STRUCTURE AND MESOMORPHYSM FOR SOME CHOLESTEROL DERIVATIVES

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abstact: The phase transition of cholesteryl p-phenoxy-phenyl carbamate, cholesteryl p-phenoxy-phenyl thiocarbonate, cholesteryl thiophenoxy-phenyl carbamate and cholesteryl p-thiophenoxy-phenyl thiocarbonate have been measured with the aid of differential scanning calorimetry. The texture of the mesophases have been determined with a hot stage equipped polarizing microscope. The phase transition schemes have been described.

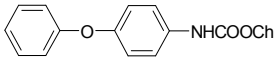
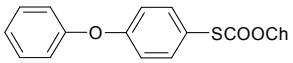
Introduction

Cholesteric liquid crystals have estabilished application in many advanced technologies like liquid crystal displays, optical filters, imaging systems, radiatuin visualization, optical storage systems, temperature sensors and medical thermography.

Aim of the article consist in thermodynamics study of variety of cholesteryl derivates which have in their structure a identical structural group and different derived of carbamates and thiocarbonates. The compounds have been recently prepared and purified in Organic Chemical Laboratory of University of Pitesti and analysed by IR and NMR Spectroscopy and Thin Layer Cromatography [1,2]. Due to the liquid crystalline properties of this type of compounds which are responsible for their requirement in various fields to increase their synthesis in a large amount and developing the scientific research in this area.

The structure of studied compounds is shown in Table 1.

Table 1. The structure of cholesteryc derivates

Comp.*	Molecular formula	Molecular weight	Structure	Macroscopic shape
I	$C_{40}H_{55}O_3N$	597		light pink elongated droplet
II	$C_{40}H_{54}O_3S$	614		yellow-white plates

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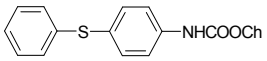
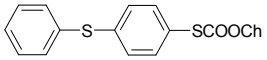
III	$C_{40}H_{55}O_2NS$	613		yellow plates
IV	$C_{40}H_{54}O_2S_2$	630		yellow agglomerated crystals

* I - cholesteryl p-phenoxy-phenyl carbamate; II - cholesteryl p-phenoxy-phenyl thiocarbonate; III - cholesteryl thiophenoxy-phenyl carbamate; IV - cholesteryl p-thiophenoxy-phenyl thiocarbonate.

Experimental

The thermodynamic study was performed by Differential Scanning Calorimetry by thermal flow monitoring vs. temperature and dynamic conditions of temperature (heating and cooling) and in a highly purified argon atmosphere [3,4].

The mesophases textures have been also monitored under thermal dynamic condition by Böetius termomicroscopy [5].

Results and Disscusion

The results obtained by DSC and TM are given in Table 2.

Table 2. The structure of cholesteryl derivates

Comp.	DSC		TM	
	heating	cooling	heating	cooling
	T_{tr} (°C)	T_{tr} (°C)		
I	156,84	127,34	-light-pink elongated berries; -152-155°C melting	65-70°C conglomerate
II	115,04	-	-yellow-white plates -90°C shifting crystals 105°C shifting crystals 116°C melting	yellow plates at room temperature
III	125,54 129,24	-	-yellow blade crystals -70°C reorganisation -117°C shifting -126°C yellow melt	remain as yellow melt
IV	101,34 116,09		-unregular shape yellow crystals conglomerate -82°C shifting -92°C crystals joining -103-113°C colourless melt	88°C unregular shape like waves

The structure of polymorph mesophase had been identified comparing the structures recorded by thermomicroscopy with textural pattern of Demus and Richter [6]. So, 1st, 3rd and 4th compounds are estimated textural types as indicated in figures 1, 2 and 3.

Fig. 1*:* Polygonal texture for 1st compound

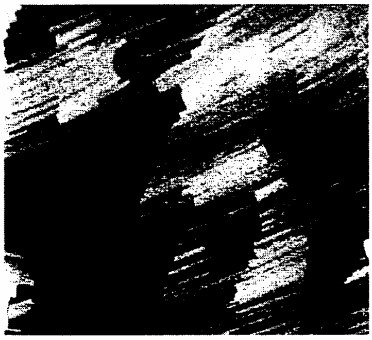


Fig. 1*:* Fan – shaped type texture for 3rd compound

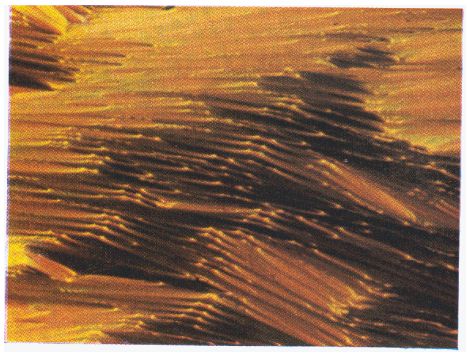
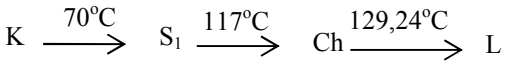
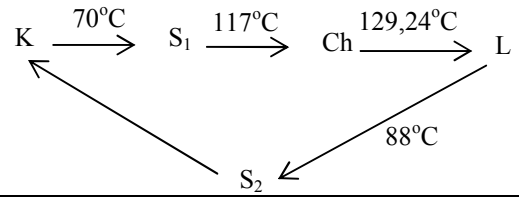


Fig. 3*:* Wave type texture, focal conic with tight eclipses compound

After results combining we proposed original polymorphs schemes shown in Table 3.

Table 3. Polymorphs schemes

Compound	Scheme
I	K $\xrightarrow{154{,}84^{o}C}$ L; L $\downarrow 127{,}34^{o}C$ Ch; Ch $\rightarrow$ K
II	K $\xrightarrow{90^{o}C}$ Ch $\xrightarrow{115{,}04^{o}C}$ L

III	
IV	

K – Crystal; S – Smectyc phase; Ch – Cholesteryl phase; L – Isotropic liquid

It has been observed that cholesteryl p-phenoxy-phenyl carbamate shows a monotropic cholesteryl phase while cholesteryl p-phenoxy-phenyl thiocarbonate shows a enantiotropic mesophase.

The differences between the structure of carbamate and thiocarbonate consist in increasing of cholesteryl interval, so:

- for cholesteryl p-phenoxy-phenyl carbamate the interval is around 27°C and for cholesteryl p-phenoxy-phenyl thiocarbonate the interval it is around 25°C;
- for cholesteryl thiophenoxy-phenyl carbamate it was revealed a cholesteryl inteval of 12°C and for cholesteryl p-thiophenoxy-phenyl thiocarbonate 9°C.

The isotropisation points for carbamates are higher then carbonates so thermal stability decreasing of carbamates could be assign to the increasing of flexibility in lateral 3β chain by the introduction of one oxygen atom beside the carbonyl group.

This hypothesis is sustained by the replacement of sulphur with one –NH- group yielding the respective cholesteryl carbamate which has a high conjugation capacity with phenyl chain as well as with carbonyl group resulting in a high rigidity in this region of the molecule.

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