International Journal of Modern Physics B
Vol. 20, No. 21 (2006) 2999–3013
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THE INFLUENCE OF NEW D-SECO-ESTRONE DERIVATIVES ON THE BEHAVIOR OF THE CHOLESTERIC LIQUID CRYSTALS BINARY MIXTURES

D. Ž. OBADOVIĆ*,†, M. STOJANOVI†, S. JOVANOVIĆ-ŠANTA‡, D. LAZAR†,
A. VAJDA§ and N. ÉBER§

†*Department of Physics, Faculty of Sciences, Trig D.Obradov'ca 4,*
21000 Novi Sad, Serbia
‡*Department of Chemistry, Faculty of Sciences, Trg D.Obradov'ca 3,*
21000 Novi Sad, Serbia
§*Research Institute for Solid State Physics and Optics of the Hungarian Academy of Sciences,*
H–1525 Budapest, P.O. Box 49, Hungary
* *obadovic@im.ns.ac.yu*

Received 13 July 2004

We have studied the influence of the new chiral nonmesogenic seco-estrone derivatives **1-7**, synthesized in several synthetic steps starting from estrone, onto 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 the added chiral non-mesogenic additives **1-7** (45%-45%-10%; **Mix.1-Mix.7**, respectively). A considerable shift of the I → Ch phase transition temperature, as well as of the temperature of the SmA* phase formation, was observed. X-ray diffraction data enabled the determination of the molecular structures of the compounds **3**, **5**, **6** and **7**, 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 **Mix.1-Mix.6**: 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, on the basis of solved molecular structures, the most probably conformation of the other compounds (**1**, **2** and **4**) used in this work is determined. We have also investigated the influence of these chiral additives onto the pitch of the cholesteric helix of a binary mixture of cholesteric liquid crystals.

Keywords: 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 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 different chiral molecules to an achiral solvent can result in completely different helical pitches.[5] Chiral dopants with very high helical twisting powers are useful for cholesteric liquid crystal mixtures and are of great industrial importance.[6]

The addition of some of the D-seco-estrone derivatives to cholesteric compounds or to their binary mixtures in different concentrations resulted in a significant shift of the temperature of phase transitions toward the direction of lower temperatures with respect to that of the initial components.[7] Comparing the results of optical microscopy and X-ray diffraction data from an unoriented sample we have identified the type and the 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 distances $x = (d$ and $D)$ 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 solved molecular structures, using molecularmechanic calculations, the most probably conformation of compounds **1**, **2** and **4**, were also determined. The pitch of the cholesteric helix ($P = \lambda/\bar{n}$, λ is the maximum of the reflectance spectra and $\bar{n}$ is the mean refraction index) and the macroscopic helical twisting power, β_M,[8] was determined on the basis of reflection spectral analysis.

2. Experimental

2.1. *General*

The optical study was performed using a polarization microscope Carl Zeiss (Jena) in the transparent light with a 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$\hat{\alpha}$ radiation at 0.154 nm, with an automatic high temperature kit Paar HTK-10.

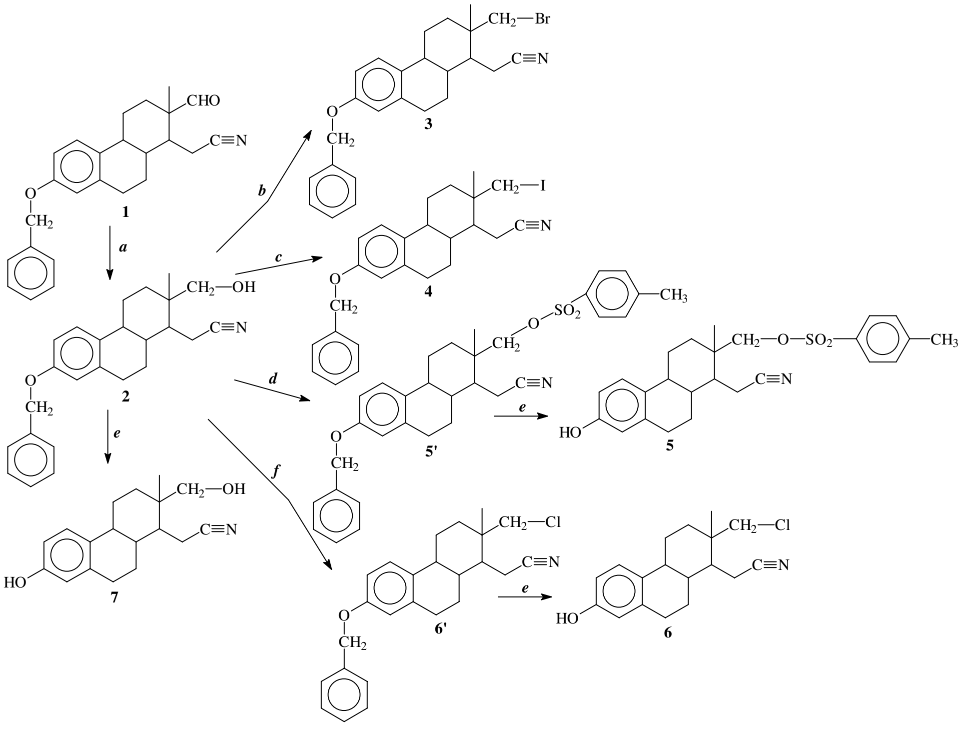
The molecular and crystal structures of the chiral additives **3**, **5**, **6** and **7** in their crystal phase were determined by the standard procedures of the single crystal structure determination. Due to poor crystal quality of **5** the crystal structure refinement was limited to an isotropic stage. For this crystal the molecular energy minimum conformation was determined by the molecular–mechanic calculations (MMC) (PCMODEL, Serena Software, 1989), starting from the rough molecular model. From the other additives (**1**, **2** and **4**) no single crystals could be grown, therefore a structure determination by X-ray was not possible. Instead MMC were used to obtain the minimal energy conformations of these molecules.

