

Unsymmetrical Bent-core Liquid Crystals Based on Resorcinol Core

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Two series of unsymmetrical bent-core liquid crystals were obtained by using resorcinol as central core. The two classes of compounds were obtained by reacting 3-(benzyloxy)phenol with some 4-(4-alkyloxyphenylazo)benzoic acids and 4-((4-(alkyloxy)benzoyl)oxy)benzoic acids both possessing six to ten carbon atoms in the flexible tail. The chemical structure was confirmed by spectroscopic techniques ($^1\text{H-NMR}$, $^{13}\text{C-NMR}$, FTIR and MS) while the mesomorphic properties were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The series containing an azo aromatic moiety as linking group presented liquid crystalline properties only in the cooling cycle while the other series, where an esteric group was introduced an enantiotropic behavior for compounds possessing an even number of carbon atoms in the flexible terminal chain. All the investigated compounds proved to be thermally stable up to 300°C.

Keywords: bent-core, liquid crystals, resorcinol, azo linking group

Unconventional chiral liquid crystals have been intensively investigated in the past years because of their applications in modern technology based on special functions such as ferroelectricity and antiferroelectricity. Although are non-chiral molecules, the bent-core liquid crystals exhibit antiferroelectricity without electro-optical switching. The bent-core compounds exhibit as well unusual features and symmetry properties [1-7]. While in conventional smectic liquid crystals one axis is needed to define the orientation of molecules into layers, for bent-core molecules two axes define the orientation into layers. The bent shape of these mesogens requires a secondary direction for orientational ordering, orthogonal to the long molecular axis.

The structure of bent-core compounds can be symmetrical, with the same mesogenic unit on both arms or unsymmetrical, with different mesogenic units on the arms [8, 9]. The mesogenic units bounded to central core may contain ester, imino or azo bounds while terminal flexible chains can be of alkyl or alkyloxy type. Among the connection groups between cycles, the azo linkage distinguishes especially by photoinduced phase transitions that occur in azobenzene derivatives, property of great interest because it leads to promising materials for light-assisted switches devices. Several bent-core derivatives with liquid crystals properties containing azo linking group have been synthesized in our research group [4, 5].

The mesophases exhibited by bent-core compounds are similar to calamitic ones, being of nematic and smectic ordering, but more banana types (B mesophases) can be observed, alone or combined with calamitic ones. The occurrence of mesophase type depends on the angle between the two arms of the bent-core molecule. The B mesophases have been identified in compounds containing 1,3-phenylene or 2,7-naphthalene as central units [6].

The purpose of this paper deals with the synthesis, structural characterization and investigation of the liquid crystalline properties of several biaxial liquid crystals unsymmetrical disubstituted, with resorcinol as central unit and containing azo-aromatic or ester linking groups.

Experimental part

Materials and methods

All the reagents used in the chemical reactions and purification processes were commercial available: benzyl chloride, resorcinol (Aldrich), potassium iodine, potassium carbonate (Fluka), tetrabutylammonium hydrogensulfate (TBAHS) (Aldrich), 1,3-dicyclohexylcarbodiimide (DCC) (Aldrich), 4-(Dimethylamino)pyridine (DMAP) (Aldrich), 3-(Benzyloxy)phenol (**1**) [12], 4-((4-(alkyloxy) benzoyl)oxy)benzoic acids (**2a**÷**2e**) [13] respectively 4-(4-alkyloxyphenylazo)benzoic acids [14] and 4-(4-alkyloxyphenylazo)-benzoyl chlorides (**3a**÷**3e**) were obtained according to literature data [15].

All the obtained compounds were purified by column chromatography with Silica gel 60 (Merck) and for thin layer chromatography silica plates (Merck, F_{254}) were used. All organic solvents (acetone, dichloromethane, ethyl acetate, hexane) used in chemical synthesis or for column chromatography were purchased from Chemical Company were purified by using conventional methods or used as bought.

Instrumentation

Nuclear magnetic resonance spectra were recorded on a Bruker® Avance DRX 400 MHz spectrometer. Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) as internal standard. 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 FTIR spectra were recorded on a Nicolet Magna 550 spectrometer (NaCl crystal window).

