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Original scientific paper

## New cholesteryl-containing bent core liquid crystals

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**Abstract:** The paper presents the synthesis and mesomorphic behavior of two new series of bent core liquid crystalline compounds based on a 1,3-dihydroxybenzene core and containing a cholesteryl 6-oxyhexanoate wing. The two series were obtained by esterification of the cholesteryl 6-(3-hydroxyphenoxy)hexanoate core with some 4-{{[4-(*n*-alkyloxy)phenyl]azo}benzoic acids (*n*-alkyl = *n*-hexyl – *n*-dodecyl) or 4-{{[4-(*n*-alkyloxy)benzoyl]oxy}benzoic acids (*n*-alkyl = *n*-hexyl – *n*-decyl). The esterification reactions were performed *via* the corresponding acyl chlorides or with the dicyclohexylcarbodiimide/4-(*N,N*-dimethylamino)pyridine (DCC/DMAP) system. All the synthesized compounds evidenced enantiotropic liquid crystalline properties with smectic type textures when investigated by differential scanning calorimetry and polarized optical microscopy. Isotropization and isotropic to liquid crystal transitions occurred at relatively low temperatures (between 89 and 146 °C). The compounds containing the azo-aromatic linking group presented the largest range of stability of the mesophases (between 42 and 87 °C). All the investigated compounds were thermally stable in the range of the existence of mesophases.

**Keywords:** liquid crystals; banana shaped; cholesterol; resorcinol.

### INTRODUCTION

Liquid crystals have been intensively investigated for the last six decades, resulting in the discovery of many applications in modern technologies. Cholesteric liquid crystals (CLCs) are compounds with liquid crystalline properties that contain at least one chiral carbon atom in their molecule. They are so-called because such properties were first observed in cholesteric esters.<sup>1</sup>

Due to their unique optical properties, such as selective reflection of circular polarized light, high optical rotatory power and circular dichroism, CLCs have attracted the attention of chemists and physicists.<sup>2,3</sup>

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Liquid crystalline compounds containing two identical or non-identical mesogens united through a flexible spacer of varying length and parity are among the large variety of non-conventional liquid crystals reported to date.<sup>4</sup> Since the discovery of cholesteryl benzoate, the first liquid crystal,<sup>5</sup> more than 3300 monomers, oligomers and polymers with cholesterol have been synthesized and characterized.<sup>6</sup>

Chiral dimesogenic compounds consisting of two different mesogenic units with at least one containing a cholesteryl unit interlinked through a spacer are a relatively new class of liquid crystalline compounds that still require more research in order to establish the relationship between their structure and their liquid crystalline properties.<sup>7</sup> Unsymmetric dimesogenic compounds containing a cholesteryl ester moiety and azobenzene mesogenic groups may be suitable for use in liquid crystalline displays and optical–electric functional devices.<sup>8,9</sup> Molecules containing azo groups show reversible *trans/cis* isomerization upon UV–Vis irradiation.<sup>10,11</sup> Tamaoki and Mallia reported the synthesis of dimesogenic compounds containing the cholesteryl-azobenzene moiety linked by a flexible alkyl chain of 6 to 14 carbon atoms in length, the majority of these compounds exhibited only the cholesteric mesophase.<sup>12</sup>

Very characteristic for liquid crystals with strong chiral pro-mesogenic units (as in the case of cholesterol with 8 chiral centers) are the blue phases (BP I, BP II, BP III). They appear between the isotropic and chiral nematic or smectic textures, within a narrow temperature range<sup>13,14</sup> and the twist grain boundary phase (TGBA, TGBC, TGBC<sup>\*</sup>), observed at the phase transition from isotropic liquid or chiral nematic to the smectic A or chiral smectic C phases.<sup>13</sup>

TGB and BP phases are examples of frustrated mesophases and derive from an antagonistic situation when the molecules are trying to form a helical structure with the chiral nematic helix axis perpendicular on the long axes of the molecules simultaneously with their tendency to form a lamellar structure.<sup>15</sup> The discovery of these types of new mesophases raises up the interest for future practical applications of liquid crystals containing chiral groups in their molecules.<sup>16</sup>