Optical reflectance spectra were measured in the 10,000–30,000 cm^{-1} range, in the phase transition temperature region of the investigated compounds, using a monochromator SPM-2 (Veb Zeiss, Jena) with an R-45/0 type reflection cell. MgO was used as "white" standard.

The refraction index was measured by Abbes refractometer (Zeiss–Jena).

2.2. *Synthesis of the new chiral additives*

The initial compound, 3-benzyloxy-17-oxo-16,17-secoestra-1,3,5(10)-trien-16-nitrile (**1**, scheme 1) was synthesized in several synthetic steps, starting from estrone.[3] The sodium borohydride reduction of compound **1** afforded 3-benzyloxy-17-hydroxy-16,17-secoestra-1,3,5(10)-trien-16-nitrile (**2**), which was the key intermediate in the synthesis of all other chiral additives.[3] 3-Benzyloxy-17-bromo-16,17-secoestra-1,3,5(10)-trien-16-nitrile (**3**) was obtained by the substitution



a $NaBH_4$ / CH_3OH, RT
b CBr_4, PPh_3 / Py, 60 °C
c I_2, PPh_3, imidazole / toluene, reflux
d TsCl / Py, RT
e H_2, Pd/C/ CH_2Cl_2, CH_3OH, RT
f CBr_4, PPh_3 / Py, 60 °C

Scheme 1.

Table 1. The phase sequence of initial substances.

Substances	Phases and transition temperature (°C)
Cholestryl laurate	I 93 Ch 90 SmA* 83.5 Cr
Cholestryl enantate	I 114 Ch 99.5 SmA* 72.9 Cr
1	Cr 137-138 I
2	Cr 135-136.5 I
3	Cr 157-157.5 I
4	Cr 139-140 I
5	Cr 138-140 I
6	Cr 196-198 I
7	Cr 198-199 I

reaction of **2** with tetrabromo methane in pyridine, in the presence of triphenylphosphine. 3-Benzyloxy-17-iodo-16,17-secoestra-1,3,5(10)-trien-16-nitrile (**4**), was synthesized in similar reaction conditions, using iodine, imidazole and triphenylphosphine. Tosylation of **2** was carried out in dry pyridine, yielding 3-benzyloxy-17-tosyloxy-16,17-secoestra-1,3,5(10)-trien-16-nitrile (**5′**), which under reaction conditions of hydrogenolysis gave 3-hydroxy-17-tosyloxy-16,17-secoestra-1,3,5(10)-trien-16-nitrile (**5**). 3-Hydroxy-17-chloro-16,17-secoestra-1,3,5(10)-trien-16-nitrile (**6**), was prepared by hydrogenolysis of 3-benzyloxy-17-chloro-16,17-secoestra-1,3,5(10)-trien-16-nitrile (**6′**), which was obtained in similar reaction conditions like the 17-bromo derivative, using tetrachloro methane in pyridine. At last, hydrogenolysis of derivative **2** yielded 3,17-dihydroxy-16,17-secoestra-1,3,5(10)-trien-6-nitrile (**7**).[3,4] X-ray structure analysis of **3**, **5**, **6**, **7** revealed their absolute configuration as (17*R*).