Transition temperatures were determined using a Linkam heating stage connected with a Linksys 32 temperature control unit in conjunction with a Axioscop 40 Zeiss polarizing optical microscope and Qimaging/Retiga-1000R camera for image capture, the transitions being confirmed by DSC analysis (Mettler Toledo DSC1). Heating and cooling cycles were run at rates of 10°C/min under nitrogen atmosphere, with sample measured in closed lid aluminum pans.

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All the thermal analysis were run in the same conditions, on 2.8 - 4.3 mg samples on a Mettler-Toledo® TGA SDTA851® derivatograph in N₂ atmosphere, with a flow rate of 20 ml/min and a heating rate of 10°C/min from 25 to 900°C.

Synthesis

General method for the preparation of 3-(benzyloxy)phenyl 4-((4-(alkyloxy)phenyl) diazenyl) benzoates (**4a÷4e**)

Compounds were prepared by adapting literature data [16]. A mixture of 3-(benzyloxy)phenol (0.999 mmol), 4-(4-alkyloxyphenylazo)-benzoyl chloride (1.098 mmol), potassium carbonate (1.331 mmol), tetrabutylammonium hydrogensulfate (0.023 mmol), in dichloromethane (150 mL) and water (40 mL) was vigorously stirred for 24 h. The organic layer was separated, washed several times with distilled water, dried on anhydrous magnesium sulphate and concentrated on rotaevaporatory. Compounds were purified by column chromatography on Silica Gel using a mixture of methylene chloride : hexans 3:1 as eluent. Orange products were obtained.

3-(benzyloxy)phenyl 4-((4-(hexyloxy)phenyl) diazenyl) benzoate (**4a**)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 0.378g (1.098 mmol) 4-(4-hexyloxyphenylazo)-benzoyl chloride, 0.184g (1.331 mmol) K₂CO₃, 0.008 g (0.023 mmol) TBAHS, Yield = 57% (0.290 g). ¹H-NMR (CDCl₃, δ / ppm): 8.32 (d, 2H, ArH, J=8.34 Hz), 7.97 (d, 4H, ArH, J=8.98 Hz), 7.45-7.32 (m, 6H, ArH), 7.02 (d, 2H, ArH, J=8.99 Hz), 6.91 (d, 2H, ArH, J=7.45 Hz), 6.85 (d, 1H, ArH, J=8.55 Hz), 5.08 (s, 2H, Ar-CH₂-O-), 4.06 (t, 2H, -O-CH₂-), 1.83 (cv, 2H, -CH₂-), 1.49 (cv, 2H, -CH₂-), 1.36 (m, 4H, aliphatic), 0.92 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.62, 162.50, 159.77, 155.78, 151.87, 146.84, 136.60, 131.20, 130.41, 129.94, 128.60, 128.05, 127.51, 125.33, 122.50, 114.83, 114.17, 112.71, 108.59 (1C esteric + 18 C aromatic), 70.23 (Ar-CH₂-O-), 68.46 (-O-CH₂-), 31.55, 29.12, 25.67, 22.58, 14.02 (5 C, aliphatic), m/z (CDCl₃): 509.18 [M+Na]⁺. FT-IR (KBr, cm⁻¹): 3028.28 (ν CH aromatic), 2953.01, 2935.65 (ν CH, aliphatic), 1732.07 (ν O-C=O), 1404.17 (ν N=N).

3-(benzyloxy)phenyl 4-((4-(heptyloxy)phenyl) diazenyl) benzoate (**4b**)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 0.393g (1.097 mmol) 4-(4-heptyloxyphenylazo)-benzoyl chloride, 0.184g (1.331 mmol) K₂CO₃, 0.008 g (0.023 mmol) TBAHS, Yield = 56% (0.293 g). ¹H-NMR (CDCl₃, δ / ppm): 8.32 (d, 2H, ArH, J=8.33 Hz), 7.97 (d, 4H, ArH, J=8.99 Hz), 7.45-7.32 (m, 6H, ArH), 7.02 (d, 2H, ArH, J=8.77 Hz), 6.91 (d, 2H, ArH, J=7.01 Hz), 6.86 (d, 1H, ArH, J=8.99 Hz), 5.08 (s, 2H, Ar-CH₂-O-), 4.06 (t, 2H, -O-CH₂-), 1.83 (cv, 2H, -CH₂-), 1.48 (cv, 2H, -CH₂-), 1.33 (m, 6H, aliphatic), 0.91 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.62, 162.50, 159.77, 155.78, 151.87, 146.83, 136.60, 131.20, 130.41, 129.94, 128.60, 128.05, 127.51, 125.33, 122.50, 114.83, 114.17, 112.71, 108.59 (1C esteric + 18 C aromatic), 70.23 (Ar-CH₂-O-), 68.46 (-O-CH₂-), 31.75, 29.15, 29.03, 25.96, 22.59, 14.06 (6 C, aliphatic), m/z (CDCl₃): 523.20 [M+Na]⁺. FT-IR (KBr, cm⁻¹): 2960.73 (ν CH aromatic), 2872, 2846.93 (ν CH, aliphatic), 1734 (ν O-C=O), 1489.04 (ν N=N).