The new field of bent core liquid crystals has also tried to exploit the properties that may be induced by the presence of a cholesteric moiety. Generally, the synthesized structures are quite complex, two typical rigid mesogenic groups being attached to the core molecule while the cholesteryl part acts more as a terminal chain.<sup>6</sup>

In order to develop the class of cholesterol-containing bent core liquid crystals, this paper presents the synthesis, structural characterization and mesomorphic properties of two new series of chiral liquid crystals based on a resorcinol core. In order to obtain as simple as possible bent core liquid crystalline compounds containing cholesteric units, the synthesized compounds possess only one typical mesogenic wing, formed by two aromatic rings, connected *via* ester or

azo linking groups, and containing alkyloxy terminal flexible chains. The other arm is formed by a cholesteryl unit linked by a pentamethylen flexible spacer to the core molecule.

## EXPERIMENTAL

### *Materials, instruments and methods*

All reagents and solvents were purchased from Aldrich or Merck and were used without further purification unless otherwise noted. Cholesteryl 6-bromohexanoate was synthesized accordingly to a literature procedure.<sup>17</sup> The 4-[[4-(alkyloxy)phenyl]azo]benzoic acids<sup>18</sup> and the 4-[4-(alkyloxy)benzoyloxy]benzoic acids<sup>19</sup> were obtained by adapting literature data. All reactions involving dicyclohexylcarbodiimide (DCC) and 4-(*N,N*-dimethylamino)pyridine (DMAP) were performed in anhydrous dichloromethane, under a dry nitrogen atmosphere. Silica gel 60 (Merck) was used for column chromatography.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker® Avance DRX 400 MHz spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) as an internal standard. The infrared (IR) spectra were recorded using a Nicolet® Magna 550 FT-IR spectrometer (NaCl crystal window). The mass spectra were recorded on a quadrupole–time of flight mass spectrometer equipped with an electrospray ion source (Agilent® 6520 Accurate Mass Q-TOF LC/MS). The transition temperatures were determined using a Linkam heating stage and Linksys 32 temperature control unit in conjunction with an Axioscop 40 Zeiss polarizing optical microscope and Qimaging/Retiga-1000R camera for image capture. The transitions were confirmed by DSC analysis (Mettler Toledo DSC1). Heating and cooling cycles were run at rates of 10 °C min<sup>-1</sup> under a nitrogen atmosphere. The samples were measured in closed lid aluminum pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase standards.<sup>20</sup>

All the thermal gravimetric analyses were performed on 2.5–4.5 mg samples on a Mettler-Toledo® TGA SDTA851<sup>e</sup> instrument under a dynamic N<sub>2</sub> atmosphere, flow rate of 20 ml min<sup>-1</sup>, at a heating rate of 10 K min<sup>-1</sup> from 25 to 900 °C. In order to obtain comparable data, constant operational parameters were employed for all samples.

The melting points were recorded using a melting point meter Krüss Optotronic KSPI – N and are uncorrected.

### *Synthesis of cholesteryl 6-(3-hydroxyphenoxy)hexanoate (1)*

A mixture of resorcinol (0.91 g, 8.25 mmol) and K<sub>2</sub>CO<sub>3</sub> (4.55 g, 33 mmol) in 2-butanone (40 mL) was stirred at reflux temperature for 30 min and then cholesteryl 6-bromohexanoate (3.1 g, 5.5 mmol) dissolved in 2-butanone (10 mL) was added dropwise with a syringe. The reaction mixture was kept over night at reflux temperature, cooled down to room temperature, filtrated and concentrated under vacuum. Purification by column chromatography on silica gel using a mixture of hexane : ethyl acetate 3:1 as eluent afforded **1** as a pure substance. The physical and spectral data for **1** are given in the Supplementary material to this paper.

### *General method for the synthesis of compounds 4a–f*

Acyl chlorides **2a–f** were prepared from the corresponding acids by reaction with thionyl chloride and were used immediately for the synthesis of **4a–f**. A mixture of one equivalent of **1**, 1.08 equivalents of 4-[[4-(alkyloxy)phenyl]azo]benzoyl chloride **2** and tetrabutylammonium hydrogensulfate (TBAHS) in dichloromethane (40 mL) and 1.28 equivalents of potassium carbonate in water (10 mL) were vigorously stirred for 24 h at room temperature. The organic layer was separated, washed several times with distilled water, dried over anhydrous

magnesium sulfate and concentrated on a rotary evaporator. Compounds **4a–f** were purified by column chromatography on silica gel using a mixture of dichloromethane : ethyl acetate 20:1 as eluent.

