

## THERMODYNAMIC STUDY AND STRUCTURE-MESOMORPHISM CORRELATION FOR NEW SITOSTERYL BENZOATE COMPOUNDS

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Two new sitosteryl benzoate compounds with liquid crystals properties were thermodynamically characterized by DSC and by thermomicroscopy. The thermal parameters and some thermodynamic functions associated to polymorphic transition were determined in correlation with the molecular bases. Relative polymorphism diagrams were constructed to clarify the thermodynamic phase stability of each derivative.

### INTRODUCTION

Although the liquid crystals existence has been known for more than one century, until 1960 studies in this area were not very important because they didn't envisage practical application. After that, because of liquid crystals applications, the research has known an explosive development in top of scientific domains.

Liquid crystals present an intermediary order degree between regular crystals and isotropic liquid. Because the liquid crystals have some positional order degree likes the solids, they show a large variety of defects and discontinuities in their macroscopic structure. Moreover, like the properties of the liquids, liquid crystals can undergo strong modifications of their long axis of the molecules ordering.

If mesomorphic phases appear at temperature variation, then liquid crystals are thermotropic. Mesomorphism can be monotropic if mesophases arise only at cooling of isotropic liquid or enantiotropic if this arises at cooling of isotropic liquid as well as at heating of crystal.

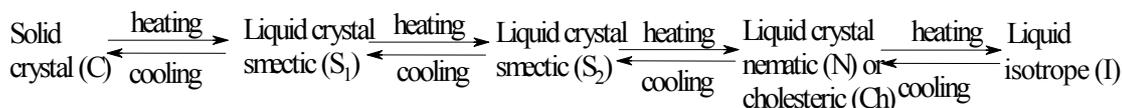
Most thermotropic liquid crystals are formed from certain organic molecules, with some common physico-chemical characteristics. Some important properties of the liquid crystals are:

elongated form of the molecules and molecular aggregates; rigid structure with molecules having double and triple bonds which makes evident the long axis of the molecule; existence of strong permanent electric dipoles; presence of some slight dipolar groups placed at the extremity of the molecules, etc.

Systematic investigations of different type of thermotropic liquid crystals structure lead to their classification in: nematic liquid crystals (N) with non-stratification structure, smectic crystals ( $S_A - S_H$ ) with stratification plan structure and cholesteric crystals (Ch) with stratification helicoidal structure.<sup>1-3</sup>

Thermotropic nematic liquid crystals are formed by elongated molecules with the long axis aligned parallel to a preferential direction. Smectic mesophases are characterized by a reduced order of the long molecular axis and a disposal in equidistant planes of the molecular liquid centers. Cholesteric liquid crystals can be considered as having a structure of a twist nematic. For this reason some investigators do not consider the cholesteric phase different from the nematic phase.

The decreasing of molecule ordering degree with temperature variation implies simple or complex first order phase transitions which can be presented in the general transition scheme:



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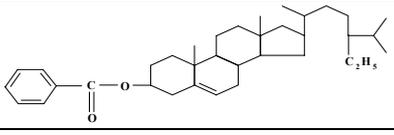
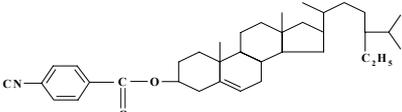
In the last decades, a series of derivatives from  $\beta$ -sitosterol have been synthesized, and their mesomorphism has been marked out.<sup>4,5</sup>

This paper presents a thermodynamic study of two sitosteril benzoates with structures shown in Table 1.

The studied substances were synthesized, purified and spectrally characterized in the Organic Chemistry Laboratory of the Faculty of Chemistry from the University of Bucharest<sup>6</sup>.

Table 1

Chemical structure of the studied sitosteryl benzoates

Compound	Molecular formula	Molecular weight	Structure
sitosteryl benzoate	$C_{36}H_{54}O_2$	518.83	
sitosteryl <i>para</i> -ciano-benzoate	$C_{37}H_{53}O_2N$	543.72	

## RESULTS AND DISCUSSION

The thermodynamic study was accomplished by Differential Scanning Calorimetry (DSC) and Boëtius thermomicroscopy (TM).<sup>7,8</sup>

The temperature dependence of the heat flow ( $dH/dt$ ) for sitosteryl benzoate is presented in Fig. 1.

