Nonsymmetric Liquid Crystalline Cholesteric Dimers Derived from Resorcinol

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Two new series of cholesterol based dimers were designed and synthesized. The final compounds were obtained by a two steps reaction: first, mono esterification of a resorcinol unit with cholesteryl hydroxysuccinate and second, the remaining phenolic unit was linked with two mesogenic groups containing an acid function. The molecular structure was confirmed by ^{1}H-NMR, ^{13}C-NMR, mass spectrometry and FT-IR investigations. The liquid crystalline behaviour of the synthesized dimers was investigated by differential scanning calorimetry (DSC) coupled with polarizing optical microscopy (POM). All of the dimers showed liquid crystal properties with smectic textures and cholesteric & smectic mesophases, respectively.

Keywords: cholesterol, bent-core dimers, resorcinol

Liquid crystal (LC) phases are an intermediate state of matter located between the solid (crystalline) and liquid (isotropic) phases. The liquid crystalline compounds display a different, intermediate state, also referred to as the fourth state of matter, or the mesophase [1] and form an important class of phase change materials wherein the supramolecular organization is controlled by a variety of weak noncovalent forces [2]. Mesogenic dimers or twin mesogens, which consist of molecules containing two mesogenic units, are currently of great interest since they exhibit complex and novel phase behaviour not usually observed in conventional LC architectures [3-5]. Because are often met in nature, steroids, despite their light-sensitive nature, are used to generate chiral liquid crystals. Not surprisingly, they have been used in transforming macroscopic chirality and its associated effects on mesomorphism. In the last time periods cholesterol has been integrated in the architecture of molecules due to its commercial availability as an inexpensive natural product, rigid structure with eight chiral centers and ease with which the structure can be derivatized [6].

From the discovery of the first liquid crystal by Reinitzer in 1888, cholesteryl benzoate [7], more than 3300 monomers, oligomers and polymers with cholesterol have been synthetised and characterized for their properties [6]. Cholesterol molecule is known as a good mesogen since most of cholesterol esters exhibited liquid crystal phase and it has high optical activity to form helical mesomorphism [8]. Among these, the dimers are the most reported cases in literature. Characteristically for cholesterol dimers is the possibility to form uncommon incommensurate phases [9, 10] such as blue phases (BP) and twisted grain boundary phases (TGB) [11, 12]. There are three distinct BPs, blue phase I (BPI), blue phase II (BPII) and blue phase III (BPIII) appearing between the isotropic (I) phase and chiral nematic (N*) / smectic (Sm) phases, over a short temperature range only of a few degrees Celsius. From these, BPI and BPII have cubic symmetry while in the BPIII phase the orientational order of molecules is not periodic and the symmetry is the same as that of the isotropic phase. Likewise, three types of TGB phases, namely TGBA, TGBC and TGBC* are seen in chiral systems. The mesophase ordering occurs between isotropic liquid or chiral nematic and smectic A or chiral smectic C phases with the temperature interval being strongly dependent on the optical purity [6]. For these, the smectic textures of the blocks are of the orthogonal SmA, tilted SmC and helical SmC* variety respectively.

These types of mesophases are very interesting because they arise from antagonistic situations in which the molecules try to organize into a certain manner and can be used for electro-optical applications. Mallia and Tamaoki reported the photochemically driven phase transition in dimesogenic compounds consisting of azobenzene and cholesterol [13, 14].

In this paper two new series of nonsymetric dimesogenic compounds with resorcinol as central unit are reported. To promote the liquid crystalline behaviour, a cholesteric moiety has been incorporated into one of the wings, while on the other a calamitic mesogenic group has been connected. To understand the relation between the molecular structure-liquid crystalline properties, the nature of the connecting groups between aromatic rings of mesogens has been varied from azo to esteric, with the length of terminal tails. Differential scanning calorimetry (DSC) and polarizing optical microscopy (POM) have been applied to study the mesomorphic properties.

Experimental part

Materials

All reagents, solvents and starting materials were purchased from Aldrich and Merck and were used without further purification unless otherwise noted. Cholesteryl succinate was synthesized following a procedure described in the literature [15]. The two mesogenic groups were obtained by adapting literature data: (2a÷f) 4-(4-alkoxyphenylazo)-benzoic acids [19] and 4-(4-alkoxybenzoyloxy)-benzoic acids (3a÷e) [17]. All reactions involved DCC and DMAP were performed in anhydrous dichloromethane, under a dry atmosphere of nitrogen. Silicagel 60 (Merck®) was used for column chromatography.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker® Avance DRX 400 MHz spectrometer.

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Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) as internal standard. IR spectra were recorded using a Nicolet® Magna 550 FT-IR spectrometer (NaCl crystal window). 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). Optical textures were observed using an Axioscop 40 Zeiss polarizing optical microscope and Qimaging/Retiga-1000R camera for image capture in conjunction with Linkam heating stage and Linksys 32 temperature control unit. The transitions were confirmed by DSC analysis (Mettler Toledo DSC1). Heating and cooling cycles were run at rates of 10^0C/min under nitrogen atmosphere, with sample measured in closed lid aluminum pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase standards.

All the thermal analysis were performed on 2.5 - 4.5 mg samples on a Mettler-Toledo® TGA SDTA851e derivatograph in N_2 atmosphere, with a flow rate of 20 mL/min, with a heating rate of 10 K/min from 25 to 900°C. In order to obtain comparable data, constant operational parameters were kept for all samples.

Synthesis

3-hydroxyphenyl cholesteryl succinate (1)