*3-[[6-(cholesteryloxy)-6-oxohexyl]oxy]phenyl 4-[[4-(hexyloxy)phenyl]azo]benzoate (4a)*

Quantities: compound **1** (0.21 g, 0.35 mmol), 4-[[4-(hexyloxy)phenyl]azo]benzoyl chloride (0.130 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), and K<sub>2</sub>CO<sub>3</sub> (0.48 g, 0.45 mmol) in water (10 mL).

*3-[[6-(cholesteryloxy)-6-oxohexyl]oxy]phenyl 4-[[4-(heptyloxy)phenyl]azo]benzoate (4b)*

Quantities: compound **1** (0.21 g, 0.35 mmol), 4-[[4-(heptyloxy)phenyl]azo]benzoyl chloride (0.135 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), and K<sub>2</sub>CO<sub>3</sub> (0.48 g, 0.45 mmol) in water (10 mL),

*3-[[6-(cholesteryloxy)-6-oxohexyl]oxy]phenyl 4-[[4-(octyloxy)phenyl]azo]benzoate (4c)*

Quantities: compound **1** (0.21 g, 0.35 mmol), 4-[[4-(octyloxy)phenyl]azo]benzoyl chloride (0.141 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), and K<sub>2</sub>CO<sub>3</sub> (0.48 g, 0.45 mmol) in water (10 mL).

*3-[[6-(cholesteryloxy)-6-oxohexyl]oxy]phenyl 4-[[4-(nonyloxy)phenyl]azo]benzoate (4d)*

Quantities: compound **1** (0.21 g, 0.35 mmol), 4-[[4-(nonyloxy)phenyl]azo]benzoyl chloride (0.146 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), and K<sub>2</sub>CO<sub>3</sub> (0.48 g, 0.45 mmol) in water (10 mL).

*3-[[6-(cholesteryloxy)-6-oxohexyl]oxy]phenyl 4-[[4-(decyloxy)phenyl]azo]benzoate (4e)*

Quantities: compound **1** (0.21 g, 0.35 mmol), 4-[[4-(decyloxy)phenyl]azo]benzoyl chloride (0.151 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), and K<sub>2</sub>CO<sub>3</sub> (0.48 g, 0.45 mmol) in water (10 mL).

*3-[[6-(cholesteryloxy)-6-oxohexyl]oxy]phenyl 4-[[4-(dodecyloxy)phenyl]azo]benzoate (4f)*

Quantities: compound **1** (0.21 g, 0.35 mmol), 4-[[4-(dodecyloxy)phenyl]azo]benzoyl chloride (0.162 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL) and K<sub>2</sub>CO<sub>3</sub> (0.48 g, 0.45 mmol) in water (10 mL). The physical and spectral data for **4a–f** are given in the Supplementary material to this paper.

*General method for the synthesis of compounds 5a–e*

A mixture of 1 equivalent of **1**, 1.1 equivalents of 4-[[4-(alkyloxy)benzoyl]oxy]benzoic acid and 0.2 equivalents of DMAP dissolved in dry dichloromethane was stirred for a 15–20 min at room temperature, cooled to 0 °C on an ice bath and then 1.2 equivalents of DCC dissolved in dry dichloromethane were added dropwise. After 30 min, the ice bath was removed and the reaction mixture was stirred for 48 h at room temperature after which the precipitated *N,N'*-dicyclohexylurea (DCU) was filtered off. The solvent was evaporated in vacuum and the solid residue was chromatographed on silica gel using a 3:1 mixture of hexane:ethyl acetate as eluent. White products were obtained.

*4-[[3-((6-(cholesteryloxy)-6-oxohexyl)oxy)phenoxy]carbonyl]phenyl 4-(hexyloxy)benzoate (5a)*

Quantities: compound **1** (0.20 g, 0.35 mmol), 4-[[4-(hexyloxy)benzoyl]oxy]benzoic acid (0.134 g, 0.39 mmol), DCC (0.087 g, 0.42 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40 mL).