3-(benzyloxy)phenyl 4-((4-(octyloxy)phenyl) diazenyl) benzoate (**4c**)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 0.409 g (1.098 mmol) 4-(4-octyloxyphenylazo)-benzoyl chloride, 0.184g (1.331 mmol) K₂CO₃, 0.008 g (0.023 mmol) TBAHS, Yield = 55% (0.295 g). ¹H-NMR (CDCl₃, δ /

ppm): 8.32 (d, 2H, ArH, J=8.56 Hz), 7.97 (d, 4H, ArH, J=8.76 Hz), 7.45-7.32 (m, 6H, ArH), 7.02 (d, 2H, ArH, J=8.99 Hz), 6.91 (d, 2H, ArH, J=6.58 Hz), 6.86 (d, 1H, ArH, J=8.99 Hz), 5.08 (s, 2H, Ar-CH₂-O-), 4.05 (t, 2H, -O-CH₂-), 1.83 (cv, 2H, -CH₂-), 1.49 (cv, 2H, -CH₂-), 1.30 (m, 8H, aliphatic), 0.90 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.62, 162.51, 159.77, 155.77, 151.87, 146.83, 136.60, 131.20, 130.41, 129.94, 128.60, 128.05, 127.51, 125.33, 122.50, 114.84, 114.17, 112.71, 108.59 (1C esteric + 18 C aromatic), 70.23 (Ar-CH₂-O-), 68.47 (-O-CH₂-), 31.79, 29.33, 29.21, 29.15, 25.99, 22.64, 14.08 (7 C, aliphatic), m/z (CDCl₃): 537.21 [M+Na]⁺. FT-IR (KBr, cm⁻¹): 3070.67 (ν CH aromatic), 2918.29, 2848.85 (ν CH, aliphatic), 1732.07 (ν O-C=O), 1500.62 (ν N=N).

3-(benzyloxy)phenyl 4-((4-(nonyloxy)phenyl) diazenyl) benzoate (**4d**)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 0.424 g (1.097 mmol) 4-(4-nonyloxyphenylazo)-benzoyl chloride, 0.184g (1.331 mmol) K₂CO₃, 0.008 g (0.023 mmol) TBAHS, Yield = 54% (0.298 g). ¹H-NMR (CDCl₃, δ / ppm): 8.32 (d, 2H, ArH, J=8.33 Hz), 7.97 (d, 4H, ArH, J=8.77 Hz), 7.45-7.32 (m, 6H, ArH), 7.02 (d, 2H, ArH, J=8.77 Hz), 6.91 (d, 2H, ArH, J=7.24 Hz), 6.87 (d, 1H, ArH, J=8.55 Hz), 5.08 (s, 2H, Ar-CH₂-O-), 4.05 (t, 2H, -O-CH₂-), 1.83 (cv, 2H, -CH₂-), 1.49 (cv, 2H, -CH₂-), 1.30 (m, 10H, aliphatic), 0.90 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.61, 162.50, 159.76, 155.77, 151.86, 146.83, 136.59, 131.19, 130.40, 129.93, 128.59, 128.05, 127.51, 125.32, 122.49, 114.83, 114.16, 112.70, 108.59 (1C esteric + 18C aromatic), 70.22 (Ar-CH₂-O-), 68.46 (-O-CH₂-), 31.86, 29.50, 29.37, 29.24, 29.14, 25.99, 22.65, 14.09 (8 C, aliphatic), m/z (CDCl₃): 551.23 [M+Na]⁺. FT-IR (KBr, cm⁻¹): 3068.74 (ν CH aromatic), 2918.29, 2850.78 (ν CH, aliphatic), 1734 (ν O-C=O), 1406.1 (ν N=N).

