diffraction studies on unoriented samples of the binary (**Mixbin**), as well as of the three-component (**Mix1** to **Mix3**) mixtures, in all phases they exhibited. The relevant structural parameters obtained from the X-ray diffraction data are listed in Table 3. As examples, diffraction profiles of unoriented samples of **Mixbin** and of one ternary mixture (**Mix3**) are depicted in Figure 3 for different temperatures.

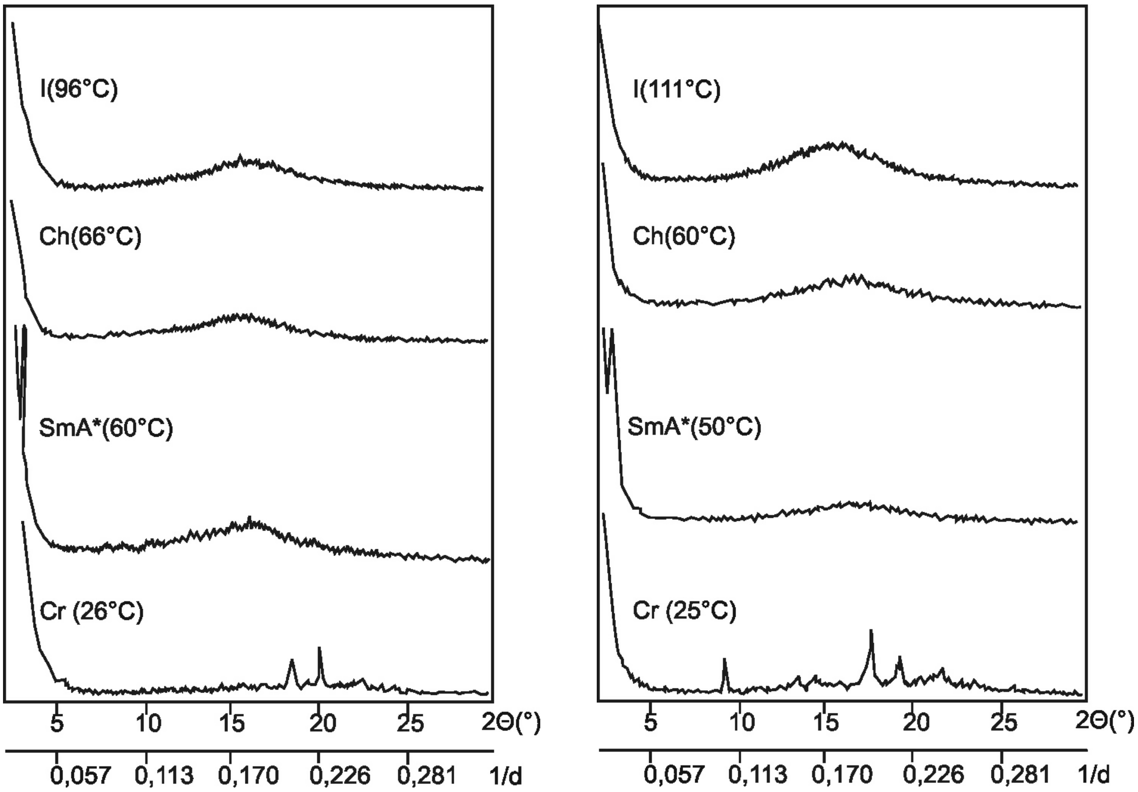


Figure 3a

Figure 3b

Figure 3. X-ray diffraction profiles for: a) **Mixbin** and b) **Mix3**

The analysis of X-ray diffraction profile of the SmA* phase showed the presence of a strong reflection at small angles, indicating the presence of a layer structure with layer spacing d; the diffuse broad peak appearing in the 2θ range of $10 - 25\,°$, with a maximum at $16.5\,°$ corresponding to the average intermolecular distance (D).

One can notice in Table 3 that the chiral additive **3** induces an increase in the smectic layers thickness in the SmA* phase compared to that of **Mixbin**. It is probably due to the steric influence of bulky substituents at positions 3 and 17 of the backbone of the chiral additive **3**, which in the ternary mixture **Mix3** alters the packing of the host molecules of **Mixbin**.

Table 3. Structural parameters of investigated mixtures for all observed phases at temperature T [°C]: angles corresponding to the reflection peaks 2θ [°], smectic layer thickness d [Å] (error of measurements δ_d was about ±0.1 Å), average intermolecular distance D [Å] (error of measurements δ_d was about ±0.03Å).

Mixture	T [°C]	2θ [°]	d [Å]	D [Å]
Mixbin	96 (I)	16.0		5.53
	66 (Ch)	16.4		5.4
	60 (SmA*)	2.9	30.4	
		16.5		5.37
Mix1	111 (I)	16.0		5.53
	63.5 (Ch)	16.4		5.4
	51 (SmA*)	3.5	25.2	
		16.6		5.33
Mix2	93 (I)	16.2		5.46
	50 (Ch)	16.8		5.27
	42 (SmA*)	3.5	25.2	
		17.0		5.21
Mix3	111 (I)	16.0		5.53
	60.4 (Ch)	16.9		5.24
	50 (SmA*)	2.7	32.7	
		17.1		5.18

On the other hand, the d values for **Mix1** and **Mix2** are by almost 15% smaller than in **Mixbin** (Table 3). It could be because the substituents in the positions 3 and 17 of the backbone of the estradiol derivatives **1** and **2** are less bulky, so they allow better packing of the host molecules in the ternary mixtures.

In the cholesteric and isotropic phases no small angle reflections are detectable, indicating the lack of positional order; only the broad peaks at larger angles are present (Figure 3) corresponding to the average intermolecular distance D. As can be seen from Table 3, the additives have practically no influence on D in the isotropic phase. However, some reduction of D can be seen in the Ch phase of the ternary mixtures, which becomes more pronounced in the SmA* mesophase. This indicates that a higher packing density of the molecules is favoured in the presence of the additives, than in the pure cholesteric binary mixture.

4. Conclusion

The results of the studies of the ternary mixtures of cholesteric liquid crystals with non-mesogenic chiral estradiol derivatives **1** - **3** have shown a significant shift of the mesomorphic phase transitions toward lower temperatures, compared to those of the reference mixture. From the X-ray diffraction data of unoriented samples we have determined the average intermolecular distance, D, and the smectic layer spacing, d. It was shown that the smectic layer spacing in the SmA* phase of **Mix3** is bigger, while in **Mix1** and **Mix2** it is smaller than in the reference mixture. The reduction of the average intermolecular distances indicates a higher packing density of the molecules in the ternary mixtures than in the reference one.

Acknowledgments

This work was supported by research Grant No. 141020 and No. 142052B from the Ministry of Science and Technological Development of the Republic of Serbia, the Hungarian National Science Funds OTKA K61075, the ESF-COST D35 WG-13/05, and the SASA-HAS bilateral exchange project.

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