CHARACTERIZATION OF LIQUID CRYSTALLINE SITOSTEROL AND STIGMASTEROL DERIVATIVES

I. Baciu*, Viorica Meltzer, C. Topală and Elena Pincu

In order to develop liquid crystal technology and its applications sitosterol and stigmasterol esters have been synthesized and their mesomorphic phases and other physical properties have been studied. Cholesteric and smectic phases were observed in all sitosteryl and stigmasteryl derivatives. Textures of the "Blue Phase" was observed in three stigmasteryl derivatives: stigmasteryl-5-nitrobenzo[b]tiophen-2-carboxilate, 3-chlorobenzo[b]tiophen-2-carboxylate and 3,4-dichlorophenyl-stigmasteryl carbamate.

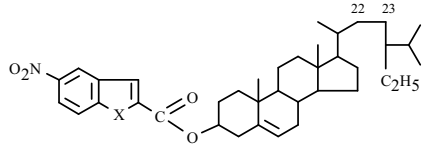
Introduction

Cholesteric liquid crystals have established application in many advanced technologies like liquid crystal displays, optical filters, imaging systems, radiatuin visualization, optical storage systems, temperature sensors and medical thermography. Keeping in view the importance of liquid crystal technology in future optical based technologies; a systematic effort is being carried out at our laboratories to develop organic liquid crystals.

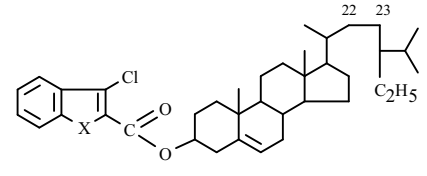
Many cholesteric and smectic materials have been synthesized and characterized which include varios 3β substituted sterol esters, Schiff bases [1-3].

Here we present our study of eight stigmasterol and sitosterol esters.

Table 1. The stigmasterol and sitosterol compound I – VIII used in the present paper.

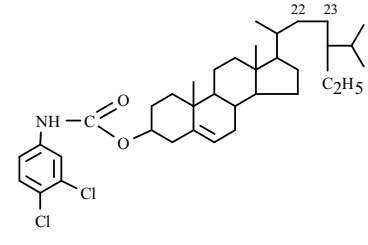


I X = S **II** X = S , $C_{22} – C_{23}$ – double bond



V X = S **VI** X = SO_2 , $C_{22} – C_{23}$ – double bond

III X = SO_2 **IV** X = SO_2 , $C_{22} – C_{23}$ – double bond



VII X = SO_2 **VIII** X = SO_2 , $C_{22} – C_{23}$ – double bond

* Faculty of Chemistry, Department of Organic Chemistry, University of Bucharest, 90-94 Şos. Panduri, Bucharest, Romania

Experimental

Synthesis

Sitosteryl and stigmasteryl esters, I – IV, were prepared by reaction of 5-nitrobenzo[b]-tiophen-2-carboxylic acid and its sulphone eith sitosterol and stigmasterol. Compound V and VI prepared from 3/chlorobenzo[b]-tiophen-2-carboxylic acid with sitosterol and stigmasterol, and compounds VII, VIII prepared from 3,4-dichlorophenyl isocyanate with sitosterol and stigmasterol. Pure crystals of the desired stigmasteryl and sitosteryl esters were obtained after re-crystallization from amyl alcohol and a mixtured benzene and ethanol. Details of the synthesis and purification procedure can be seen in reference [4-6].

The synthesis and purity of the compounds synthesized were checked by IR and NMR spectra.

Phase Characterization

Phase characterization was carried out using a polarising microscope equipped with a hot stage. DSC curves were obtained with a Perkin-Elmer 2 calorimeter under argon purge. The temperature was calibrated with the melting point of indium standard. The temperature of the phase transition could be reproduced with the accuracy of ±1K. Distinct recognizable textures were observed for different molecular ordering in all the samples, which are discussed in following section.

Results and Discussion

The melting behaviour, determined from DSC and TM [7, 8], of all the compounds studied is summarized in Table 2.

Table 2. Phase transitions in Liquid Crystal Compounds.