The phase sequences of the synthesized chiral additives (**1-7**) are given in Table 1.

3. Results and Discussion

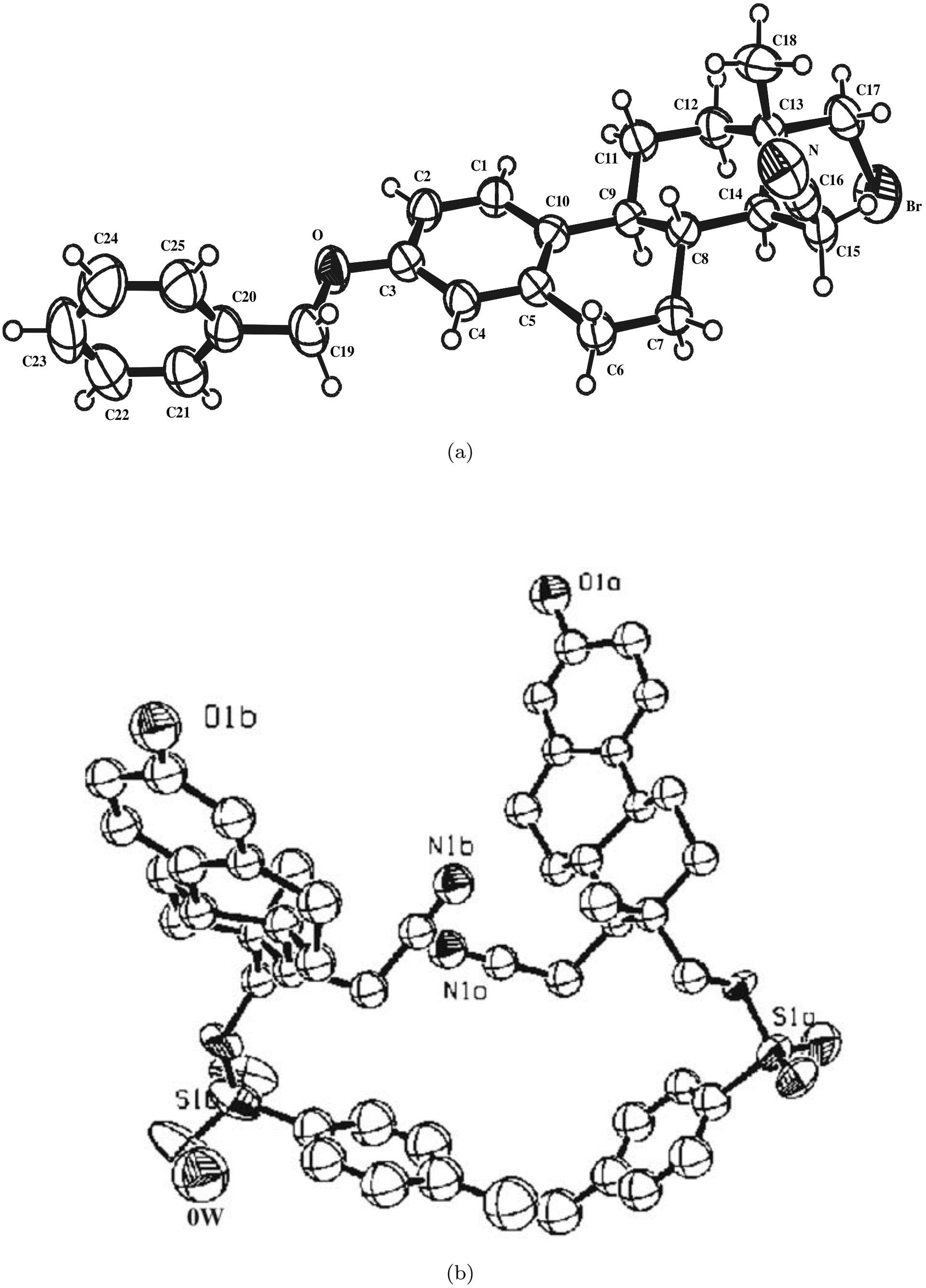
The molecular structures of the compounds **3**, **5**, **6** and **7** (Scheme 1) were determined by X-ray diffraction and they are presented in Fig. 1. The basic crystallographic data are given in Table 2.

The analysis of **3**, **6** and **7** has been completed and crystallographic data deposited at the Cambridge Crystallographic Data Center (CCDC 205268, CCDC 205269 and CCDC 205270, respectively).

The X-ray measurement of **5** was aborted after collecting about 50% of data because the check reflections had fallen below 50% of their initial intensity. Therefore the structure of **5** 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 **5** and the water molecule [see Fig. 1(b)].