3-(benzyloxy)phenyl 4-((4-(decyloxy)phenyl) diazenyl) benzoate (**4e**)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 0.440 g (1.099 mmol) 4-(4-decyloxyphenylazo)-benzoyl chloride, 0.184g (1.331 mmol) K₂CO₃, 0.008 g (0.023 mmol) TBAHS, Yield = 53% (0.300 g). ¹H-NMR (CDCl₃, δ / ppm): 8.32 (d, 2H, ArH, J=8.55 Hz), 7.97 (d, 4H, ArH, J=8.98 Hz), 7.45-7.32 (m, 6H, ArH), 7.02 (d, 2H, ArH, J=8.99 Hz), 6.91 (d, 2H, ArH, J=7.45 Hz), 6.86 (d, 1H, ArH, J=8.55 Hz), 5.08 (s, 2H, Ar-CH₂-O-), 4.05 (t, 2H, -O-CH₂-), 1.83 (cv, 2H, -CH₂-), 1.49 (cv, 2H, -CH₂-), 1.30 (m, 12H, aliphatic), 0.90 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.61, 162.51, 159.77, 155.77, 151.87, 146.83, 136.60, 131.20, 130.41, 129.93, 128.60, 128.05, 127.51, 125.34, 122.50, 114.84, 114.17, 112.71, 108.59 (1C esteric + 18 C aromatic), 70.23 (Ar-CH₂-O-), 68.47 (-O-CH₂-), 31.88, 29.55, 29.36, 29.30, 29.14, 25.99, 22.66, 14.09 (8 C, aliphatic), m/z (CDCl₃): 565.24 [M+Na]⁺. FT-IR (KBr, cm⁻¹): 3064.88 (ν CH aromatic), 2922.15, 2850.78 (ν CH, aliphatic), 1734 (ν O-C=O), 1469.75 (ν N=N).

General method for the preparation of 4-((3-(benzyloxy)phenoxy)carbonyl)phenyl 4-(alkyloxy)benzoates (**5a÷5e**)

Compounds were prepared by adapting literature data [7]. A mixture of 1 equivalent of 3-(benzyloxy)phenol, 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 20:1 mixture of dichloromethane : hexane as eluent. White products were obtained.

4-((3-(benzyloxy)phenoxy)carbonyl)phenyl 4-(hexyloxy)benzoate (5a)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 4-(4-(hexyloxy)benzoyloxy)benzoic acid (0.376 g, 1.098 mmol), DCC (0.247 g, 1.197 mmol), DMAP (0.024 g, 0.196 mmol), CH₂Cl₂ (50 mL), Yield = 50 % (0.292 g). ¹H-NMR (CDCl₃, δ / ppm): 8.27 (d, 2H, ArH, J=8.55 Hz), 8.15 (d, 2H, ArH, J=8.55 Hz), 7.45-7.31 (m, 8H, ArH), 6.99 (d, 2H, ArH, J=8.99 Hz), 6.92-6.83 (m, 3H, ArH), 5.08 (s, 2H, Ar-CH₂-O-), 4.05 (t, 2H, -O-CH₂-), 1.83 (cv, 2H, -CH₂-), 1.49 (cv, 2H, -CH₂-), 1.36 (m, 4H, aliphatic), 0.93 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.34, 163.81, 159.74, 155.36, 151.83, 136.59, 132.39, 131.77, 129.90, 128.58, 128.03, 127.50, 126.86, 122.06, 120.93, 114.40, 114.17, 112.66, 108.61 (2C esteric + 17 C aromatic), 70.21 (Ar-CH₂-O-), 68.36 (-O-CH₂-), 31.51, 29.02, 25.62, 22.55, 13.99 (5 C, aliphatic), m/z (CDCl₃): 525.18 [M+Na]⁺. FT-IR (KBr, cm⁻¹): 3032.09 (ν CH aromatic), 2916.36, 2852.71 (ν CH, aliphatic), 1734, 1730.14 (ν O-C=O).