A mixture of resorcinol (0.91 g, 8.25 mmol) cholesteryl succinate (3.1 g, 5.5 mmol) and DMAP (0.13 g, 1.1 mmol) were vigorously stirred at room temperature for 30 min in dry dichloromethane (30 mL). The reaction mixture was cooled at 0°C on an ice bath and DCC (1.25 g, 6 mmol) was added dropwise. After one hour the ice bath was removed and the mixture was kept for 48 h at room temperature and then the precipitated N,N'-dicyclohexylurea (DCCU) was filtered off. The solvent was evaporated in vacuum an. Compound 1 was purified by column chromatography on Silica Gel using a mixture of hexane : ethyl acetate 3:1 as eluent. White product. η= 64.24% (2.3 g), mp= 128°C; **^{1}H-NMR (400 MHz, CD_3COCD_3)** δ_H ppm 8.60 (s, 1H, -OH), 7.21 (m, 1H, aromatic), 6.73 (m, 1H, aromatic), 6.63 (m, 1H, aromatic), 6.60 (m,1H, aromatic), 5.40 (d, *J* = 3.8 Hz, 1H, cholesteric), 4.59 (m, 1H, cholesteric), 2.85 (t, *J* =6.6 Hz, 2H, -CH_2-), 2.70 (t, *J* =6.6 Hz , 2H, -CH_2-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.10 – 0.74 (complex signals, 30H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.74 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, CD_3COCD_3)** δ_C ppm 172.11, 171.48, 159.20, 153.02, 140.74, 130.64, 123.27, 113.62, 113.54, 110.00 (2C esteric, 2C cholesteric, 6C aromatic), 74.82, 57.64, 57.11, 51.10, 43.17, 40.68, 40.33, 38.94, 37.89, 37.43, 37.05, 36.70, 32.77, 32.68, 30.03, 29.01, 28.77, 28.56, 25.00, 24.63, 23.18, 22.93, 21.82, 19.74, 19.23, 12.32 (26C cholesteric and aliphatic carbon atoms).

General method for the synthesis of 4a÷4f compounds

Acyl chlorides were prepared and introduced immediately into synthesis. A mixture of 1 equiv. of 3-hydroxyphenyl cholesteryl succinate **(1)**, 1.1 equiv. of 4-(4-alkyloxyphenylazo)-benzoyl chloride (**2**), 1.28 equiv of potassium carbonate, tetrabutylammonium hydrogensulfate (TBAHS) in dichloromethane (40 mL) and water (10 mL) were vigorously stirred for 24 h at room temperature. The organic layer was separated, washed several times with distilled water, dried on anhydrous magnesium sulfate and concentrated on rotary evaporator. Compounds (4a÷4f) were purified by column chromatography on Silica Gel using a mixture of dichloromethane: ethyl acetate 20:1 as eluent. Orange products were obtained.

cholesteryl 3-(4-((4-(hexyloxy)phenyl)azo)benzoyloxy) phenyl succinate (4a)

Quantities: 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-hexyloxyphenylazo) benzoyl chloride (0.131 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), K_2CO_3 (0.48 g, 0.45 mmol) in water (10 mL), orange product, η = 55.88 % (0.171 g), liquid crystal: 105°C (K/LC), 155°C (LC/I), 137 °C (I/LC). **^{1}H NMR (400 MHz, $CDCl_3$) δ ppm** 8.31 (d, *J* = 8.5 Hz, 2H, aromatic), 8.02 – 7.90 (m, 4H, aromatic), 7.44 (m, 1H, aromatic), 7.16 (dd, J_1 = 8.0, J_2= 1.9 Hz, 1H, aromatic), 7.09 (m, 1H, aromatic), 7.06 (dd, J_1 = 8.5, J_2= 1.9 Hz, 1H, aromatic), 7.02 (d, *J* = 9.0 Hz, 2H, aromatic), 5.36 (d, *J* = 4.4 Hz, 1H, cholesteric), 4.66 (m, 1H, cholesteric), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.73 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.66 (complex signals, 54H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.66 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** ppm 171.35, 170.60, 164.25, 162.49, 155.85, 151.33, 151.25, 146.25, 139.47, 131.22, 130.11, 129.78, 125.31, 122.74, 122.53, 119.18, 119.06, 115.59, 114.81, 74.57 (3C esteric, 14C aromatic, 2C cholesteric), 74.57 (cholesteric), 68.44 (-OCH_2-), 56.64, 56.11, 49.96, 42.27, 39.69, 39.50, 38.06 (7C cholesteric), 36.91, 36.54, 36.16, 35.77, 31.86, 31.81, 31.55, 29.68, 29.44, 29.41, 29.12, 28.20, 27.99, 27.74, 25.67, 24.26, 23.82, 22.81, 22.58, 22.55, 20.99, 19.28, 18.69, 14.02, 11.83 (25C cholesteric and aliphatic carbon atoms). ***m/z (CHCl$_3$):*** 892.59 [M-1+Li]$^+$, **FT-IR (KBr, cm^{-1}):** 1757.15, 1737.86, 1728.22 (ν >C=O, ester)

cholesteryl 3-(4-((4-(heptyloxy)phenyl)azo) benzoyloxy)phenyl succinate (4b)

Quantities: 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-heptyloxyphenylazo) benzoyl chloride (0.136 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), K_2CO_3 (0.48 g, 0.45 mmol) in water (10 mL), orange product, η = 51.44 % (0.161 g), liquid crystal: 65 °C (K/K), 95 °C (K/LC), 104 °C (LC/LC), 147 °C (LC/I), 131 °C (I/LC), 63 °C (LC/K), 17 °C (K/K). **^{1}H-NMR (400 MHz, $CDCl_3$) δ** 8.31 (d, *J* = 8.5 Hz, 2H, aromatic), 8.02 – 7.90 (m, 4H, aromatic), 7.44 (m, 1H, aromatic), 7.16 (dd, J_1 = 8.0, J_2= 1.9 Hz, 1H, aromatic), 7.09 (m, 1H, aromatic), 7.06 (dd, J_1 = 8.5, J_2= 1.9 Hz, 1H, aromatic), 7.02 (d, *J* = 9.0 Hz, 2H, aromatic), 5.36 (d, *J* = 4.4 Hz, 1H, cholesteric), 4.66 (m, 1H, cholesteric), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.73 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.66 (complex signals, 54H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.66 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** 171.36, 170.62, 164.27, 162.50, 155.86, 151.33, 151.17, 146.85, 139.48, 131.23, 130.12, 129.80, 125.32, 122.75, 122.54, 119.19, 119.07, 115.59, 114.82 (3C esteric, 14C aromatic, 2C cholesteric), 74.58 (cholesteric), 68.45 (-OCH_2-), 56.64, 56.11, 49.97, 42.28, 39.69, 39.51, 38.07 (7C cholesteric), 36.92, 36.55, 36.17, 35.78, 31.87, 31.82, 31.76, 29.69, 29.43, 29.16, 29.04, 28.21, 28.00, 27.74, 25.96, 24.26, 23.82, 22.81, 22.60, 22.55, 21.00, 19.29, 18.70, 14.08, 11.84 (25C cholesteric and aliphatic carbon atoms). ***m/z (CHCl$_3$):*** 906.3 [M-1+Li]$^+$, **FT-IR (KBr, cm^{-1}):** 1757.15, 1737.86, 1728.22 (ν >C=O, ester)

cholesteryl 3-(4-((4-(octyloxy)phenyl)azo)benzoyloxy) phenyl succinate (4c)

