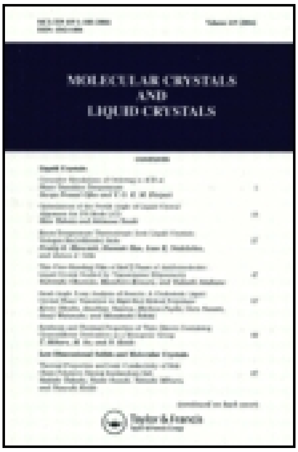

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Study of Binary Cholesteric Liquid Crystalline Mixtures Doped with Some Chiral Nonmesogenic Estradiol Derivatives

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We investigated the influence of some estradiol derivatives on the thermal and structural properties of binary mixtures of cholesteryl enantate and cholesteryl myristate. The characterization of the mesophases was made by polarizing optical microscopy, differential scanning calorimetry and X-ray diffraction. A considerable shift of the phase transition temperature I→Ch, as well as the temperature of formation of the SmA phase was observed. Besides phase sequences and phase transition temperatures the measurements enabled the determination of some molecular parameters of the mixtures: the thickness of smectic layers and the longitudinal spacing distance in the cholesteric phase (*d*) and the average distance between the long axes of neighboring molecules (*D*).*

Keywords Cholesteric liquid crystals; estradiol derivatives; X–ray diffraction

1. Introduction

In a continuation of our studies on cholesteric liquid crystal mixtures doped with some chiral non-mesogenic additives [1,2], undertaken with the aim to obtain liquid crystalline materials with phase transition temperature close to room temperature, we investigated the influence of some estradiol derivatives on the thermal and structural properties of binary mixtures of cholesteryl enantate (**ChE**) and cholesteryl myristate (**ChM**). 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. On the other hand,

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in natural biological systems estradiol and estradiol derivatives play a significant physiological role [3]. Microscopic observations, differential scanning calorimetry, and X-ray diffraction measurements were used in this investigation. The mesomorphic and physical properties of these mixtures are discussed.

2. Experimental Methods

Melting points of the chiral additives were determined in open capillary tubes on a Büchi SMP apparatus; the values are uncorrected. The optical studies were performed with a polarizing microscope (POM) (Carl Zeiss, Jena) in transparent light using crossed polarizers. A hot stage allowed controlled heating and cooling of the sample. Homeotropic alignment of the liquid crystal was obtained by evaporation of metal (Au) onto the glass plate using the vacuum evaporator JEOL JEE-4B. Thermal properties of the samples were measured using a differential scanning calorimeter (DSC), model Q20, TA Instruments, USA with hermetically sealed aluminum pans containing 3–5 mg of sample. The samples (capsules) were scanned from room temperature to 150°C in a dynamic ramp program with a heating rate of 10°C/min using an empty pan as a reference blank. Calibration of the equipment was carried out by indium as a temperature standard. Unoriented samples were investigated by X–ray diffraction in the transmission geometry by means of 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.

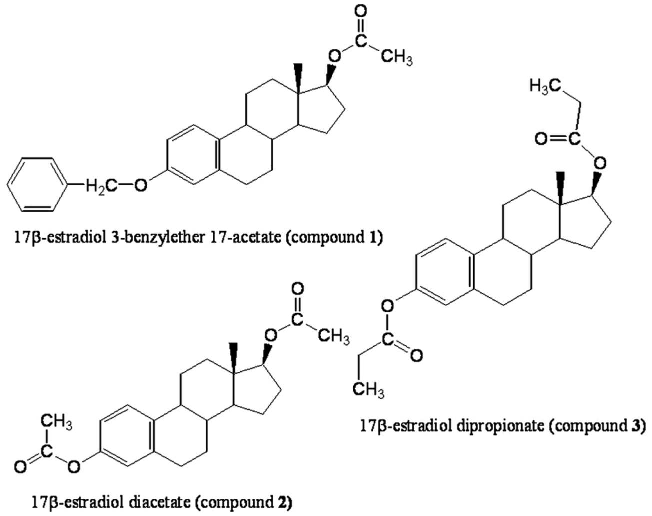
3. Results and Discussion

3.1. *Synthesis*

The investigated chiral additives, 17β-estradiol 3-benzylether 17-acetate (**1**), 17β-estradiol diacetate (**2**) and 17β-estradiol dipropionate (**3**), are known compounds [4]. 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 yielded benzyl ether of estradiol by acetic anhydride in dry pyridine. Compounds **2** and **3** were synthesized from estradiol, by 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.