Table 2. The basic crystallographic data.

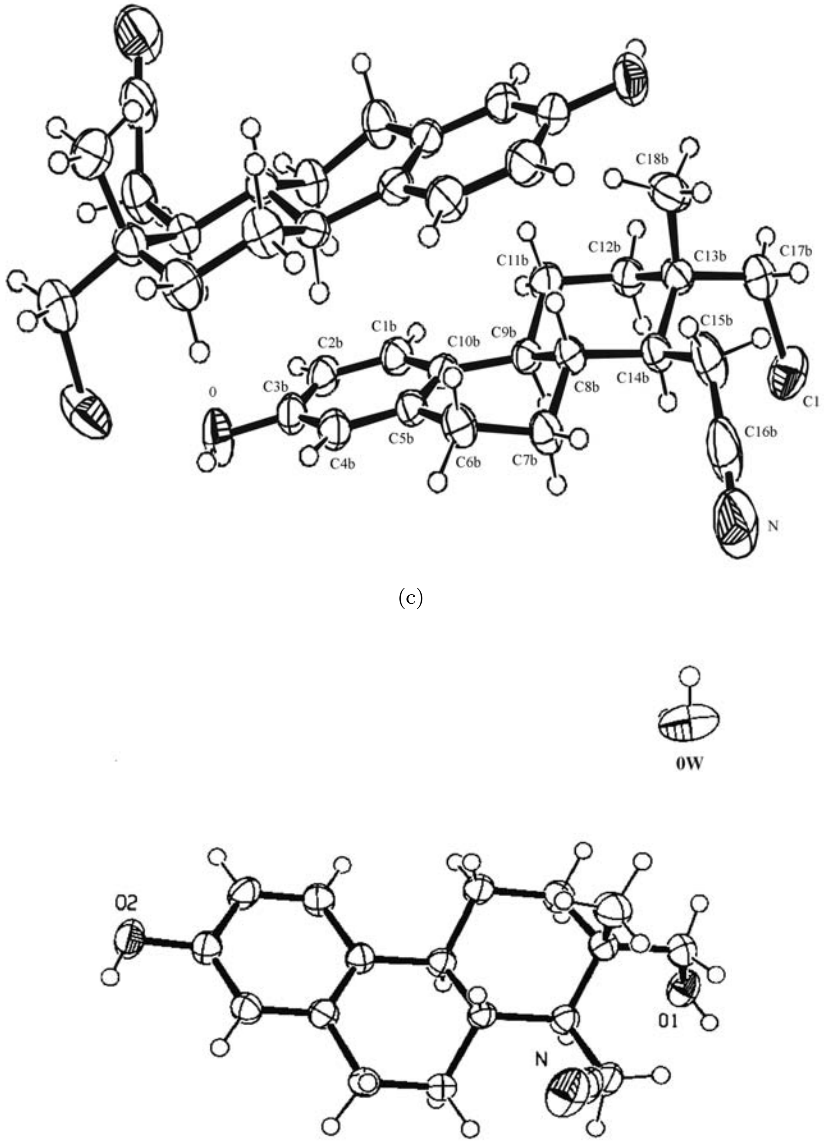
Compound	**3**	**5**	**6**	**7**
Radiation	MoK$_\alpha$	MoK$_\alpha$	MoK$_\alpha$	MoK$_\alpha$
System	Monoclinic	Monoclinic	Monoclinic	Orthorombic
Space group	$P2_1$	$P2_1$	$P2_1$	$P2_12_12_1$
a (Å)	7.6721(6)	10.1937(8)	12.2930(12)	8.0576(6)
b (Å)	14.7616(10)	7.7656(6)	8.9470(10)	9.3546(7)
c (Å)	10.1234(6)	30.158(2)	14.635(2)	21.129(1)
β (°)	108.198(6)	99.343(7)	97.876(5)	—
R	0.0325 2598 ref. $F_o > 4\sigma(F_o)$	0.1026 3512 ref. $F_o > 4\sigma(F_o)$	0.0314 7452 ref. $F_o > 4\sigma(F_o)$	0.0349 3286 ref. $F_o > 4\sigma(F_o)$



(a)

(b)

Fig. 1. Molecular structure of chiral additives: (a) **3**, (b) **5**, (c) **6**, (d) **7**.