Quantities**:* 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-octyloxyphenylazo) benzoyl chloride (0.141 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), K_2CO_3 (0.48 g, 0.45 mmol) in water (10 mL), orange product, η = 52.21 % (0.165 g), liquid crystal: 16 °C (K/K), 102 °C (K/LC), 109 °C (LC/LC), 134°C (LC/I), 134 °C (I/LC), 123°C (LC/LC), 53 °C (LC/K), 16°C (K/K). **^{1}H-NMR (400 MHz, $CDCl_3$) δ** 8.31 (d, *J* = 8.5 Hz, 2H, aromatic), 8.02 – 7.90 (m, 4H, aromatic), 7.44 (m, 1H, aromatic), 7.16 (dd, J_1= 8.0, J_2= 1.9 Hz, 1H, aromatic), 7.09 (m, 1H, aromatic), 7.06 (dd, J_1 = 8.5, J_2= 1.9 Hz, 1H, aromatic), 7.02 (d, *J* = 9.0 Hz, 2H, aromatic), 5.36 (d, *J* = 4.4 Hz, 1H, cholesteric), 4.66 (m, 1H, cholesteric), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.73 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.66 (complex signals, 56H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.66 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** 171.36, 170.62, 164.27, 162.51, 155.85, 151.34, 151.17, 146.85, 139.48, 131.23, 130.12, 129.80, 125.32, 122.75, 122.53, 119.20, 119.07, 115.59, 114.82 (3C esteric, 14C aromatic, 2C cholesteric), 74.59 (cholesteric), 68.46 (-OCH_2-), 56.65, 56.11, 49.97, 42.29, 39.69, 39.51, 38.07 (7C cholesteric), 36.92, 36.56, 36.17, 35.78, 31.87, 31.82, 31.80, 29.44, 29.42, 29.34, 29.22, 29.15, 28.21, 28.00, 27.74, 26.01, 24.27 , 23.82, 22.81, 22.65, 22.56, 21.00, 19.29, 18.70, 14.10, 11.84 (26C cholesteric and aliphatic carbon atoms). ***m/z (CHCl$_3$): 920.2 [M-1+Li]$^+$**, FT-IR (KBr, cm^{-1}):** 1757.15, 1737.86, 1728.22 (ν >C=O, ester)

cholesteryl 3-(4-((4-(nonyloxy)phenyl)azo)benzoyloxy) phenyl succinate (4d)

Quantities**:* 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-nonyloxyphenylazo) benzoyl chloride (0.147 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), K_2CO_3 (0.48 g, 0.45 mmol) in water (10 mL), orange product, η = 48.59 % (0.157 g), liquid crystal: 80 °C (K/K), 113 °C (K/LC), 134 °C (LC/I), 126 °C (I/LC), 79 °C (LC/K). **^{1}H-NMR (400 MHz, $CDCl_3$) δ** 8.31 (d, *J* = 8.5 Hz, 2H, aromatic), 8.02 – 7.90 (m, 4H, aromatic), 7.44 (m, 1H, aromatic), 7.16 (dd, J_1= 8.0, J_2= 1.9 Hz, 1H, aromatic), 7.09 (m, 1H, aromatic), 7.06 (dd, J_1 = 8.5, J_2= 1.9 Hz, 1H, aromatic), 7.02 (d, *J* = 9.0 Hz, 2H, aromatic), 5.36 (d, *J* = 4.4 Hz, 1H, cholesteric), 4.66 (m, 1H, cholesteric), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.73 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.66 (complex signals, 58H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.66 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** 171.36, 170.61, 164.26, 162.50, 155.85, 151.33, 151.17, 146.85, 139.48, 131.23, 130.12, 129.79, 125.32, 122.74, 122.53, 119.20, 119.07, 115.59, 114.82 (3C esteric, 14C aromatic, 2C cholesteric), 74.58 (cholesteric), 68.46 (-OCH_2-), 56.64, 56.11, 49.97, 42.28, 39.69, 39.51, 38.07 (7C cholesteric), 36.92, 36.55, 36.16, 35.77, 31.86, 31.81, 29.51, 29.43, 29.40, 29.37, 29.24, 29.15, 28.20, 28.10, 27.74, 25.99, 24.26, 23.82, 22.81, 22.66, 22.56, 21.00, 19.29, 18.70, 14.10, 11.83 (26C cholesteric and aliphatic carbon atoms). ***m/z (CHCl$_3$): 934.31 [M-1+Li]$^+$, **FT-IR (KBr, cm^{-1}):** 1757.15, 1737.86, 1728.22 (ν >C=O, ester)

cholesteryl 3-(4-((4-(decyloxy)phenyl)azo)benzoyloxy) phenyl succinate (4e)

Quantities**:* 3-hydroxyphenyl cholesteryl succinate (0.20 g; 0.34 mmol), 4-(4-decyloxyphenylazo) benzoyl chloride (0.152 g; 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) in dichloromethane (40 mL), K_2CO_3 (0.48 g, 0.45 mmol) in water (10 mL), orange product, η = 49.38 % (0.161 g), liquid crystal: 87 °C (K/K), 117 °C (K/LC), 128 °C (LC/LC), 140 °C (LC/I), 138 °C (I/LC), 126°C (LC/LC), 85 °C (LC/K). **^{1}H-NMR (400 MHz, $CDCl_3$) δ** 8.31 (d, *J* = 8.5 Hz, 2H, aromatic), 8.02 – 7.95 (m, 4H, aromatic), 7.44 (m, 1H, aromatic), 7.15 (dd, J_1= 8.0, J_2= 1.97 Hz, 1H, aromatic), 7.09 (m, 1H, aromatic), 7.05 (dd, J_1 = 8.5, J_2= 1.9 Hz, 1H, aromatic), 7.02 (d, *J* = 9.0 Hz, 2H, aromatic), 5.36 (d, *J* = 4.4 Hz, 1H, cholesteric), 4.66 (m, 1H, cholesteric), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.73 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.66 (complex signals, 60H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.66 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** 171.34, 170.60, 164.24, 162.49, 155.84, 151.32, 151.17, 146.84 , 139.47, 131.22, 130.11, 129.78, 125.31, 122.74, 122.53, 119.18, 119.06, 115.58, 114.81(3C esteric, 14C aromatic, 2C cholesteric), 74.56 (cholesteric), 68.45 (-OCH_2-), 56.63, 56.10, 49.96, 42.27, 39.69, 39.50, 38.06 (7C cholesteric), 36.91, 36.54, 36.16, 35.77, 31.89, 31.81, 29.54, 29.43, 29.40, 29.36, 29.31, 29.15, 28.20, 27.99, 27.73, 25.99, 24.25, 23.82, 22.81, 22.67, 22.55, 20.99, 19.28, 18.69, 14.10, 11.83 (26C cholesteric and aliphatic carbon atoms). ***m/z (CHCl$_3$): 948.2 [M-1+Li]$^+$. **FT-IR (KBr, cm^{-1}):** 1757.15, 1737.86, 1728.22 (ν >C=O, ester)

cholesteryl 3-(4-((4-(dodecyloxy)phenyl)azo) benzoyloxy)phenyl succinate (4f)