3.2. *DSC and POM*

In the first phase the miscibility of pure **ChE** and **ChM** was investigated by preparing binary mixtures with different weight percent ratios (80%-20%, 60%-40%, 50%-50%, 40%-60%, and 20%-80%; denoted as **Mix1** – **Mix5**, respectively). From among these **Mix3** was selected as a reference mixture for further studies. In the second phase ternary mixtures of cholesteric liquid crystals (**Mix6, Mix7** and **Mix8**) were prepared, composed of **Mix3** (90% by weight) and one of the chiral additives (10% by weight of **1, 2** and **3**, respectively). Before preparing the binary mixtures, its pure components, **ChE** and **ChM**, have been checked by POM and DSC measurement (Table 1). The obtained phase sequences and phase transition temperatures of binary



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

17β-estradiol diacetate (compound 2)

17β-estradiol dipropionate (compound 3)

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

mixtures are given in Figure 2. The results of POM and DSC measurements, for all investigated mixtures are listed in Tables 2 and 3. In **Mix1** and **Mix2** there is direct melting into the isotropic phase in heating, which indicates that their mesophases are monotropic.

In all investigated mixtures focal conic polygonal textures were observed. Figure 3a presents an example for this texture of the cholesteric (Ch) phase observed in a homeotropic cell. 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. At this type of orientation the surface area is occupied by the polygonal base of a focal conic domain. However, formation of such domains, although it reduces the surface energy, is also accompanied by an increase of the "bulk" energy due to director distortions. The energy balance dictates that the focal conic domains have to be larger than some critical size in order to become stable [6–9].

The focal conic texture of the SmA* phase are shown in Figure 3b. 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 center of the focal conic, *i.e.*, layers orient tangentially in a circular focal conic domain. In a thin layer of a liquid

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

Compounds	Phases and transition temperatures (°C)	Ref.
ChE	I 114 Ch 99.5 SmA* 92.5 Cr	[5]
ChM	I 86.5 Ch 81 SmA* 71 Cr	[5]
1	Cr 101-103 I	
2	Cr 121-123 I	
3	Cr 102-104 I	

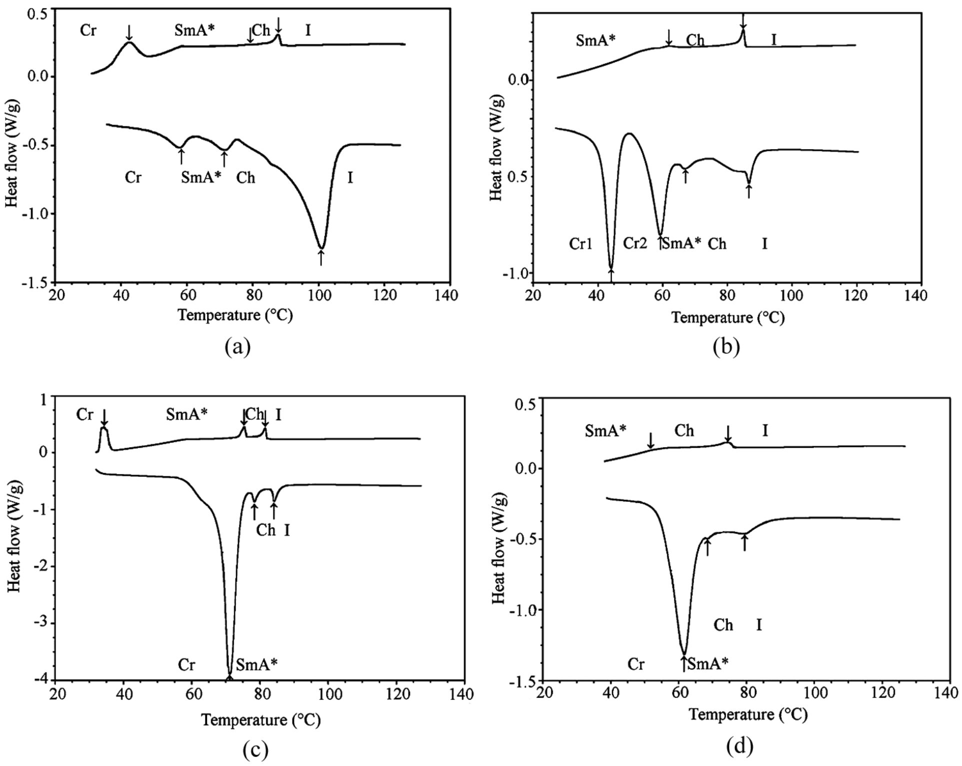


Figure 2. DSC plots for some studied compounds: a) **Mix1**; b) **Mix3**; c) **Mix5**, and d) **Mix6**. Arrows indicate the phase transitions.

crystal at the cholesteric-isotropic transition, when the cholesteric layer have the homeotropic boundary alignment, spherulitic domains were generated in some mixtures, when the sample was heated to the isotropic phase and then after 20 minutes it was quickly cooled (Fig. 3c). The convex shape of the spherulites is due to the homeotropic anchoring. They exist either as isolated localized states or form regular lattices [10,11].