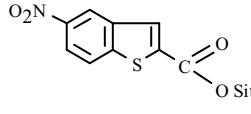
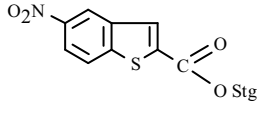
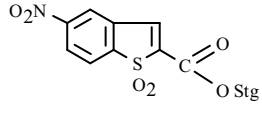
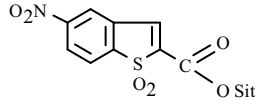
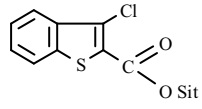
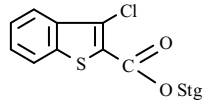
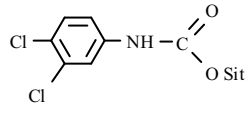
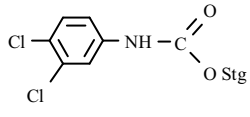
Symbol text	Compound	On Heating [°C]	On Cooling [°C]
I		229.87 C – Ch 258 Ch – I	210.89 Ch – S [7]
II		235.59 C – S_1 242.14 S_1 – Ch 260. 59 Ch – I	173.34 Ch – S_2 [8]
III		163 C – Ch 231 Ch – I	210 I – Ch 196 Ch – S 167 No change

Table 2. (*continued*)

Symbol text	Compound	On Heating [°C]	On Cooling [°C]
IV		171.90 C – Ch 175 Ch - I	146 I – Ch 110 Ch – S 70 No change
V		109.66 C – S_1 137.21 S_1 – S_2 150 S_2 – Ch 214 Ch - I	85.14 Ch – S_3 70 No change
VI		170 C – Ch 171.90 Ch - I	146 I – Ch [8] 110 Ch – S_1 37.02 S_1 – S_2
VII		128 C – Ch 145 Ch - I	No change [6]
VIII		170. 34 C – S_1 177.84 S_1 – Ch 187 Ch - I	No change [6]

I→ Isotropic phase; Ch → Cholesteric phase; S_1, S_2 → Smectic phase;
C → Crystalline phase; Stg – stigmasterol; Sit – sitosterol.

Nematic, chiral nematic and smectic liquid crystalline phases are known to have characteristic textures when observed under a polarization microscope (9a). The cholesteric phase was identified by the well-known focal conic texture and the planar texture [10].

The blue phase has been observed for three derivatives **II**, **VI** and **VIII** in a small temperature region, immediately below the clearing point. The name is derived from the occurrence of scattered blue light, which can be noticed more easily in reflection than in transmission. Because of its small range of existence, a structure determination seems to be somewhat difficult. The optical isotropy points to some kind of cubic lattice with a large elementary cell (9b).

The blue phase has been observed for three derivatives: **II**, **VI** and **VIII**, in a small temperature region, immediately below the clearing point. Plate 1 and 2 show this phenomenon. Under the microscope, the blue phase appears in the form of a platelet texture. These platelets exhibit colours between crossed polarizes, but also with only one polarizer or without polarizers at all. Accordingly, the colours of the platelets cannot be interpreted in terms of the usual interference coloure of thin layers, particularly if the fact is considered that the blue phase is optically isotropic [11].

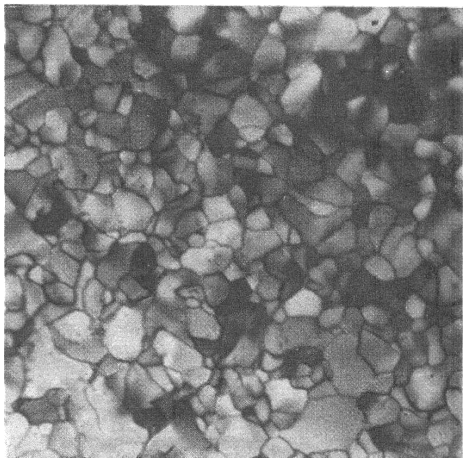


Fig. 1: *Blue phase, platelet texture obtained for* **II** *at* 242.14°C.

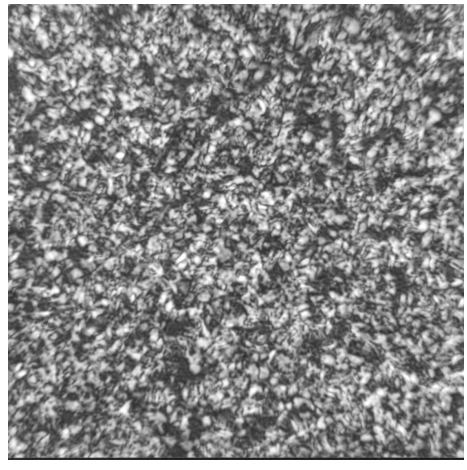


Fig. 2: *Polarized optical micrographs of* **VI**, *on cooling at* 37.02°C.