*4-[[3-((6-(cholesteryloxy)-6-oxohexyl)oxy)phenoxy]carbonyl]phenyl 4-(heptyloxy)benzoate (5b)*

Quantities: compound **1** (0.20 g, 0.35 mmol), 4-[[4-(heptyloxy)benzoyl]oxy]benzoic acid (0.140 g, 0.39 mmol), DCC (0.085 g; 0.41 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40 mL).

*4-[[3-((6-(cholesteryloxy)-6-oxohexyl)oxy)phenoxy]carbonyl]phenyl 4-(octyloxy)benzoate (5c)*

Quantities: compound **1** (0.20 g, 0.35 mmol), 4-[[4-(octyloxy)benzoyl]oxy]benzoic acid (0.145 g, 0.39 mmol), DCC (0.085 g, 0.41 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40 mL).

*4-[[3-((6-(cholesteryloxy)-6-oxohexyl)oxy)phenoxy]carbonyl]phenyl 4-(nonyloxy)benzoate (5d)*

Quantities: compound **1** (0.20 g, 0.35 mmol), 4-[[4-(nonyloxy)benzoyl]oxy]benzoic acid (0.150 g, 0.39 mmol), DCC (0.085 g, 0.41 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40 mL).

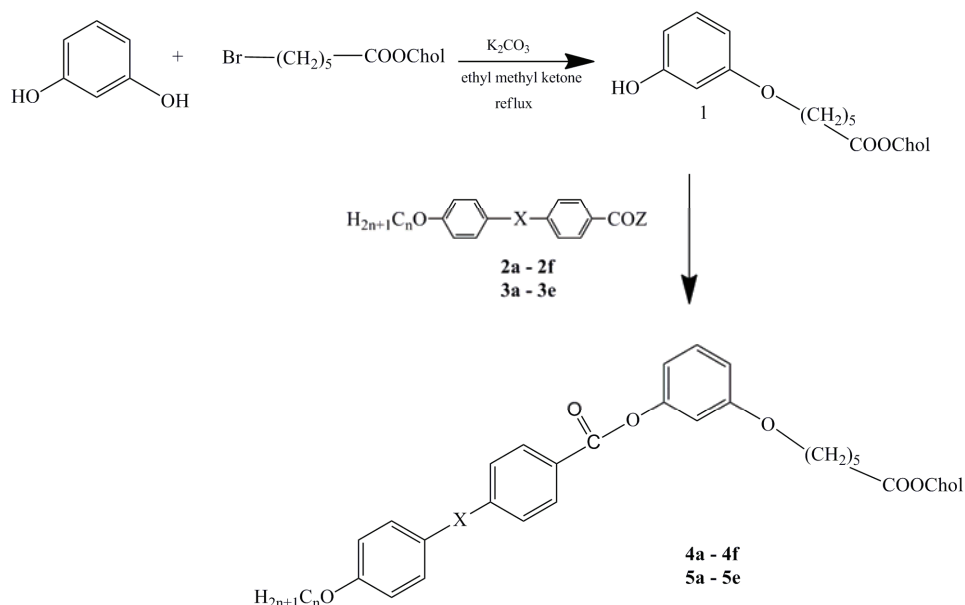
*4-[[3-((6-(cholesteryloxy)-6-oxohexyl)oxy)phenoxy]carbonyl]phenyl 4-(decyloxy)benzoate (5e)*

Quantities: compound **1** (0.20 g, 0.35 mmol), 4-[[4-(decyloxy)benzoyl]oxy]benzoic acid (0.155 g, 0.39 mmol), DCC (0.085 g, 0.41 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40 mL).