Quantities**:* 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-dodecyloxyphenylazo) benzoyl chloride (0.163 g, 0.38 mmol) and TBAHS (5.7 mg, 0.017 mmol) dichloromethane (40 ml), K_2CO_3 (0.48 g, 0.45 mmol) in water (10 mL), orange product, η = 46.42 % (0.156 g), liquid crystal: 106 °C (K/LC), 111 °C (LC/LC), 131 °C (LC/I), 130 °C (I/LC), 103°C (LC/LC), 94 °C (LC/K), 27 °C (K/K). **^{1}H-NMR (400 MHz, $CDCl_3$) δ** 8.31 (d, *J* = 8.5 Hz, 2H, aromatic), 8.02 – 7.90 (m, 4H, aromatic), 7.44 (m, 1H, aromatic), 7.16 (dd, J_1 = 8.0, J_2=1.97 Hz, 1H, aromatic), 7.09 (m, 1H, aromatic), 7.06 (dd, *J* = 8.5, J_2= 1.9 Hz, 1H, aromatic), 7.02 (d, *J* = 9.0 Hz, 2H, aromatic), 5.36 (d, *J* = 4.4 Hz, 1H, cholesteric), 4.66 (m, 1H, cholesteric), 4.06 (t, *J* = 6.6 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.73 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.66 (complex signals, 64H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.66 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** 171.35, 170.61, 164.26, 162.51, 155.85, 151.34, 151,18, 146.85, 139.48, 131.23, 130.13, 129.79, 125.32, 122.74, 122.53, 119.19, 119.07, 115.59, 114.82 (3C esteric, 14C aromatic, 2C cholesteric), 74.58 (cholesteric), 68.46 (-OCH_2-), 56.65, 56.12, 49.98, 42.29, 39.70, 39,52, 38.07 (7C cholesteric), 36.92, 36.55, 36.17, 35.78, 31,93, 31,87, 31,83, 29.66, 29.63, 29.59, 29.56, 29.44, 29.41, 29.37, 29.35, 28.21, 28.00, 27.74, 26.00, 24.27, 23.83, 22.81, 22.68, 22.55, 21.00, 19.29, 18.70, 14.11, 11.84 (29C cholesteric and aliphatic carbon atoms). ***m/z (CHCl$_3$): 975.96 [M-1+Li]$^+$. **FT-IR** (KBr, cm^{-1}): 1757.15, 1737.86, 1728.22 (ν>C=O, ester).

General method for the synthesis of 5a÷5e compounds

A mixture of 1 equiv. of 3-hydroxyphenyl cholesteryl succinate (**1**), 1.1 equiv. of 4-(4-alkoxyphenylazo)-benzoic acid (**3**), and 0.2 equiv. of DMAP, dissolved in dry dichloromethane, was stirred for a 20-25 min at room temperature, cooled at 0^{0}C on an ice bath and then 1.2

equiv. of DCC dissolved in dry dichloromethane was added dropwise. After half an hour the ice bath was removed and the reaction mixture was stirred for 48 h at room temperature and then the precipitated N,N'-dicyclohexylurea (DCCU) was filtered off. The solvent was evaporated in vacuum and the solid was chromatographed on silicagel using a 3:1 mixture of hexane:ethyl acetate as eluent. White products were obtained.

cholesteryl 3-(4-(4-(hexyloxy)benzoyloxy)benzoyloxy) phenyl succinate (5a)

Quantities*:* 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-hexyloxybenzoyloxy)benzoic acid (0.126 g, 0.37 mmol), DCC (0.085g, 0.41 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40mL), white product, η= 52.88 % (0.165 g), liquid crystal: **24** °C (K/K), 157 °C (K/I), 71 °C (I/LC), 15°C (K/K). **^{1}H-NMR (400 MHz, $CDCl_3$) δ** 8.26 (d, *J* = 8.7 Hz, 2H, aromatic), 8.15 (d, *J* = 8.8 Hz, 2H, aromatic), 7.43 (m, 1H, aromatic), 7.37 (d, *J* = 8.6 Hz, 2H, aromatic), 7.13 (dd, J_1=8.34 Hz, J_2=1.98 Hz, 1H aromatic), 7.06-7.03 (m, 2H, aromatic), 6.99 (d, *J* = 8.8 Hz, 2H, aromatic), 5.37 (d, *J* = 3.8 Hz, 1H, cholesteric), 4.62 (m, 1H, cholesteric), 4.06 (t, *J* = 6.5 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.72 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.67 (complex signals, 52H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.67 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** 171.36, 170.61, 164.27 , 164, 163.82, 155.45, 151.30, 151.15, 139.49, 132.40, 131.81, 129.77, 126.58, 122.73, 122.11, 120.91, 119.19, 119.05, 115.58, 114.40, (4C esteric, 14C aromatic, 2C cholesteric), 74.56 (cholesteric), 68.36 (-OCH_2-), 56.64, 56.10, 49.96, 42.27, 39.69, 34.49, 38.05 (7C cholesteric), 36.91, 36.54, 36.16, 35.76, 31.86, 31.81, 31.52, 30.17, 29.67, 29.39, 29.02, 28.20, 27.99, 27.73, 25.63, 24.25, 23.80, 22.80, 22.56, 22.54, 20.99, 19.28, 18.69, 14.05, 11.83 (25 cholesteric and aliphatic carbon atoms). ***m/z*** *($CHCl_3$):* 930.26 [M-2+Na+Li]$^+$. **FT-IR** (KBr, cm^{-1}): 1751.36, 1735.93, 1724,36 (ν >C=O, ester).

cholesteryl 3-(4-(4-(heptyloxy)benzoyloxy)benzoyloxy) phenyl succinate (5b)