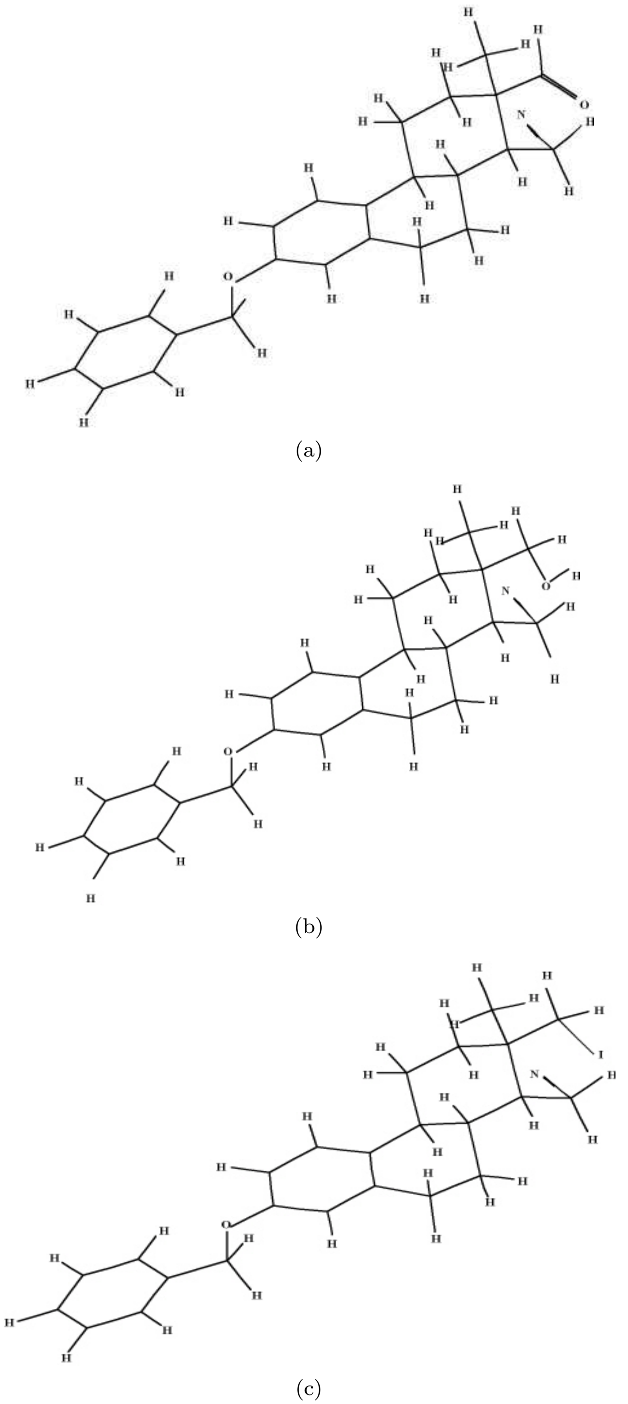
(c)

(d)

Fig. 1 (*Continued*)

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 molecularmechanic calculations (MMC).

MMC were also performed to define the conformation of **3**, **6** and **7** in terms of energy minima starting from the crystal molecule. Furthermore, the combinations



(a)

(b)

(c)

Fig. 2. Minimal energy molecular conformations of molecules (a) **1**, (b) **2** and (c) **4** generated by the molecular-mechanic calculations.

Table 3. Molecular length, ℓ, and molecular width, d^* of the chiral additives.

Substances	ℓ (nm)	d^* (nm)
1	~17	4.5
2	15.5	5.8
3	15.8	6.3
4	15.9	6.5
5	14.5	8.1
6	10.5	6.2
7	9.2	5.8

of the energy minimum molecular structures of **3**, **5**, **6** and **7** enabled us to generate the minimum energy structures of another three molecules, i.e. **1**, **2**, **4** by MMC, which are given in Fig. 2.

The molecular length, ℓ, of the compound **5** was determined as the distance between the O atom connected to the position 3 and the CH_3 from the 17-tosyloxy moiety. The molecular width, d^*, was estimated as the distance between the O atoms of the SO_2 group and the nitrile N atom. The ℓ and d^* values of other compounds were determined in the same way taking the terminal atoms in the molecules. These parameters for all compounds are given in Table 3.

The optical microscopic studies have been started with checking the pure substances: cholesteryl laurate and cholesteryl enantate. The properties of the cholesteric substances have shown good agreement with existing literature data.[9] Then the melting points of the new chiral additives **1-7** have been identified. The phase transition temperatures of all pure substances are listed in Table 1. After that we have prepared the binary mixture, **Mixbin**, which contained cholesteryl enantate and cholesteryl laurate, 50–50% by weight. This binary mixture was used as the reference compound for testing the chiral additives. Therefore three-component mixtures (**Mix.1**–**Mix.7**), containing **Mixbin** (90%), and one of the chiral derivatives (**1-7**, 10%) have been prepared.

