

The Influence of Some D-Seco-Estrone Derivatives on the Phase Transitions of Binary Mixtures of Cholesteric Liquid Crystals

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Abstract

We have studied the influence of the new chiral non-mesogenic seco-estrone derivatives 2 and 4, synthesized in several synthetic steps starting from estrone, on the physical characteristics of the binary mixtures of cholesteric liquid crystals. We have examined the phase transitions of the mixture of cholesteryl laurate and cholesteryl enantate with addition of chiral non-mesogenic additives 2 and 4 (45 % – 45 % – 10 %; Mix.1 and Mix.2, respectively). X-ray diffraction data enabled the determination of the molecular structures of the compounds 2 and 4, the crystal lattice parameters of the new chiral additives and their molecular length (l) and width (d^*), as well as some 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 neighbouring molecules (D). Using molecular-mechanic calculations, based on the solved molecular structures, the most probable conformation of the compound 2 was determined.

Key words: X-ray diffraction, D-seco-estrone derivatives, cholesteric liquid crystals

1. Introduction

This work represents the continuation of our studies [1, 2] of binary and multicomponent mixtures of cholesteric liquid crystals, undertaken with an aim to obtain the systems with stable mesophase transitions and transition temperatures close to room temperature. Taking into account the suitable steroidal configuration of investigated D-seco-estrone derivatives, as well as their antiestrogenic activity with no estrogenic effect [3, 4], we have undertaken the study of a binary mixture of cholesteryl laurate and cholesteryl enantate with these derivatives. These chiral additives do not have any liquid crystalline phases.

The addition of some of the D-seco-estrone derivatives to cholesteric compounds or their binary mixtures in different concentrations resulted in significant shift of the temperature of phase transitions towards lower temperatures with respect to that of the initial components [5]. Comparing the results of optical microscopy and X-ray diffraction data from unoriented sample we have identified the type and temperature of the phase transition and outlined the phase diagrams. The layer spacing (d) in SmA* phase and the average intermolecular distance (D) (i.e. the mean distance between the long axes of neighbouring parallel molecules) were determined using the Bragg law: $\lambda = 2x \sin \theta$, where the distances $x = d$ and $x = D$ were calculated from the positions of the small angle and the large angle diffraction peak, respectively. In the case of a cholesteric phase, d corresponds to the average longitudinal (along the director) spacing distance, which is approximately equal to the length of the molecule. X-ray diffraction data enabled the determination of the crystal lattice parameters, molecular structures and the molecular length (l) and width (d^*) of some new chiral additives. On the basis of the solved molecular structures, using molecularmechanic calculations, the most probable conformation of compound 2 was also determined.

2. Experimental details

General

The optical study was performed using a polarization microscope Carl Zeiss (Jena) in the transparent light with special additional facility for the controlled heating and cooling of the sample, Mettler FP5.

Unoriented samples were investigated by X-ray diffraction in the transmission geometry by means of a conventional powder diffractometer, Seifert V-14, using CuK $_{\alpha}$ radiation at 0.154 nm, with an automatic high temperature kit Paar HTK-10.

The molecular and crystal structure of the chiral additive 4 in crystal phase was determined by the standard procedures of the single crystal structure determination. Because of the poor crystal quality of 4, the crystal structure refinement was limited to isotropic stage. For this crystal the molecular energy minimum conformation was determined by the molecularmechanic calculations (MMC) (PCMODEL, Serena Software, 1989), starting from the rough molecular model. From the additive 2 no single crystals could be grown, therefore a structure determination by X-ray was not possible. Instead, MMC was used to obtain the minimal energy conformations of this molecule.

Synthesis of the new chiral additives

The starting compound, 3-benzyloxy-17-oxo-16,17-secoestra-1,3,5(10)-trien-16-nitrile (1, Scheme 1) was synthesized in several steps, starting from estrone. The sodium borohydride reduction of compound 1 afforded 3-benzyloxy-17-hydroxy-16,17-secoestra-1,3,5(10)-trien-16-nitrile (2). Tosylation of the 17-hydroxy function of derivative 2, carried out in dry pyridine, yielded 3-benzyloxy-17-tosyloxy-16,17-secoestra-1,3,5(10)-trien-16-nitrile (3). Further, under reaction conditions of hydrogenolysis, this compound gave 3-hydroxy-17-tosyloxy-16,17-secoestra-1,3,5(10)-trien-16-nitrile (4).

The phase sequences of the synthesized chiral additives (2 and 4) are given in Table 1.

Table 1. The phase sequence of initial substances.