4-((3-(benzyloxy)phenoxy)carbonyl)phenyl 4-(heptyloxy)benzoate (5b)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 4-(4-(heptyloxy)benzoyloxy)benzoic acid (0.391 g, 1.097 mmol), DCC (0.247 g, 1.197 mmol), DMAP (0.024 g, 0.196 mmol), CH₂Cl₂ (50 mL), Yield = 61 % (0.362 g). ¹H-NMR (CDCl₃, δ / ppm): 8.27 (d, 2H, ArH, J=8.77 Hz), 8.15 (d, 2H, ArH, J=8.99 Hz), 7.45-7.31 (m, 8H, ArH), 6.99 (d, 2H, ArH, J=8.99 Hz), 6.92-6.83 (m, 3H, ArH), 5.08 (s, 2H, Ar-CH₂-O-), 4.05 (t, 2H, -O-CH₂-), 1.83 (cv, 2H, -CH₂-), 1.49 (cv, 2H, -CH₂-), 1.36 (m, 6H, aliphatic), 0.91 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.36, 164.31, 163.82, 159.76, 155.38, 151.85, 136.61, 132.40, 131.79, 129.91, 128.59, 128.04, 127.51, 126.87, 122.07, 120.95, 114.41, 114.19, 112.67 (2C esteric + 17 C aromatic), 70.23 (Ar-CH₂-O-), 68.38 (-O-CH₂-), 31.73, 29.08, 29.00, 25.93, 22.58, 14.05 (6C, aliphatic), m/z (CDCl₃): 539.19 [M+Na]⁺. FT-IR (KBr, cm⁻¹): 3032.09 (ν CH aromatic), 2945.3, 2920.22 (ν CH, aliphatic), 1737.86, 1734 (ν O-C=O).

4-((3-(benzyloxy)phenoxy)carbonyl)phenyl 4-(octyloxy)benzoate (5c)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 4-(4-(octyloxy)benzoyloxy)benzoic acid (0.407 g, 1.099 mmol), DCC (0.247 g, 1.197 mmol), DMAP (0.024 g, 0.196 mmol), CH₂Cl₂ (50 mL), Yield = 63 % (0.194 g). ¹H-NMR (CDCl₃, δ / ppm): 8.27 (d, 2H, ArH, J=8.77 Hz), 8.15 (d, 2H, ArH, J=8.77 Hz), 7.45-7.31 (m, 8H, ArH), 6.98 (d, 2H, ArH, J=8.77 Hz), 6.92-6.83 (m, 3H, ArH), 5.07 (s, 2H, Ar-CH₂-O-), 4.05 (t, 2H, -O-CH₂-), 1.83 (cv, 2H, -CH₂-), 1.48 (cv, 2H, -CH₂-), 1.30 (m, 8H, aliphatic), 0.90 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.36, 164.31, 163.82, 159.76, 155.38, 151.85, 136.61, 132.40, 131.79, 129.91, 128.59, 128.04, 127.51, 126.87, 122.07, 120.95, 114.41, 114.18, 112.67, 108.62 (2C esteric + 18 C aromatic), 70.23 (Ar-CH₂-O-), 68.38 (-O-CH₂-), 31.78, 29.30, 29.19, 29.07, 25.97, 22.63, 14.07 (7 C, aliphatic), m/z (ν CH aromatic), 2922.15, 2854.64 (ν CH, aliphatic), 1734 (ν O-C=O).

4-((3-(benzyloxy)phenoxy)carbonyl)phenyl 4-(nonyloxy)benzoate (5d)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 4-(4-(nonyloxy)benzoyloxy)benzoic acid (0.424 g, 1.097