The optical and DSC 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 **Mix6** – **Mix8** compared to **Mix3**. The largest temperature shifts of I→Ch phase transition have been recorded due to the addition of the chiral non-mesogenic additive **1**. Only additive **3** induced a broadening of the Ch phase range (Table 2).

3.3. *X-Ray Diffraction*

The relevant structural parameters were obtained from the X–ray diffraction data using Bragg's 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

Table 2. Phase transition temperatures T and transition enthalpies ΔH on heating from DSC

Code	Cr1	T (°C) [ΔH (J/g)]	Cr2	T (°C) [ΔH (J/g)]	Cr3	T (°C) [ΔH (J/g)]	SmA	T (°C) [ΔH (J/g)]	Ch	T (°C) [ΔH (J/g)]	I
ChE	•									110.2 [68.6]	•
Mix1	•	59.6 [1.7]	•	72.7 [1.5]	•					100.9 [30.0]	•
Mix2	•	56.9 [18.2]	•	67.0 [0.8]	•					87.2 [11.2]	•
Mix3	•	44.1 [17.9]	–		•	59.1 [13.3]	•	67.5 [0.7]	•	86.7 [5.3]	•
Mix4	•					57.9 [57.0]	•	71.0 [0.8]	•	84.1 [2.0]	•
Mix5	•					71.2 [101.6]	•	78.4 [1.7]	•	84.2 [2.4]	•
ChM	•					74.7 [74.3]	•	80.3 [1.5]	•	85.2 [1.8]	•
Mix6	•					61.5 [36.6]	•	68.9 [1.6]	•	79.8 [1.6]	•
Mix7	•					61.9 [38.4]	•	73.3 [1.8]	•	83 [not res.]	•
Mix8	•	40.7 [4.0]			•	57.8 [28.5]	•	79.0 [2.2]	•	83 [not res.]	•

(Table3). As examples, diffraction profiles of unoriented samples of **Mix3** and of one ternary mixture (**Mix6**) are depicted in Figure 4 for different temperatures. 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 range $2\theta \sim 9$–26° with the maximum at $2\theta \sim 17{,}5°$ corresponds to the average intermolecular distance (*D*).

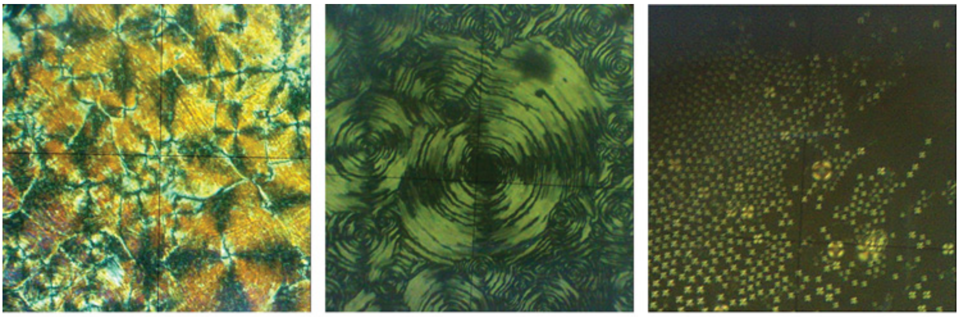
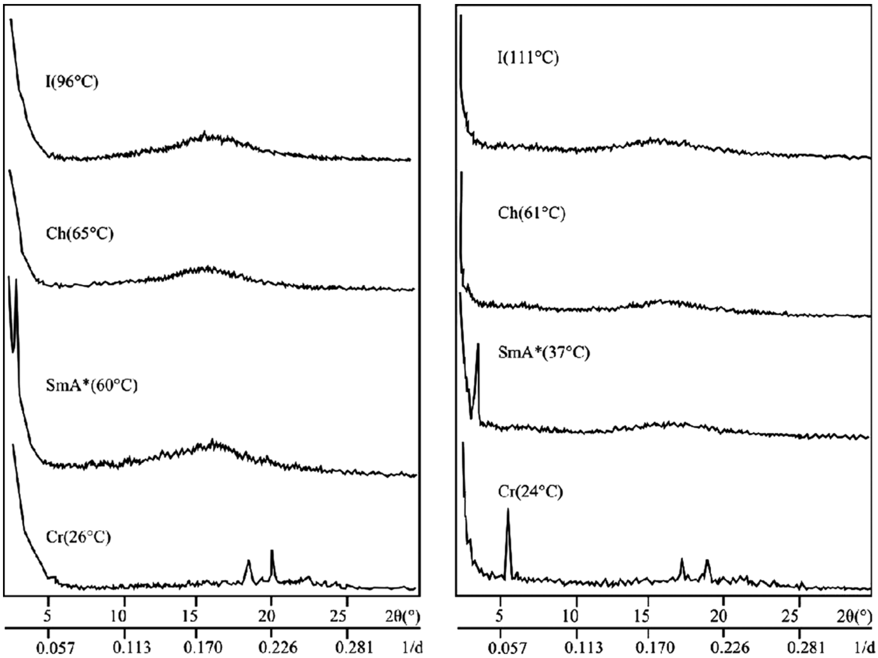