## RESULTS AND DISCUSSION

A two-step reaction was necessary to obtain the desired compounds (Scheme 1). In the first step, cholesteryl 6-(3-hydroxyphenoxy)hexanoate (**1**) was obtained by refluxing cholesteryl 6-bromohexanoate and resorcinol (in a 1:1.5 molar ratio) in 2-butanone, in the presence of potassium carbonate.<sup>17</sup> In the second step, the free phenolic group of **1** was esterified with two series of mesogenic acids containing two aromatic rings, connected *via* an azo or an ester linking group and containing alkyloxy ending chains. For the esterification reactions, two methods were used. In the case of the **4a-f** series, poor results were obtained when the more convenient DCC/DMAP system was used. In this case, the esterification reactions were realized with the corresponding acid chlorides in aqueous K<sub>2</sub>CO<sub>3</sub>/dichloromethane at room temperature for 24 h, using tetrabutylammonium hydrogen sulfate (TBAHS) as a phase transfer catalyst.<sup>21</sup> In the case of **5a-e** series, the esterification was performed with DCC and DMAP in dry dichloromethane at room temperature for 48 h.<sup>19</sup> All the obtained compounds were purified by column chromatography using dichloromethane:ethyl acetate (20:1) or hexane:ethyl acetate (3:1) as eluents. The yields were similar for both series (around 50 %). The structure and purity of the obtained final compounds were checked and confirmed by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, FT-IR and mass spectrometry (data given in the Supplementary material to this paper).

Taking into consideration the importance of thermal stability for the whole interval of the existence of the mesophase, thermogravimetric studies were performed for both the **4a-f** and **5a-e** series. Thermogravimetric data evidenced very good thermal stability for all the compounds, the  $T_{\text{onset}}$  values (temperatures at which the degradation processes begin) being more than 150 °C higher than the isotropization values ( $T_{\text{onset}}$  values in Tables I and II). These values are comparable with those other classes of bent core compounds containing azo or ester linking groups.<sup>18,22</sup>



Scheme 1. Synthesis of the cholesteric liquid crystals; **2a-f**, X = -N=N-, Z = -Cl,  $n = 6-10$ , 12, aq.  $\text{K}_2\text{CO}_3$ , TBAHS, 24 h; **3a-e**, X = -COO-, Z = -OH,  $n = 6-10$ , DCC, DMAP,  $\text{CH}_2\text{Cl}_2$ , 48 h; **4a-f**, X = -N=N-,  $n = 6-10$ , 12; **5a-e**, X = -COO-,  $n = 6-10$ ; Chol = cholesteryl.

TABLE I. Transition temperatures ( $^{\circ}\text{C}$ ), and associated transition enthalpies ( $\text{J g}^{-1}$ ) for compounds **4a-f**; abbreviations: Cr, crystalline; LC, liquid crystal; I, isotropic;  $t_{\text{onset}}$ : the initial temperature at which the degradations processes begin

Cmpd.	$T / ^{\circ}\text{C} [\Delta H / \text{J g}^{-1}]$						$t_{\text{onset}} / ^{\circ}\text{C}$
	Heating			Cooling			
	Cr/LC	LC/I	Mesophase interval, $^{\circ}\text{C}$	I/LC	LC/Cr	Mesophase interval, $^{\circ}\text{C}$	
<b>4a</b>	59 [-24.94]	146 [-2.45]	87	131 [1.57]	-	-	327
<b>4b</b>	83 [-25.66]	142 [-1.89]	59	118 [3.21]	-	-	326
<b>4c</b>	77 [-22.66]	133 [-6.28]	56	130 [5.28]	-	-	329
<b>4d</b>	78 [-35.58]	133 [-3.66]	55	125 [4.02]	8 [1.26]	117	318
<b>4e</b>	80 [-36.05]	122 [-2.55]	42	115 [2.37]	34 [19.38]	71	326
<b>4f</b>	82 [-39.45]	97 [-1.12]	15	89 [0.55]	43 [15.08]	46	329

The phase transition temperatures and the associated enthalpies for **4a-f** are presented in Table I. During the DSC investigations, compounds **4a-f** showed

TABLE II. Transition temperatures (°C), and associated transition enthalpies (J g<sup>-1</sup>) for compounds **5a–e**: abbreviations: Cr, crystalline; LC, liquid crystal; I, isotropic; *t*<sub>onset</sub>, the initial temperature at which the degradations processes begin