Quantities*:* 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-heptyloxybenzoyloxy)benzoic acid (0.131 g, 0.37 mmol), DCC (0.085g, 0.41 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40 mL), white product, η = 50.63% (0.160 g), liquid crystal: 30°C (K/K), 89 °C (K/K), 139 °C (K/I), 91 °C (I/LC), 72°C (LC/LC), 43 °C (LC/K), 13 °C (K/K). **^{1}H-NMR (400 MHz, $CDCl_3$) δ** 8.26 (d, *J* = 8.7 Hz, 2H, aromatic), 8.15 (d, *J* = 8.8 Hz, 2H, aromatic), 7.43 (m, 1H, aromatic), 7.37 (d, *J* = 8.6 Hz, 2H, aromatic), 7.13 (dd, J_1=8.34 Hz, J_2=1.98 Hz, 1H aromatic), 7.06-7.03 (m, 2H, aromatic), 6.99 (d, *J* = 8.8 Hz, 2H, aromatic), 5.37 (d, *J* = 3.8 Hz, 1H, cholesteric), 4.62 (m, 1H, cholesteric), 4.06 (t, *J* = 6.5 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.72 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric) 2.05 – 0.67 (complex signals, 54H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.67 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** 171.36, 170.61, 164.27 , 164, 163.82, 155.45, 151.30, 151.15, 139.49, 132.40, 131.81, 129.77, 126.58, 122.73, 122.11, 120.91, 119.19, 119.05, 115.58, 114.40, (4C esteric, 14C aromatic, 2C cholesteric), 74.55(cholesteric), 68.36 (-OCH_2-), 56.64, 56.09, 49.96, 42.27, 39.69, 39.49, 38.05 (7C cholesteric), 36.91, 36.54, 36.16, 35.77, 32.86, 31.88, 31.74, 29.68, 29.41, 29.07, 29.01, 28.21, 27.99, 27.72, 25.92, 24.26, 23.81, 22.80, 22.58, 22.55, 20.99, 19.28, 18.69, 14.07, 11.83 (25C cholesteric and aliphatic carbon atoms). ***m/z*** *($CHCl_3$):* 944.16 [M-2+Na+Li]$^+$, **FT-IR** (KBr, cm^{-1}): 1751.36, 1735.93, 1730.14, 1724.36(ν >C=O, ester)

cholesteryl 3-(4-(4-(octyloxy)benzoyloxy)benzoyloxy) phenyl succinate (5c)

Quantities*:* 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-octyloxybenzoyloxy)benzoic acid (0.136 g, 0.37 mmol), DCC (0.085g, 0.41 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40 mL), white product, η = 49.38 % (0.158 g), liquid crystal: 18 °C (K/K), 91 °C (K/I), 86 °C (I/LC), 58°C (LC/LC), 29 °C (LC/K). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 8.26 (d, *J* = 8.7 Hz, 2H, aromatic), 8.15 (d, *J* = 8.8 Hz, 2H, aromatic), 7.43 (m, 1H, aromatic), 7.37 (d, *J* = 8.6 Hz, 2H, aromatic), 7.13 (dd, J_1=8.34 Hz, J_2=1.98 Hz, 1H aromatic), 7.06-7.03 (m, 2H, aromatic), 6.99 (d, *J* = 8.8 Hz, 2H, aromatic), 5.37 (d, *J* = 3.8 Hz, 1H, cholesteric), 4.62 (m, 1H, cholesteric), 4.06 (t, *J* = 6.5 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.72 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.67 (complex signals, 56H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.67 (s, 3H, cholesteric)). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 171.37, 170.62, 164.28 , 164.01, 163.82, 155.45, 151.31, 151.15, 139.49, 132.41, 131.82, 129.78, 126.59, 122.74, 122.12, 120.91, 119.19, 119.05, 115.58, 114.41, (4C esteric, 14C aromatic, 2C cholesteric), 74.57 (cholesteric), 68.38 (-OCH_2-), 56.65, 56.10, 49.97, 42.28, 39.70, 39.50, 38.06 (7C cholesteric), 36.92, 36.55, 36.16, 35.77, 31.87, 31.82 , 31.78, 29.69, 29.40, 29.31, 29.20, 29.07, 28.21, 28.00, 27.73, 25.97, 24.26, 23.81, 22.81, 22.64, 22.55, 21.00, 19.29, 18.69, 14.09, 11.83 (26C cholesteric and aliphatic carbon atoms). ***m/z*** *($CHCl_3$):* 958.04 [M-2+Na+Li]$^+$, **FT-IR** (KBr, cm^{-1}): 1734, 1724.36 (ν –C=O, ester)

cholesteryl 3-(4-(4-(nonyloxy)benzoyloxy)benzoyloxy) phenyl succinate (5d)

Quantities*:* 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-nonyloxybenzoyloxy)benzoic acid (0.142 g, 0.37 mmol), DCC (0.085g, 0.41 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40 mL), white product, η = 44.48 % (0.145 g), liquid crystal: 17°C (K/K), 93 °C (K/I), 76 °C (I/LC), 52°C (LC/LC), 35 °C (LC/K). **^{1}H-NMR (400 MHz, $CDCl_3$) δ** 8.26 (d, *J* = 8.7 Hz, 2H, aromatic), 8.15 (d, *J* = 8.8 Hz, 2H, aromatic), 7.43 (m, 1H, aromatic), 7.37 (d, *J* = 8.6 Hz, 2H, aromatic), 7.13 (dd, J_1=8.34 Hz, J_2=1.98 Hz, 1H aromatic), 7.06-7.03 (m, 2H, aromatic), 6.99 (d, *J* = 8.8 Hz, 2H, aromatic), 5.37 (d, *J* = 3.8 Hz, 1H, cholesteric), 4.62 (m, 1H, cholesteric), 4.06 (t, *J* = 6.5 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.72 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.67 (complex signals, 58H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.67 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** 171.36, 170.61, 164.27 , 164.01, 163.82, 155.45, 151.30, 151.15, 139.49, 132.41, 131.82, 129.77, 126.59, 122.74, 122.11, 120.91, 119.20, 119.06, 115.58, 114.40, (4C esteric, 14C aromatic, 2C cholesteric), 74.57 (cholesteric), 68.37 (-OCH_2-), 56.65, 56.10, 49.97, 42.28, 39.70, 39.50, 38.06 (7C cholesteric), 36.92, 36.55, 36.16, 35.77, 31.87, 31.82, 31.78, 29.69, 29.42, 29.40, 29.31, 29.20, 29.07, 28.21, 27.99, 27.73, 25.96, 24.26, 23.81, 22.81, 22.64, 22.55, 21.00, 19.29, 18.69, 14.10, 11.83 (27C cholesteric and aliphatic carbon atoms). ***m/z*** *($CHCl_3$):* 971.93 [M-2+Na+Li]$^+$, **FT-IR** (KBr, cm^{-1}): 1734, 1724.36 (ν>C=O, ester).