Phase sequences of the investigated mixtures are presented in Table 4. Data for **Mix.7** are not given as compound **7** did not formed homogenic mixture with these cholesteric liquid crystals.

Analysis of the phase sequences of the three-component mixtures **Mix.5** and **Mix.6**, and comparison with the binary mixture (**Mixbin**) have shown that the addition of chiral non-mesogenic additives, **5** and **6**, resulted in shifts of the temperatures of the isotropic-cholesteric (I-Ch) phase transition by 3.5°C and of the cholesteric-smectic A* (Ch-SmA*) one by ~1.3–2.5°C. In the case of **Mix.1**, **Mix.2** and **Mix.3** the shifts of the I-Ch and Ch-SmA* phase transition temperatures were 10–13°C and 7–11°C, respectively. The maximal shifts of the I-Ch and Ch-SmA* transition temperatures, observed for **Mix.4**, were 21°C and 18.8°C, respectively.

Table 4. The phase sequence of investigated mixtures. The transition temperatures are given in °C.

Mixtures	Transition temperature	Transitions temperature	Transitions temperature	Phase temperature range	Phase temperature range	ΔT	ΔT	ΔT
	I → Ch	Ch → SmA*	SmA* → Cr	Ch	SmA*	I → Ch	Ch → SmA*	SmA* → Cr
Mixbin	76.8	69.1	35	7,7	34,1			
Mix.1	66.4	61.2	30	5,2	31,2	10,4	7,9	5
Mix.2	63.6	58.5	32	5,1	26,5	13,2	10,6	3
Mix.3	65.8	62	48	3,8	14	11	7,1	−13
Mix.4	55.8	50.3	35	5,5	15,3	21	18,8	0
Mix.5	73.3	66.8	24	6,5	42,8	3,5	2,3	11
Mix.6	73.3	68.0	24	5,3	44	3,5	1,1	11

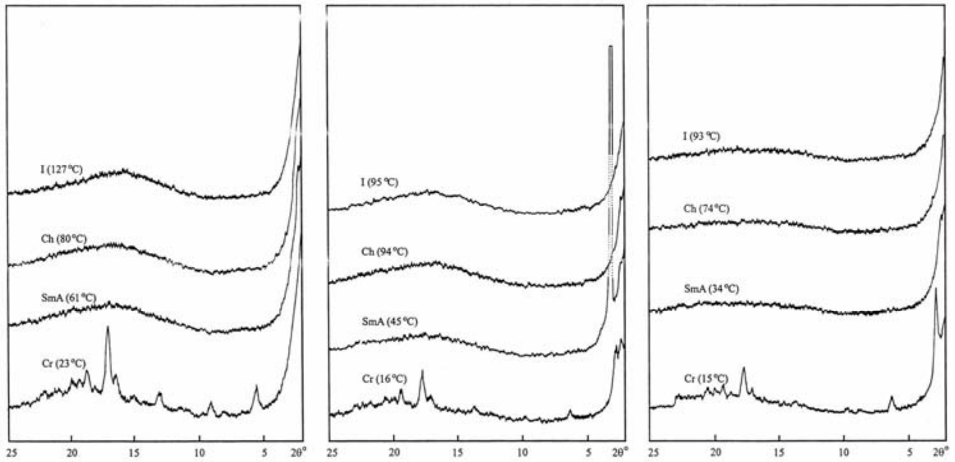


Fig. 3. X-ray diffraction profiles for: (a) **Mix.5**, (b) **Mix.4** and (c) **Mixbin**.

The largest temperature range of the SmA* phase, 44°C, was observed in mixture **Mix.6**. The SmA* phase in most of the mixtures was stable down close to the room temperature.

On the basis of the collected experimental data, we have performed the study of unoriented samples with X-ray diffraction. X-ray diffraction studies were carried out on the binary (**Mixbin**) and on the three-component mixtures (**Mix.1-6**). Relevant parameters of investigated mixtures, obtained from X-ray diffraction data, are presented in Table 5. Diffraction profiles of unoriented samples of some of the ternary mixtures, as well as of **Mixbin**, at different temperatures, are given in Fig. 3.