Cmpd.	T / °C [ $\Delta H$ / J g <sup>-1</sup> ]														<i>t</i> <sub>onset</sub> °C
	Heating							Cooling							
	Cr <sub>1</sub> /Cr <sub>2</sub>	Cr <sub>2</sub> /Cr <sub>3</sub>	Cr <sub>3</sub> /Cr <sub>1</sub>	LC <sub>1</sub> /LC <sub>2</sub>	LC <sub>2</sub> /I	Mesophase interval, °C	I/LC <sub>1</sub>	LC <sub>1</sub> /LC <sub>2</sub>	LC <sub>2</sub> /LC <sub>3</sub>	LC <sub>3</sub> /Cr	Mesophase interval, °C				
<b>5a</b>	33 [-21.5]	52 [-8.11]	91 [-37.24]	109 [-1.08]	115 [-0.27]	24	114 [0.49]	107 [1.75]	91 [0.19]	-	328				
<b>5b</b>	50 [-24.0]	70 [-18.97]	87 [-0.11]	102 [-1.19]	109 [-0.41]	22	108 [0.74]	100 [1.15]	86 [0.18]	-	338				
<b>5c</b>	-	78 [-27.56]	91 [-0.13]	102 [-1.38]	110 [-0.55]	19	109 [0.75]	100 [1.23]	90 [0.16]	-	342				
<b>5d</b>	20 [-0.08]	41 [-0.12]	90 [-0.17]	99 [-1.17]	107 [-0.72]	17	106 [0.86]	97 [1.08]	90 [0.11]	18 [0.10]	330				
<b>5e</b>	24 [-0.10]	45 [-0.24]	80 [-1.28]	85 [-0.97]	100 [-0.54]	20	99 [0.85]	78 [0.92]	41 [0.32]	22 [0.15]	328				



only two transitions on both the heating and cooling cycles. For the first three compounds of this series, the crystallization temperature could not be determined either by DSC or polarized optical microscopy (POM) observations because the crystallization occurred very slowly. Generally, because of their high viscosity, all these samples crystallized very slowly at much lower temperatures than the Cr/Lc temperature transitions.

With the exception of compound **4f**, the stability range of the mesophases, on heating, is reasonably large in the case of the series of compounds **4a–f** (between 42 and 87 °C).

The DSC curves of compound **4e** (first heating and first cooling) are illustrated in Fig. 1, as examples. The POM investigations evidenced only the presence of smectic type mesophases. No typical cholesteric oily streaks textures could be observed.

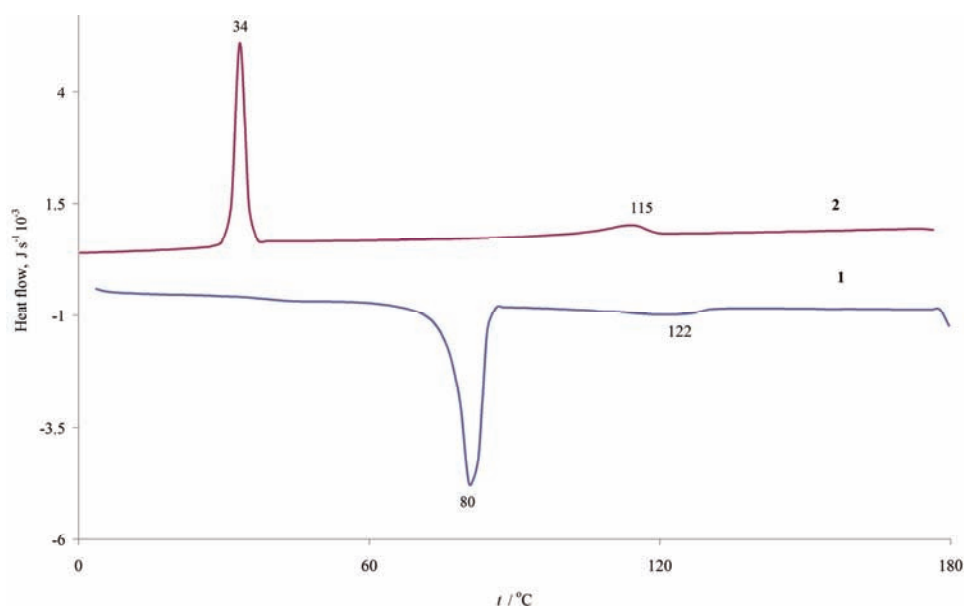


Fig. 1. DSC curves for compound **4e**: 1 – first heating, 2 – first cooling.