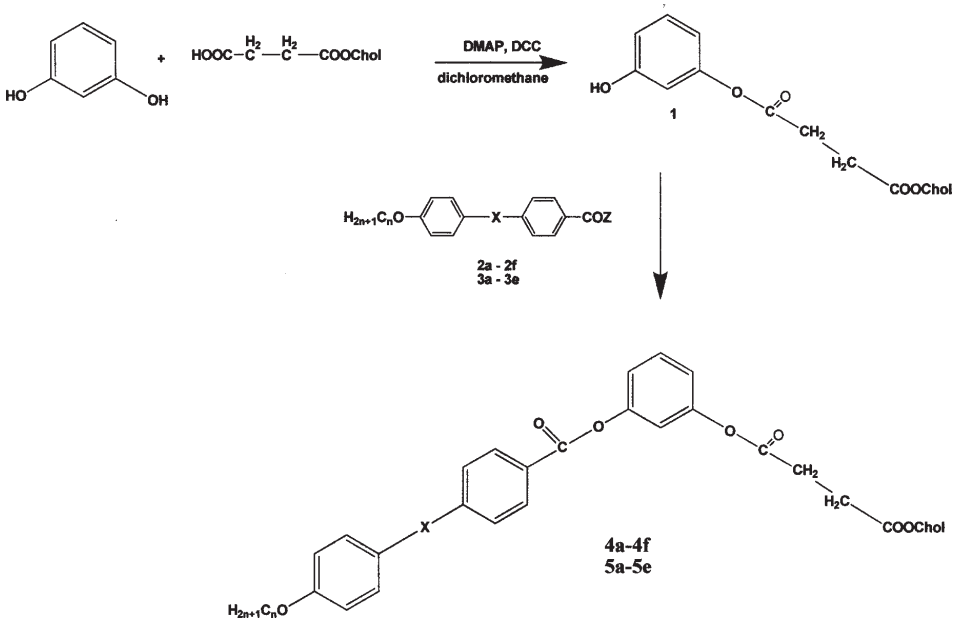

Fig. 1. Synthesis of the cholesteric liquid crystals:
2a ÷ 2f, X= -N=N-, Z = -Cl, n = 6÷10, 12, aq K_2CO_3, TBAHS, 24h
3a ÷3e, X= -OOC-, Z = - OH, n = 6÷10, DCC, DMAP, CH_2Cl_2, 48h
4a ÷4f, X= -N=N-, n = 6÷10, 12
5a÷5e, X= -OOC-, n = 6÷10
Chol = cholesteryl unit

cholesteryl 3-(4-(4-(decyloxy)benzoyloxy)benzoyloxy) phenyl succinate (5e)

***Quantities**:* 3-hydroxyphenyl cholesteryl succinate (0.20 g, 0.34 mmol), 4-(4-decyloxybenzoyloxy)benzoic acid (0.149 g, 0.37 mmol), DCC (0.085g, 0.41 mmol), DMAP (0.0085 g, 0.07 mmol), dry dichloromethane (40 mL), white product, η= 47.49 % (0.156 g), liquid crystal: 26 °C (K/K), 86°C (K/K), 101°C (K/I), 99 °C (I/LC), 55°C (LC/LC), 47 °C (LC/K), 40 °C (K/K). **^{1}H-NMR (400 MHz, $CDCl_3$) δ** 8.26 (d, *J* = 8.7 Hz, 2H, aromatic), 8.15 (d, *J* = 8.8 Hz, 2H, aromatic), 7.43 (m, 1H, aromatic), 7.37 (d, *J* = 8.6 Hz, 2H, aromatic), 7.13 (dd, J_1=8.34 Hz, J_2=1.98 Hz, 1H aromatic), 7.06-7.03 (m, 2H, aromatic), 6.99 (d, *J* = 8.8 Hz, 2H, aromatic), 5.37 (d, *J* = 3.8 Hz, 1H, cholesteric), 4.62 (m, 1H, cholesteric), 4.06 (t, *J* = 6.5 Hz, 2H, -OCH_2-), 2.88 (t, *J* = 6.7 Hz, 2H, -$COOCH_2$-), 2.72 (t, *J* = 6.6 Hz, 2H, -$COOCH_2$-), 2.34 (d, *J* = 7.6 Hz, 2H, cholesteric), 2.05 – 0.67 (complex signals, 60H, selected signals: 1.01 (6H, s, cholesteric), 0.87 (dd, 6H, J_1=6,6 Hz, J_2=1,5 Hz, cholesteric), 0.67 (s, 3H, cholesteric)). **^{13}C-NMR (101 MHz, $CDCl_3$) δ** 171.36, 170.61, 164.27 , 164.00, 163.82, 155.45, 151.30, 151.15, 151.22, 139.49, 132.40, 131.81, 129.77, 126.58, 122.73, 122.11, 120.91, 119.19, 119.05, 115.58, 114.40, (4C esteric, 14C aromatic, 2C cholesteric), 74.56 (cholesteric), 68.37 (-OCH_2-), 56.65, 56.10, 49.97, 42.28, 39.69, 39.50, 38.06 (7C cholesteric), 36.92, 36.55, 36.16, 35.77, 31.87, 31.82, 31.52, 29.39, 29.03, 28.21, 27.99, 27.73, 25.64, 24.26, 23.81, 22.81, 22.56, 22.55, 21.00, 19.29, 18.69, 14.01, 11.83 (23C cholesteric and aliphatic carbon atoms). ***m/z (CHCl$_3$)**:* 985.8 [M-2+Na+Li]$^+$, **FT-IR** (KBr, cm^{-1}): 1735.93, 1724.36 (ν>C=O, ester).