Substances	Phases and transition temperature (°C)
Cholesteryl laurate	I 93 Ch 90 SmA* 83.5 Cr
Cholesteryl enantate	I 114 Ch 99.5 SmA* 72.9 Cr
2	Cr 137-138 I
4	Cr 138-140 I

3. Results and discussion

The molecular structure of compound 4 (Scheme 1) was determined by X-ray diffraction and it is presented in Figure 1. The basic crystallographic data are given in Table 2.

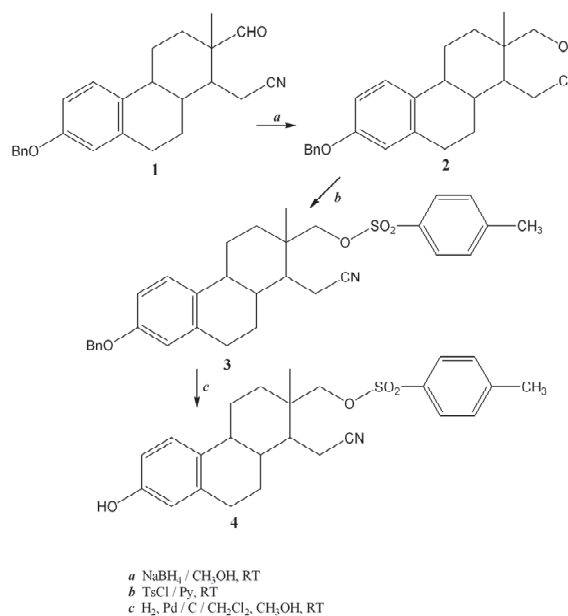
The X-ray measurement of 4 was aborted after collecting about 50 % of data because the check reflections had fallen below 50 % of their initial intensity. Therefore the structure of 4 could be solved with partial data only and isotropically refined to $R = 0.103$. This analysis has shown that the asymmetric unit contains two independent molecules of 4 and the water molecule (see Fig. 1b).

In spite of the poor data and less precisely defined molecular parameters, the revealed structure enabled us to define its minimum energy conformation by the MMC.

The combinations of the energy minimum molecular structures of 4 enabled us to generate the minimum energy structures of molecule 2 by MMC, which is given in Figure 1a.

Table 2. The basic crystallographic data.

Compound	4
Radiation	MoK α
System	Monoclinic
Space group	P2 $_1$
a (Å)	10.1937(8)
b (Å)	7.7656(6)
c (Å)	30.158(2)
β (°)	99.343(7)
R	0.1026
	3512 ref. $F_o > 4\sigma(F_o)$

**Scheme 1.**

The molecular length of compound 4 was determined as the distance between the O atom on the C-3 and the CH $_3$ group from the 17-tosyloxy moiety ($l \sim 17$ nm). The molecular width was estimated as the distance between the O atoms of the SO $_2$ group and the nitrile N atom ($d^* \sim 4.5$ nm). The l and d^* values of compound 2 were determined in the same way taking the terminal atoms in the molecules ($l \sim 14.5$ nm, $d^* \sim 8.1$ nm).

The optical microscopic studies have been started with checking the pure substances: cholesteryl laurate and cholesteryl enantate. The properties of the cholesteric

Mixbin, at different temperatures, are given in Figure 2.

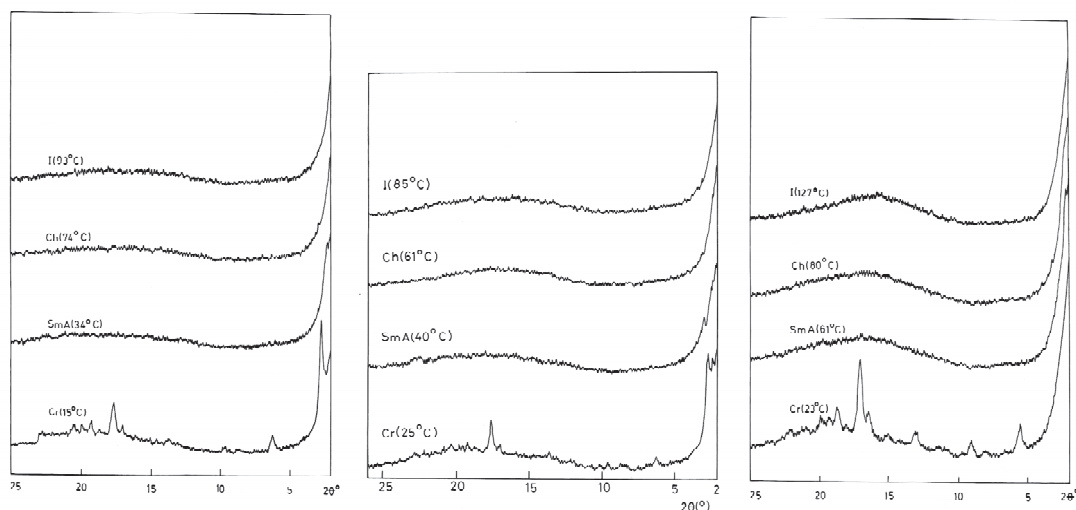


Figure 2. X-ray diffraction profiles for: a) Mixbin, b) Mix.1 and c) Mix.2.