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 diffused broad peak appearing in the range $2\theta \sim 10$–$25°$, with the maximum at $2\theta \sim 17.0°$, 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 Å and 25.2 Å for **Mixbin** and **Mix.5**, respectively. The shortest longitudinal spacing distance among all mixtures was observed in the Ch phase of **Mix.5**. It is probably due to the steric influence of the long tosyloxy group in position 17 of the compound **5**, 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 mixtures with chiral additives **1-4** and **6** are smaller than in **Mixbin**. It is probably due to the conformation of the additives, that the packing of the host molecules in ternary mixtures alters compared to that in **Mixbin**. Chiral additives **1** and **2** have CHO and OH groups, respectively, at position 17. On the other hand, chiral additive **5** possesses a longer tosyloxy group at the same position. It may be

Table 5. Molecular parameters of investigated mixtures for all observed phases at a fixed temperature T [°C]: angles corresponding to the reflection peaks 2θ [degrees], effective layer thickness d [Å] (error of measurements δ_d was about ± 0.1 Å), average repeat distance D [Å] (error of measurements δ_D was about ± 0.03 Å), macroscopic helical twisting power β_M [μm^{-1}] are presented. In the cholesteric phase d represents longitudinal spacing distance. λ is the wavelength of the maximum of the reflection peak and P is the pitch of the cholesteric helix.

Mixture	T (°C)	2θ (°)	d (Å)	D (Å)	P (nm)/λ (nm)	β_M (μm^{-1})
Mixbin	93(I)	16.6		5.33		
	74(Ch)	2.9	30.4		−282.0/476	
		3.1	28.5			
		17.0		5.21		
	34(SmA*)	2.2	40.1			
		17.8		4.98		
Mix.1	77(I)	15		5.90		
	64(Ch)	3.2	27.6		−268.8/450	−1.74
		16.5		5.57		
	42(SmA*)	2.75	32.1			
		16.0		5.53		
Mix.2	85(I)	17.0	5.21			
	61(Ch)	3.0	29.4		−263.6/442	−2.48
		17.0		5.21		
	40(SmA*)	2.9	30.4			
		17.5		5.06		
Mix.3	70(I)	16.9		5.24		
	64(Ch)	3.3	26.7			
		17.8		4.98		
	60(SmA*)	3.2	27.6			
		18.1		4.89		
Mix.4	95(I)	16.5		5.37		
	53(Ch)	2.3	38.7		−251.5/423	−4.30
		16.9		5.24		
	40(SmA*)	3.0	29.4			
		18.00		4.92		
Mix.5	86(I)	15.7		5.64		
	70(Ch)	3.5	25.2		−261.1/439	−2.84
		16.5		5.37		
	52(SmA*)	2.2	40.1			
		17.0		5.21		
Mix.6	80(I)	18.2		4.87		
	70(Ch)	3.1	28.5			
		18.3		4.84		
	52(SmA*)	3.3	26.74			
		18.5		4.82		

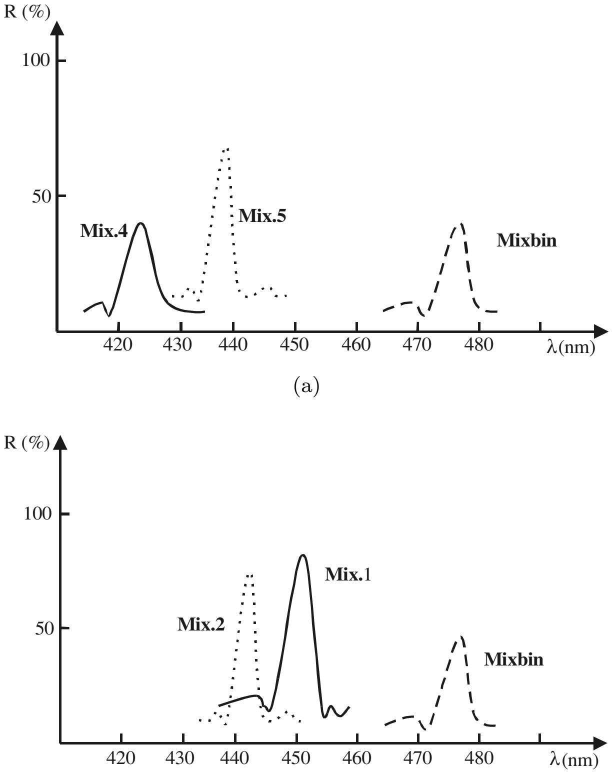
the consequence of this sterical modification and the presence of more single bonds in the case of chiral additive **5** is that the d layer thicknesses of **Mixbin** and **Mix.5** in the SmA* phase are practically the same, while in **Mix.1** and **Mix.2** they are nearly 25% smaller. The smallest d-distances in the SmA* phase were observed in mixtures with the chiral additives **3**, **4** and **6**.