Results and discussions

Synthesis

In order to obtain the desired compounds a two steps reaction was necessary (fig. 1). In the first step, cholesteryl hydroxysuccinate, resorcinol, DMAP and DCC in dry dichloromethane were stirred for 48 h at room temperature [15]. In the second step, the free phenolic group of **1** was esterificated with two series of mesogenic acids with two aromatic rings, connected *via* azo or esteric linking groups and containing alkyloxy ending groups. For the esterification reactions two methods were used. In the case of the **4a÷4f** series, poor results were obtained when using the more convenient system DCC / DMAP. In this case, the esterification reactions were realized with the corresponding acid chlorides in aqueous K_2CO_3/ dichloromethane, at room temperature, for 24 h , using tetra-buthylammonium hydrogen sulfate (TBAHS) as phase transfer catalyst [16]. In the case of **5a÷5e** series, the esterification was performed with DCC and DMAP in dry dichloromethane, at room temperature, for 48 h [17]. All the obtained compounds were purified by column chromatography using dicloromethane/ethyl acetate= 20:1 for **4a-4f** series and hexane: ethyl acetate= 3:1 for **5a-5e** series as eluents. The obtained compounds were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR and mass spectrometry. Yields were similar for both series (around 50%).

Liquid crystaline properties

The mesomorphic behaviour for all the compounds belonging to **4a÷4f** and **5a÷5e** series was investigated by polarizing optical microscopy (POM) in association with differential scanning calorimetry (DSC). Peak transition temperatures from the DSC thermograms, heating and cooling cycles at a rate of 10°C/min, were in agreement with those observed during the optical experiments.

All of the compounds of the series for **4a÷4f** exhibited enantiotropic behaviour with a broader mesophase range on cooling (36-81°C) than on heating (25-50°C) (table 1). The observed textures were assigned by visual comparison (under the microscope) with literature data [18].

The thermogravimetric data evidenced a very good thermal stability for all the investigated compounds, the temperatures at which degradation processes begun (T_{onset}) being situated with around 150°C higher than the isotropisation temperatures (table 1).

The DSC curves of compound **4e** showed on the second heating four endothermic peaks (fig. 2). The first one at 87°C is associated with a crystal-crystal transition the last one at 139°C corresponds to isotropisation and the remaining two peaks are characteristical for the appearance of the mesophase. On cooling, the first peak at 138°C is related to the entrance of the sample from isotropic liquid into mesophase, the second at 126°C marked a changing of the mesophase and the last one at 85°C is attributed to the crystallization of the sample.

Compound	T/°C [ΔH/Jg^{-1}]										T onset
	Heating					Cooling					
	K_1/ K_2	K_2/ LC	LC/ LC	LC/ I	Phase interval	I/ LC	LC/ LC	LC/ K_2	K_2/ K_1	Phase interval	
4a	-	105 [-4.43]	-	155 [-0.98]	**50**	137 [1.66]	-	-	-	-	311
4b	65 [-0.08]	95 [-0.39]	104 [-1.04]	147 [-2.10]	**52**	131 [2.25]	-	63 [0.15]	17 [0.16]	68	315
4c	16 [-0.39]	102 [-1.73]	109 [-2.37]	134 [-1.69]	**32**	134 [0.59]	123 [0.96]	53 [0.11]	16 [0.26]	81	306
4d	80 [-0.12]	113 [-4.77]	-	134 [-2.65]	**21**	126 [0.17]	-	79 [0.24]	-	47	315
4e	87 [-0.18]	118 [-0.99]	128 [-1.37]	139 [-0.72]	**23**	138 [0.66]	126 [1.62]	85 [0.24]	-	54	318
4f	-	106 [-26.69]	111 [-0.65]	131 [-0.56]	**25**	130 [0.72]	103 [0.81]	94 [1.12]	27 [5.76]	36	320

T_{onset} (°C) the initial temperature of thermal degradation processes, K=crystal, LC= liquid crystal, I=isotropic

Table 1
TRANSITION TEMPERATURES (°C) AND ASSOCIATED ENTHALPIES [Jg^{-1}] FOR **4a÷4f** SERIES

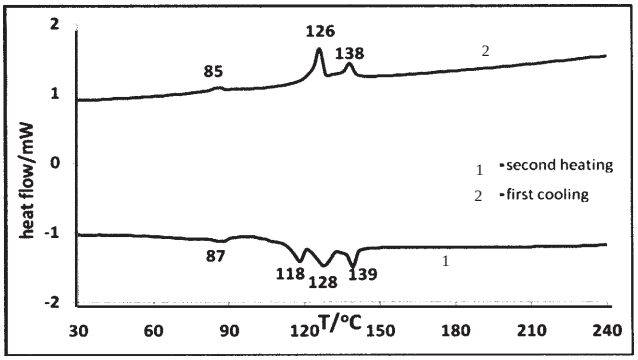

Fig. 2. DSC curves for 4e

According to POM, on cooling, compound **4e** presented two liquid crystalline transitions: the first one, with smectic textures, begun at 138°C and ended at 126°C; the second one, also smectic, started at 126°C and maintained until crystallization (85°C) (figs. 3a and 3b). On heating the same sample (**4e**) exhibited smectic textures, between 118°C and 139°C (fig. 3c). For compound **4d** smectic textures have been observed as well on cooling (fig. 3d). For all the compounds, the mesomorphic behavior on cooling was predominantly influenced by cholesterol moiety that caused glass transition.

Phase transition temperatures and associated enthalpies for **5a÷5e** series are presented in table 2. These compounds presented cholesteric and smectic mesophases over a wide temperature range only on cooling, so they are monotropic liquid crystals. The thermogravimetric studies showed a good thermal stability for all investigated samples with high degradation temperatures (T_{onset}) situated above 300°C. The observed textures were assigned by visual comparison (under the microscope) with literature data [18].

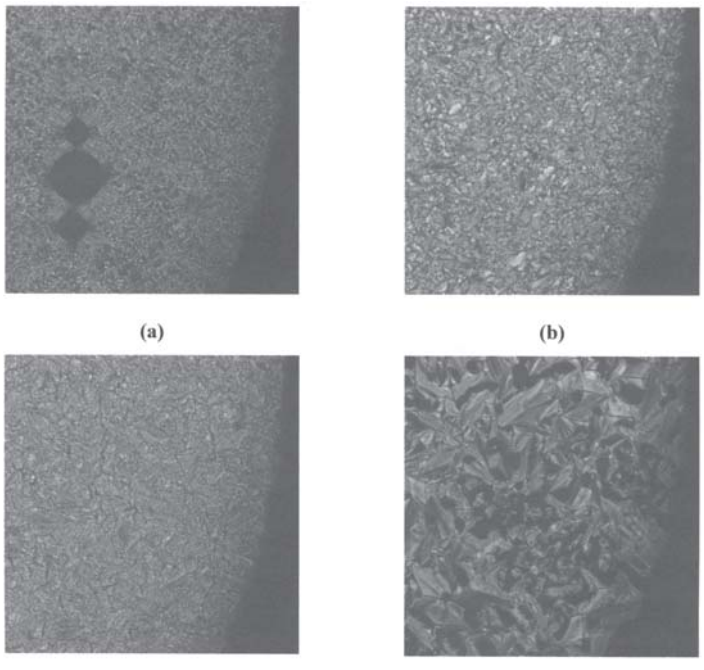

Fig. 3. Microphotographs textures: (a) **4e** first cooling 124°C, (b) **4e** first cooling 89°C, (c) **4e** second heating 128°C, (d) **4d** cooling 127°C