Table 4. Molecular parameters of investigated mixtures for all observed phases at a fixed temperature T : angles corresponding to the reflection peaks 2θ , effective layer thickness d (error of measurements δ_d was about $\pm 0.1 \text{ \AA}$), average repeat distance D (error of measurements δ_D was about $\pm 0.03 \text{ \AA}$).

Mixture	T ($^{\circ}\text{C}$)	2θ ($^{\circ}$)	d (\AA)	D (\AA)	
Mixbin	93(I)	16.6		5.33	
		2.9	30.4		
		3.1	28.5		
		17.0		5.21	
34(SmA*)		2.2	40.1		
		17.8		4.98	
		15		5.90	
Mix.1	77(I)	15		5.90	
		64(Ch)	3.2	27.6	
42(SmA*)		16.5		5.57	
		2.75	32.1		
		16.0		5.53	
		15.7		5.64	
		70(Ch)	3.5	25.2	
Mix.2	86(I)	15.7		5.64	
		70(Ch)	3.5	25.2	
		16.5		5.37	
52(SmA*)		2.2	40.1		
		17.0		5.21	

The analysis of X-ray diagrams of the SmA* phase showed the presence of a strong reflection at small angles, indicating the presence of a layer structure, and the diffuse broad peak appearing in the range of $2\theta \sim 10 - 25^{\circ}$, with the maximum at $2\theta \sim 17.0^{\circ}$, corresponding to the average intermolecular distance (D).

The calculation of the longitudinal spacing distance (d) in the cholesteric phase gives the value of 30.4 \AA and 25.2 \AA for Mixbin and Mix.2, respectively. The shortest longitudinal spacing distance was observed in the Ch phase of Mix.2. It is probably due to the steric influence of the long tosyloxy group in position 17 of compound 2, and the higher number of single bonds, which enabled better packing in the mixture.

One can notice that the thickness of smectic layers (d) in the SmA* phase of investigated mix-

ture with chiral additive 2 is smaller than in Mixbin. It is probably due to the conformation of the additive, that the packing of the host molecules in ternary mixtures is altered compared to that in Mixbin. Chiral additive 2 has a OH group at the position 17. On the other hand, chiral additive 4 possesses a longer tosyloxy group at the same position. It may be a consequence of this sterical modification and the presence of more single bonds in the case of chiral additive 4 is that the d layer thicknesses of Mixbin and Mix.2 in the SmA* phase are practically the same, while in Mix.1 they are nearly 25 % smaller.

As can be seen from Table 4, the maximum of the broad peak, corresponding to D in the SmA* mesophase, shifted towards larger angle values in Mix.1 and Mix.2, than in Mixbin. This indicates that in chiral-containing additives a higher packing density of the molecules is energetically more favourable, than in the pure cholesteric binary mixture.

Comparing Mix.1 and Mix.2 it was established that the phase transitions temperatures I→Ch and Ch→SmA* decrease with the increasing width of molecules (d^*), as well as with the decreasing molecular length (l) of the chiral additives.

4. Conclusion

The results of the studies on the ternary mixtures of cholesteric liquid crystals with new, non-liquid crystalline, chiral seco-estrone derivatives 2 and 4 have shown a significant shift of the mesomorphic phase transitions toward lower temperatures, with respect to the ones of the pure cholesteric binary mixture. The molecular structure of derivative 4 was solved by the standard procedure of single crystal structure determination, while molecularmechanical calculations were used to obtain similar data for derivative 2 forming poor quality crystals. The molecular length and width (l and d^* values, respectively) of the compounds were determined taking terminal atoms in the molecules. On the basis of X-ray diffraction data on the crystalline powder of unoriented samples we have determined the intermolecular distance, D , and the layer spacing or the longitudinal spacing distance, d . It was shown that the thickness of smectic layers, d , in the SmA* phase of the investigated mixtures with chiral additive 2 is smaller than in the binary mixture, while in Mix.2 was practically the same. The maximum of the broad peak, corresponding to the intermolecular distance in the SmA* mesophase, shifts towards smaller angle values in Mix.1 and Mix.2 than in Mixbin, which indicates that a highest packing density of the molecules is in the binary mixture. It was found that the phase transition temperatures decrease with increasing molecular length of the chiral additives.

Acknowledgments

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