On the basis of crystallographic data it was concluded that molecules of compounds **3** and **4** are approximately of the same length, as it can be seen in Table 3, while derivative **6** has the smallest ℓ-distance, due to the slightly bent form of the molecule [see Fig. 1(c)]. At position 17 of these molecules Br, I or Cl atoms are bonded which, in the mixtures, most probably force significant bending of the hydrocarbon chains in the molecules of the cholesteric compounds in order to achieve an energetically most favourable stereo chemical distribution.

As it can be seen from Table 5, the maximum of the broad peak, corresponding to D in the SmA* mesophase, moved toward larger angle values in **Mix.3**, **Mix.4** and **Mix.6**, than in mixtures with other chiral additives or **Mixbin**. This indicates that in halogen containing additives a higher packing density of the molecules is energetically more favourable, than in the pure cholesteric binary mixture or in the mixtures with other chiral additives.

Addition of a chiral additive to a non-chiral nematic host results in an induced cholesteric phase with a helical structure. The efficiency of helix induction of the additive is usually characterized by its macroscopic helical twisting power, β_M, defined by the relation $P^{-1} = \beta_M c$, where c is the concentration of the chiral additive and P is the resultant pitch.[8] If the host material is also chiral (cholesteric), it usually has already a finite helical pitch P_0. For this case the relation above can be straightforwardly generalized yielding $P^{-1} = \beta_M c + P_0^{-1}$, where now P is the modified pitch occuring due to the influence of the additive. Thus for cholesteric hosts the pitch variation $(P - P_0)$ can also be used for the determination of β_M.

In order to explore the influence of the additives on the helical structure of **Mixbin** we have studied the optical reflection spectra of the mixtures. The spectra exhibited a sharp peak corresponding to the selective light reflection in the cholesteric phase as shown in Fig. 4. The wavelength λ of the maximum reflectance has been identified and the helical pitch has been determined. These values are also listed in Table 5. From the measurements it became obvious that the influence of the chiral additives onto the binary cholesteric mixture manifests itself in the shift of the maximum of the reflection peak (476 nm in **Mixbin**) toward lower wavelengths, but without changing the sense of rotation. The decrease of the pitch of the cholesteric helix in **Mix.1**, **Mix.2**, **Mix.4** and **Mix.5** with respect to that of the pure binary mixture ($P_0 = -282.0$ nm) were 13.2, 18.4, 30.5 and 20.9 nm, respectively. From the pitch variation the macroscopic helical twisting power (β_M) of the additives could be obtained (see Table 5) using the generalized relation introduced above. The largest shift in the wavelength of the selective light reflection peak was found in **Mix.4**, resulting in the shortest pitch of the cholesteric helix, which means that chiral additive **4** had the largest β_M. It could be a consequence of the presence



(a)

(b)

Fig. 4. Reflection spectral data compared to the **Mixbin** for: (a) **Mix.4** and **Mix.5**, (b) **Mix.1** and **Mix.2**.

of the I atoms (large ionic radius) in **4**, which demands the largest twist angle of the director **n** along the helical axis. Comparing **Mix.1**, **Mix.2** and **Mix.5** it was established that the pitch of cholesteric helix decreases (and thus the macroscopic helical twisting power increases) 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, not liquid crystalline, chiral seco-estrone derivatives **1-6** 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 derivatives **3**, **5**, **6** and **7** was solved by the standard procedure of single crystal structure determination, while molecular-mechanical calculations were used to obtain similar data for other substances 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 additives **1-6** was smaller than in the binary mixture (except in the **Mix.5**, which was practically the same). Also the maximum of the broad peak, corresponding to the intermolecular distance in the SmA* mesophase, moves towards larger angle values in **Mix.3**, **Mix.4** and **Mix.6** than in mixtures with other chiral additives or in **Mixbin**. This indicates that a highest packing density of the molecules in mixtures with these additives is energetically more convenient, than in the pure binary cholesteric mixture or in **Mix.1**, **Mix.2** and **Mix.5**. Optical reflection spectra showed that the chiral additives shifted the maxima of the selective light reflection peak of the pure cholesteric binary mixture toward lower wavelengths. It was found that the pitch of the cholesteric helix decreases and the macroscopic helical twisting power increases with increasing molecular length of the chiral additives.

Acknowledgments

This work was supported by Research Grant Nos. 141020 and 142052B from the Ministry of Science and Environment Protection of the Republic of Serbia and Hungarian National Science Funds OTKA T 030401, T 032667 and T 037336. D. Z. Obadovic, M. Stančić, A. Vajda and N. Éber are grateful for the hospitality provided within the framework of an exchange project of the Serbian Academy of Sciences and Arts and the Hungarian Academy of Sciences.

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