Compounds	T/°C [ΔH/Jg^{-1}]								T_{onset}
	Heating			Cooling					
	K/ K	K/ K	K/ I	I/ LC	LC/ LC	LC/ K	K/ K	Phase interval	
5a	24 [-5.22]	-	157 [-40,75]	71 [0.53]	-	-	15 [0.09]	-	307
5b	30 [-7.20]	89 [-18.32]	139 [-0.94]	91 [0.19]	72 [0.63]	43 [0.15]	13 [0.47]	48	308
5c	18 [-1.89]	-	91 [-14.29]	86 [0.26]	58 [0.96]	29 [0.60]	-	57	300
5d	17 [-1.36]	-	93 [-17.75]	76 [0.30]	52 [1.52]	35 [0.55]	-	41	306
5e	26 [-1.15]	86 [-8.05]	101 [-0.53]	99 [0.62]	55 [0.11]	47 [0.61]	40 [0.08]	52	315

T_{onset} (°C) the initial temperature of thermal degradation processes, K=crystal, LC= liquid crystal, I=isotropic

Table 2
TRANSITION TEMPERATURES (°C) AND ASSOCIATED ENTHALPIES [Jg^{-1}] FOR **5a÷5e** SERIES

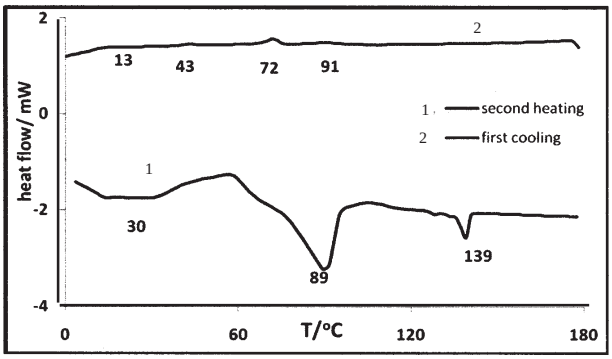

Fig. 4. DSC curves for **5b**

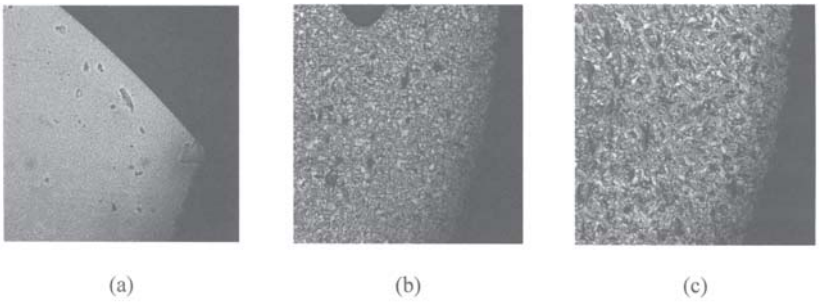

Fig. 5. Microphotographs textures: (a) **5e** first cooling 85°C cholesteric,(b) **5b** first cooling 46°C smectic, (c) **5a** first cooling 52°C

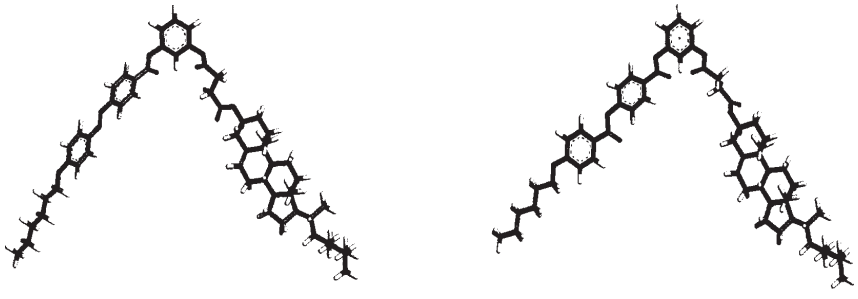

Fig. 6. Energy minimized models: a) **4a**, b) **5a**

The DSC curves for compound **5b** on heating and on cooling are showed in figure 4. The small thermal effect of the four exothermic peaks on cooling was due to slow processes that occurred, induced by the presence of cholesterol moiety. The first peak denoted a crystalline-crystalline transition and the wide peak, at 89°C characterized by a high enthalpy value, represents a polymorphism phenomenon also characteristical for crystal-crystal transitions.

Cholesteric and smectic mesophases were seen only on cooling cycle. The stability of the smectic phase is higher

for **5a** and **5b** as it was seen on POM and DSC investigations while for the higher members of the series, the cholesteric phase was more characteristical (fig. 5). Similar glass transition behaviour was maintained on cooling as with compounds of the first series (**4a÷4f)**.

The minimized energy structures of both series are illustrated in figure 6. Both series adopted a bent-core conformation with the angle between the two mesogenic groups ranging from 120.61 and 121.40°, which is in accordance with the values found in literature data for banana shaped liquid crystals [21, 22]. The values calculated for the dipole moments are between 4.82÷4.89 D for **4a÷4f** series and 6.10÷6.17 D for **5a÷5e** series.

Conclusions

Two new series of cholesterol based dimers have been synthesized and characterized. Both series contain the resorcinol core with one hydroxyl group linked by cholesteryl succinate and the other hydroxyl group esterificated with two different mesogenic groups through two synthetic pathways. Because of the presence of the cholesterol molecule, all the compounds presented glass transition on cooling. The compounds **4a÷4f** showed liquid crystal properties on heating and on cooling while **5a÷5e** displayed mesomorphic behaviour only on cooling. The observed mesophases were of smectic type for the series containing azo linkage (**4a÷4f**) and cholesteric & smectic respectively for the second series (**5a÷5e**). Thermogravimetric studies evidenced a very good thermal stability for all the investigated compounds.

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