(a) (b) (c)

Figure 3. Textures of investigated compounds in cooling: a) **Mix7** – polygonal texture at 70°C; b) **Mix5** – circular texture at 60°C; c) **Mix 5** – growth of spherulites from the isotropic phase at 80°C. (Figure appears in color online.)



(a) (b)

Figure 4. X-ray diffraction profiles for: a) **Mix3**, and b) **Mix6**.

Table 3. Phase transition temperatures T, transition enthalpies ΔH and the widths ΔT of the mesophases on cooling from DSC or POM

Code	I	T (°C) [ΔH (J/g)]	Ch	T (°C) [ΔH (J/g)]	ΔT (°C)	SmA*	T (°C) [ΔH (J/g)]	ΔT (°C)	Cr
ChE	•	92.2 [1.1]	•	85.6 [36.7]	6.5	•	82.2 [18.9]	3	•
Mix1	•	88.9 [1.9]	•	79 (POM)	10	•	40.6 [14.7]	39	•
Mix2	•	85.1 [2.0]	•	75 (POM)	10	•	39 (POM)	26	•
Mix3	•	85.6 [2.1]	•	65 (POM)	20	•	Holds phase		
Mix4	•	82.0 [2.1]	•	68.1 [1.0]	14	•	Holds phase		
Mix5	•	81.5 [2.7]	•	75.3 [3.3]	6	•	34.3 [71.6]	41	•
ChM	•	82.8 [2.0]	•	77.5 [2.9]	5	•	71 (POM)	6	•
Mix6	•	74.5 [1.9]	•	57 (POM)	17	•	Holds phase		
Mix7	•	80 (POM)	•	64.4 [4.0]	16	•	Holds phase		

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 **Mix3**. 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 **Mix8** alters the packing of the host molecules of **Mix3**. On the contrary, *d* in **Mix6** and **Mix7** are nearly 15% smaller than in **Mix3** (Table 3). In this latter case 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.

Table 4. Molecular parameters for all observed phases at a fixed temperature T: angles 2θ corresponding to the reflection peaks, effective layer thickness **d** (error of measurements δ_d was about ±0.01 nm), average repeat distance **D** (error of measurements δ_D was about ±0.003 nm)

Mixture	*T* (°C)	2θ (°)	*d* (nm)	*D* (nm)
Mix1	110(I)	16		0.553
	86(Ch)	16.3		0.543
	67(SmA*)	2.4 16.4	3.68	0.539
Mix2	88(I)	16.8		0.527
	80(Ch)	17.0		0.521
	68(SmA*)	3.1 17.5	2.84	0.506
Mix3	96 (I)	16		0.553
	65(Ch)	16.2		0.546
	60(SmA*)	2.9 16.3	3.04	0.543
Mix4	99(I)	17		0.521
	78(Ch)	17.2		0.515
	67(SmA*)	2.6 17.3	3.39	0.512
Mix5	110(I)	17.5		0.506
	78(Ch)	17.8		0.497
	74(SmA*)	3.8 18	2.32	0.492
Mix6	111(I)	16		0.553
	61(Ch)	16.5		0.537
	37(SmA*)	3.5 17.0	2.52	0.521
Mix7	93(I)	16.5		0.537
	75(Ch)	17		0.521
	42(SmA*)	3.5 17.2	2.52	0.515
Mix8	111(I)	16		0.553
	74(Ch)	16.8		0.527
	50(SmA*)	2.7 17	3.27	0.521

In the cholesteric and isotropic phases only the broad peaks at larger angles are present (Fig. 4) corresponding to the average intermolecular distance D. As it can be seen from Table 4, the additives have practically no influence on D in the isotropic phase. However, some reduction of D could 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. Conclusions and Perspectives

The results of the studies on the ternary mixtures of cholesteric liquid crystals with non-mesogenic chiral estradiol derivatives **6**–**8** have shown a significant shift of the mesomorphic phase transitions toward lower temperatures, compared to those of the reference mixture. From 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 **Mix8** is bigger, while in **Mix6** and **Mix7** it is smaller than in the reference mixture. The reduction of the average intermolecular distances indicates a highest packing density of the molecules in the ternary mixtures than in the reference one.

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