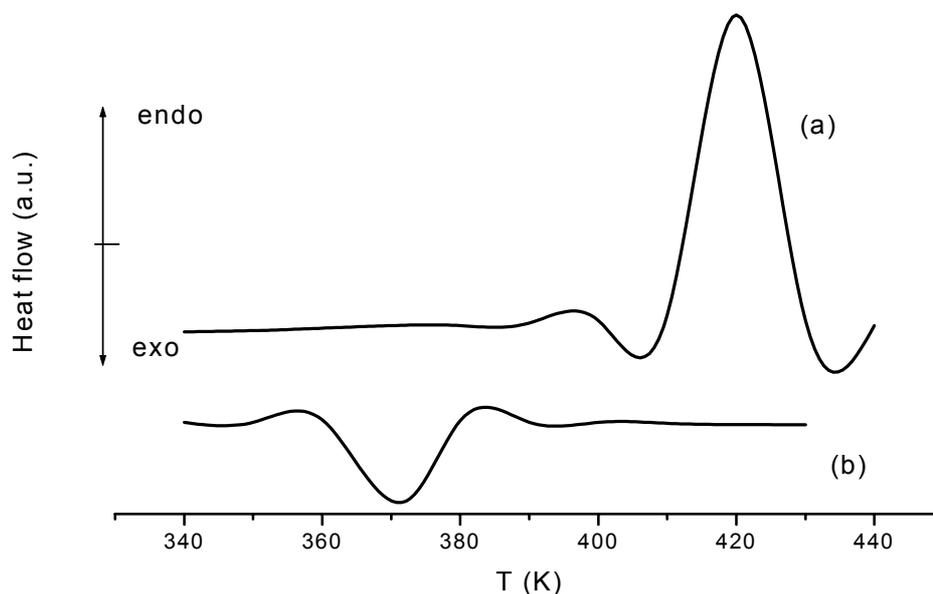


Fig. 1 – DSC curves for sitosteryl benzoate (a) at heating and (b) at cooling.

From the DSC data, the transition temperature ( $T_{tr}$ ) and the most important thermodynamic functions ( $\Delta_{tr}H$  and  $\Delta_{tr}S$ ), which characterize the transitions, were calculated.

$\Delta_{tr}H$  can be calculated using the relation:

$$\Delta_{tr}H = \frac{K \cdot A \cdot S}{m_p \cdot v_i} (\text{J} \cdot \text{g}^{-1})$$

where:  $K$  – instrument constant;  
 $A$  – peak area ( $V \cdot K$ );  
 $S$  – sensitivity of apparatus ( $mJ/s$ );  
 $m_p$  – weight of the sample ( $g$ );  
 $v_i$  – heating rate ( $K/min$ ).

From the transition temperature,  $T_{tr}$  ( $K$ ), and  $\Delta_{tr}H$  ( $J/mol$ ),  $\Delta_{tr}S$  can be calculated with the relation:

$$\Delta_{tr}S = \frac{\Delta_{tr}H}{T_{tr}} (J \cdot mol^{-1} \cdot K^{-1})$$

The peaks absence from the DSC curve obtained at cooling of the substituted compound, but, at the same time, the presence of TM transition can be explained by small structural modifications that cannot be detected by the DSC

technique. The obtained results from heating and cooling DSC curves, in the same conditions, are presented in Table 2.

The obtained TM results are presented in Table 3.

Table 2

DSC study

Compound	Heating			Cooling		
	$T_{tr}$ ( $^{\circ}C$ )	$\Delta_{tr}H$ ( $kJ \cdot mol^{-1}$ )	$\Delta_{tr}S$ ( $J \cdot mol^{-1} \cdot K^{-1}$ )	$T_{tr}$ ( $^{\circ}C$ )	$\Delta_{tr}H$ ( $kJ \cdot mol^{-1}$ )	$\Delta_{tr}H$ ( $J \cdot mol^{-1} \cdot K^{-1}$ )
sitosteryl benzoate	142.00	16.01	38.7	101.00	8.49	22.66
sitosteryl <i>para</i> -cianobenzoate	163.90	13.18	30.16			
	196.50	0.13	0.28			
	242.90	0.36	0.7			

Table 3

Thermomicroscopic study

sitosteryl benzoate	sitosteryl <i>para</i> -cianobenzoate
<ul style="list-style-type: none"> <li>▪ blade white crystals</li> <li>▪ 143 <math>^{\circ}C</math> – liquid</li> <li>▪ 96 <math>^{\circ}C</math></li> <li>– plane texture with aspect of dark and light strips oriented in the same direction</li> <li>– dispersion color change from blue to red, change characteristic to the cholesteric phase</li> </ul>	<ul style="list-style-type: none"> <li>▪ parallelepipedic crystals shining like flake of snow</li> <li>▪ 164 <math>^{\circ}C</math> – smectic phase <math>S_A</math> with plane texture</li> <li>▪ 195 <math>^{\circ}C</math></li> <li>– cholesteric phase stable under 242 <math>^{\circ}C</math> (Fig. 2)</li> <li>– dispersion color change from blue to red, change characteristic to the cholesteric phase</li> <li>▪ 55 <math>^{\circ}C</math> – mosaic texture characteristic to the smectic phase <math>S_B</math> (Fig. 3)</li> </ul>

From the data presented in Tables 2 and 3 one can observe that sitosteryl benzoate presents a polymorphism in which the cholesteric phase is monotropic.