These TM observations were completed by DSC curves, presented in Fig. 3, in which near the maximum of isotropic phase appear a new maximum for blue phase.

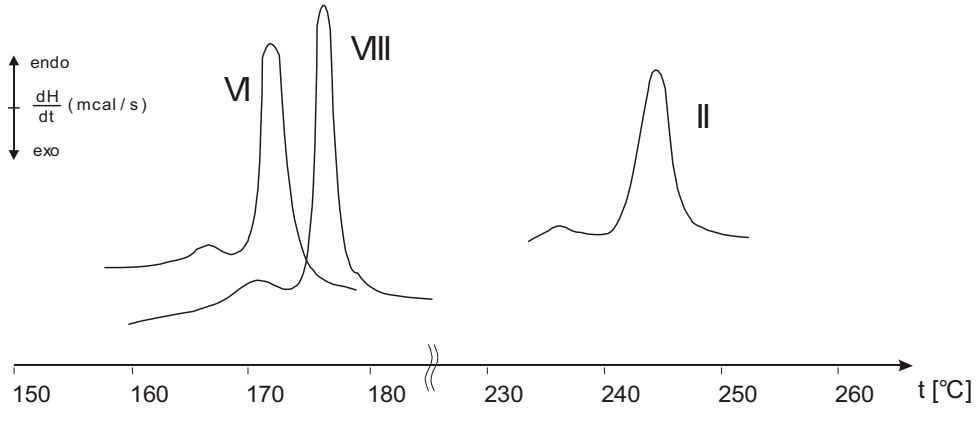


Fig. 3: *DSC curves on heating for compounds* **II**, **VI** *and* **VIII.**

Conclusions

The results presented in this paper prove that simultaneous thermomicroscopy / DSC is very useful for studied phase characterization.

The blue phase of some stigmasteryl derivatives confirm that these mesophase exists within a small temperature range between the ordinary cholesteric phase and the isotropic phase [12, 13].

REFERENCES

1. I. Baciu, C. Drăghici, C. Cîrlănaru, N. Arsenescu, *Rev. Roum. Chim.*, **2000**, *45*, 525-529
2. I. Baciu, C. Topală, C. Drăghici, *Rev. Chim.* (Bucureşti), **2001**, *52*, 110-113
3. V. Meltzer, C. Topală, I. Baciu, E. Pincu, *Rev. Roum. Chim.*, in press
4. I. Baciu, R. Vîlcu, C. Drăghici, G. Bairaktaris, *Rev. Chim.* (Bucureşti), **2000**, *12*, 216-218
5. I. Baciu, C. Topală, C. Sferdean, C. Drăghici, M. Căproiu, *Rev. Chim.* (Bucureşti), **2001**, *52*, 14-17
6. C. Topală, V. Meltzer, E. Pincu, C. Drăghici, M. Maganu, *Rev. Chim.* (Bucureşti), **2001**, *52*, 349-352
7. R. Vîlcu, V. Meltzer, I. Baciu, G. Bairaktaris, *Rev. Chim.* (Bucureşti), **2000**, *51*, 441
8. V. Meltzer, I. Baciu, C. Topală, E. Pincu, *Rev. Roum. Chim.*, in press
9. D. Demus, L. Richter, "Textures of Liquid Crystals, Sec. Ed., VEB Deutscher Verlag f ür Grundstoffinderstrie, Leipzig, **1979**, [a]page 61-94; [b]page 25
10. W. Elser, R. D. Ennulat, "Selective Reflection of Cholesteric Liquid Crystals" in "Advances in Liquid Crystals", Ed. G. H. Brown, Academic Press, **1975**, 73-172
11. G. Pelzl, H. Sackmann, *Z. Physik. Chem*., **1973**, 254, 354
12. D. Coates, G. W. Gray, *Physic. Letters*, **1975**, *51A*, 335
13. D. Demus, H. G. Hahn, F. Kuschel, *Mol. Cryst. Liquid Cryst.*, **1978**, 44, 61