In the case of compound **4e**, polarized optical microscopy evidenced a smecticX texture between 80–122 °C during the heating process, (Figs. 2a and 2d). On cooling, smectic textures appeared again between 115–35 °C, (Figs. 2b and 2c).

The compounds of the **5a–e** series, obtained by esterification of cholesteryl 6-(3-hydroxyphenoxy)hexanoate with 4-[[4-(alkyloxy)benzoyl]oxy]benzoic acids presented enantiotropic behaviors with the existence of a stability range of mesophases of around 20 °C on heating (Table II). Compounds **5a–e** presented a rich polymorphism on heating with several crystalline/crystalline or liquid crystal/li-



liquid crystal transitions. On cooling, only two liquid crystal/liquid crystal transitions could be seen for all compounds **5a–e** (Table II). As was the case for compounds **4a–f**, no typical cholesteric textures could be observed.

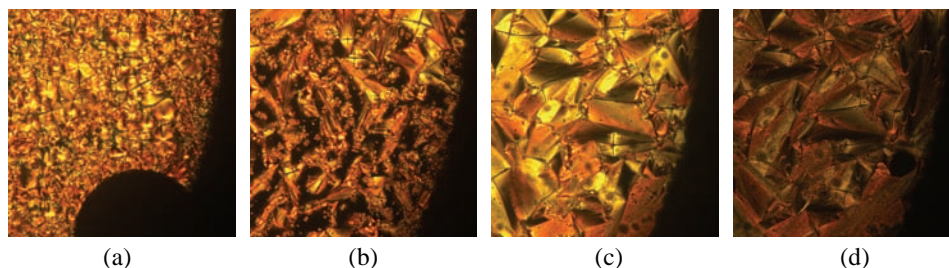


Fig. 2. Microphotographs of the mesophase textures observed for compound **4e**: a) first heating, 104 °C, b) first cooling, 111 °C, c) first cooling, 42 °C, d) second heating, 105 °C.

For the first three compounds of the series, no crystallization temperatures could be observed on the DSC curves on cooling, probably for similar reasons as was the case for compounds **4a–c**.

The DSC thermogram of compound **5e**, as a typical example for all the compounds of series **5a–e**, is presented in Fig. 3. On the second heating curve, the peaks at 24 and 45 °C corresponded to crystalline/crystalline transitions, while the peaks at 80, 82 and 100 °C corresponded to different smectic liquid crystalline transitions. On cooling, similar transitions at very similar temperatures could be observed on the DSC curves.

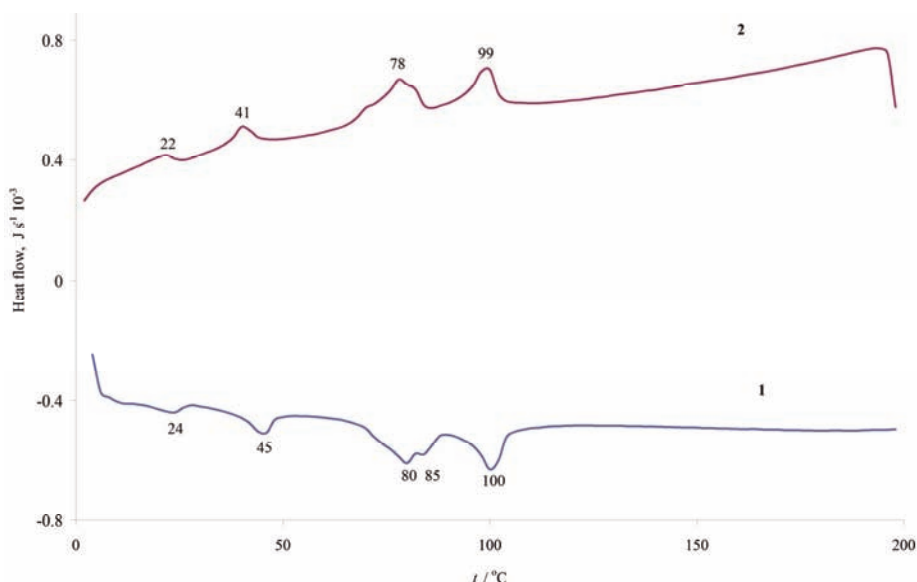


Fig. 3. DSC curves for compound **5e**: 1 – first heating, 2 – first cooling.