The data obtained for sitosteryl *para*-cianobenzoate show that at cooling, 55  $^{\circ}C$ -242  $^{\circ}C$  temperature range, two transitions appear:  $I \rightarrow Ch$

and  $Ch \rightarrow S_B$ . This fact is sustained also by the change of the dispersion color at cooling (242  $^{\circ}C$  – 195  $^{\circ}C$ ) from blue to red, change which is characteristic to the cholesteric phase.

The *p*-substituted compound presents enantiotropic polymorphism in both cholesteric and smectic phases.

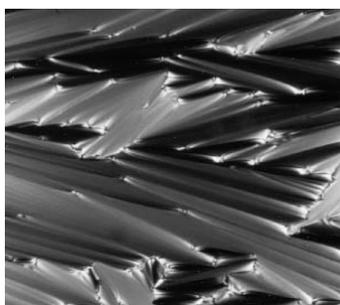
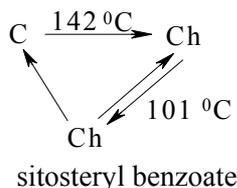


Fig. 2 – Plane texture characteristic for  $S_A$ .



Fig. 3 – Mosaic texture characteristic for  $S_B$ .

The polymorphism of these two compounds can



### EXPERIMENTAL PART

The thermal properties were determined with a Perkin-Elmer DSC 2 calorimeter under argon purge. The temperature was calibrated with the melting point of indium standard. The weights of the samples lay in the range 1-2 mg. The temperatures of the phase transitions could be reproduced with an accuracy of  $\pm 1$  K. Typical heating and cooling rates of 10 K/min were used.

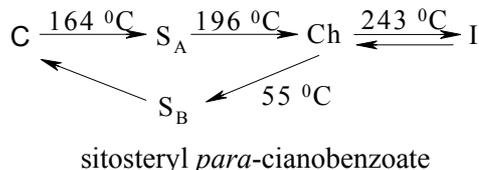
The texture of the mesophases was determined on a Boëtius hot stage apparatus.

### CONCLUSIONS

The liquid crystal phase is formed from solids in which the long axis of the molecules from the crystalline lattice is parallel. The increasing of temperature diminishes the intermolecular forces existing in the solid phase. So, the stratified lattice can form, first, a smectic phase (the layers are kept but they can drift one above the others) and then with temperature increasing the lattice will change into a cholesteric phase and after that into an isotropic liquid.

Considering the non-substituted compound as standard, one can say that the *p*-substituted compound is more rigid due to the inductive and electromeric effects, which leads to an increase of its thermal stability.

be represented by the following schemes:



The studied compounds have cholesteric properties and the mesophases are accompanied by light reflection in the visible spectrum. At the same time a change of the dispersion color from red to blue-violet is observed. This occurrence is reversible at cooling.

The transition between the smectic and cholesteric phases is characterized by small energy because it is a transition between two phases of the liquid crystal state, which means that the structural modifications are small.

### REFERENCES

1. H. Sackmann and D. Demus, *Mol. Cryst. Liquid Cryst.*, **1973**, *21*, 239.
2. S. Diele, D. Brand and H. Sackmann, *Mol. Cryst. Liquid Cryst.*, **1972**, *16*, 105.
3. A. Devries, *Mol. Cryst. Liquid Cryst.*, **1973**, *24*, 337.
4. T. Z. Risv, G. A. Adil, H.Y. Gondal and H. Sherazi, *Sci. Int. (Lahore)*, **1997**, *9*, 31.
5. S. L. Srivastava, D. Ravindra and M. Arunima, *Mol. Cryst. Liquid Cryst.*, **1996**, *297*, 139.
6. I. Baci, R. Vilcu, C. Drăghici, G. Bairaktaris and C. Sfredan, *Rev. Chim. (Bucharest)*, **2000**, *51*, 216-220.
7. V. Meltzer, I. Baci, C. Topală and E. Pincu, *Rev. Roum. Chim.*, **2001**, *46*, 1281-1284.
8. C. Topală, V. Meltzer and C. Drăghici, *Rev. Roum. Chim.*, **2005**, *50*, 125-129.