Some microphotographs taken during the POM investigations for compound **5e** are presented in Fig. 4.

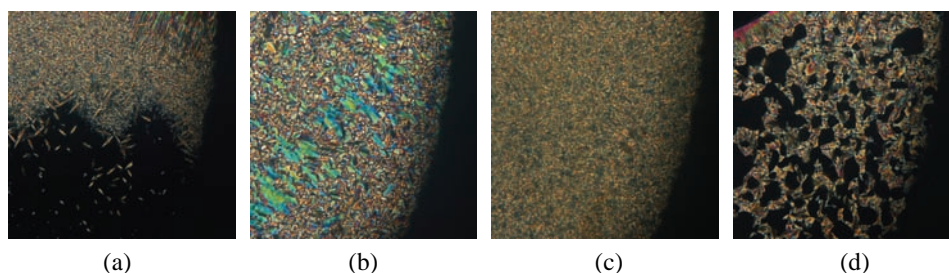


Fig. 4. Microphotographs of the textures observed for compound **5e**: a) first cooling, 60 °C, b) first cooling, 27 °C, c) second heating, 84 °C, d) second heating, 98 °C.

On both the heating and cooling cycles, smectic type textures were evidenced (Fig. 4). On the first cooling, the smectic type textures appeared at around 100 °C and remained until crystallization (Figs. 4a and 4b) and on the second heating again the same type of mesophases was seen (Figs. 4c and 4d).

#### CONCLUSIONS

Two new series of bent core liquid crystals based on a resorcinol core and containing a cholesteryl moiety connected to the core *via* a pentamethylen flexible spacer have been synthesized and characterized. The second arm consists of two aromatic rings connected *via* azo or ester groups and containing an alkyl-oxy terminal chain.

The liquid crystalline properties were investigated by polarized optical microscopy in association with differential scanning calorimetry. All the synthesized compounds presented enantiotropic liquid crystalline properties, with smectic textures. For all synthesized compounds, due to the presence of the cholesteric moiety, both main liquid crystalline transitions (isotropization and isotropic to liquid crystal) are relatively low (between 89 and 146 °C). Due to the presence of the cholesteric moiety, some difficulties were encountered in evidencing the crystallization temperature on cooling, in both the POM and DSC experiments. The largest stability range of the mesophases was met in the case of the compounds **4a–f** (between 42 and 87 °C).

The  $t_{\text{onset}}$  values obtained from thermogravimetric studies evidenced a very good thermal stability for all compounds; the degradation processes beginning more than 150 °C higher than the isotropization temperatures.

#### SUPPLEMENTARY MATERIAL

Physical and spectral data for the prepared compounds are available electronically from <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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## ИЗВОД

## НОВИ ТЕЧНИ КРИСТАЛИ КОЈИ САДРЖЕ ХОЛЕСТЕРИЛ-ГРУПУ

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У овом раду приказана је синтеза и мезоморфно понашање две нове серије једињења течних кристала базираних на 1,3-дихидроксибензеновом језгру, која садрже холестерил 6-оксихексаноатно крило. Две серије су добијене естерификацијом холестерил-6-(3-хидроксифенокс)хексаноатног језгра са 4-[[4-(*n*-алкилокси)фенил]азо]бензојевим киселинама (*n*-алкил = *n*-хексил – *n*-додецил) или 4-[[4-(*n*-алкилокси)бензоил]окси]бензојевим киселинама (*n*-алкил = *n*-хексил – *n*-децил). Реакције естерификације су изведене преко одговарајућих ацил-хлорида или са DCC/DMAP системом. Све синтетисана једињења су показивала енантиотропне особине течних кристала, са текстурама смектитног типа, приликом испитивања диференцијалном сканирајућом калориметријом и поларизованом оптичком микроскопијом. Изотропизација и прелаз из изотропне фазе ка фази течних кристала су биле и на релативно ниским температурама (између 89 и 146 °C). Једињења која садрже азо-ароматичну везујућу групу показују највећи опсег стабилности мезофаза (између 42 и 87 °C). Сва испитивана једињења су термално стабилна у опсегу у којем постоје мезофазе.

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