mmol), DCC (0.247 g, 1.197 mmol), DMAP (0.024 g, 0.196 mmol), CH₂Cl₂ (50 mL), Yield = 50 % (0.315 g). ¹H-NMR (CDCl₃, δ / ppm): 8.27 (d, 2H, ArH, J=8.55 Hz), 8.15 (d, 2H, ArH, J=8.55 Hz), 7.45-7.31 (m, 8H, ArH), 6.99 (d, 2H, ArH, J=8.77 Hz), 6.92-6.83 (m, 3H, ArH), 5.07 (s, 2H, Ar-CH₂-O-), 4.05 (t, 2H, -O-CH₂-), 1.83 (cv, 2H, -CH₂-), 1.48 (cv, 2H, -CH₂-), 1.30 (m, 10H, aliphatic), 0.89 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.35, 164.30, 163.82, 159.75, 155.37, 151.84, 136.60, 132.39, 131.78, 129.91, 128.59, 128.04, 127.50, 126.87, 122.06, 120.94, 114.40, 114.18, 112.67, 108.61 (2C esteric + 18C aromatic), 70.22 (Ar-CH₂-O-), 68.37 (-O-CH₂-), 31.84, 29.49, 29.34, 29.22, 29.07, 25.96, 22.64, 14.08 (5C, aliphatic), m/z (CDCl₃): 567.21 [M+Na]⁺. FT-IR (KBr, cm⁻¹): 3032.09 (ν CH aromatic), 2916.36, 2852.71 (ν CH, aliphatic), 1737.86, 1734 (ν O-C=O).

4-((3-(benzyloxy)phenoxy)carbonyl)phenyl 4-(decyloxy)benzoate (5e)

Quantities: 0.2 g (0.999 mmol) 3-(benzyloxy)phenol, 4-(4-(decyloxy)benzoyloxy)benzoic acid (0.437 g, 1.097 mmol), DCC (0.247 g, 1.197 mmol), DMAP (0.024 g, 0.196 mmol), CH₂Cl₂ (50 mL), Yield = 61 % (0.266 g). ¹H-NMR (CDCl₃, δ / ppm): 8.26 (d, 2H, ArH, J=8.77 Hz), 8.15 (d, 2H, ArH, J=8.77 Hz), 7.45-7.31 (m, 8H, ArH), 6.98 (d, 2H, ArH, J=8.77 Hz), 6.91-6.83 (m, 3H, ArH), 5.07 (s, 2H, Ar-CH₂-O-), 4.05 (t, 2H, -O-CH₂-), 1.82 (cv, 2H, -CH₂-), 1.48 (cv, 2H, -CH₂-), 1.28 (m, 12H, aliphatic), 0.88 (t, 3H, -CH₃). ¹³C-NMR (CDCl₃, δ / ppm): 164.37, 164.32, 163.83, 159.76, 155.38, 151.83, 136.61, 132.41, 131.80, 129.92, 128.60, 128.05, 127.52, 126.88, 122.08, 120.95, 114.42, 114.19, 112.68, 108.62 (2C esteric + 18 C aromatic), 70.24 (Ar-CH₂-O-), 68.39 (-O-CH₂-), 31.88, 29.54, 29.34, 29.30, 29.08, 25.97, 22.66, 14.09 (8 C, aliphatic), m/z (CDCl₃): 581.22 [M+Na]⁺. FT-IR (KBr, cm⁻¹): 3072 (ν CH aromatic), 2922.15, 2854.64 (ν CH, aliphatic), 1735.93, 1734 (ν O-C=O).

Results and discussions

The synthetic routes to the final **4a÷4e** and **5a÷5e** compounds are presented in Scheme 1. In the first step resorcinol was reacted with benzyl chloride to afford 3-(benzyloxy)phenol [16].

The attempts to obtain **4a÷4e** compounds by reacting 4-(4-alkyloxyphenylazo)benzoic acids with 3-(benzyloxy)phenol (**1**) in the presence of DCC and DMAP failed. The acids were converted into 4-(4-alkyloxyphenyl-azo)benzoyl chlorides (**3a÷3e**) and the reaction with 3-(benzyloxy)phenol was performed in a heterogeneous system (dichloromethane / water), in the presence of K₂CO₃ and using TBAHS as phase transfer catalyst. Compounds were purified by column chromatography on Silica Gel using a mixture of methylene chloride : hexanes 3:1 as eluent. Yields between 53 and 57%. Compounds **5a÷5e** were obtained by reacting 4-((4-(alkyloxy)benzoyl)oxy)benzoic acids (**2a÷2e**) with 3-(benzyloxy)phenol in the condition of Steglich reaction (DCC, DMAP in dry dichloromethane). Compounds were chromatographed on Silica Gel using a 20:1 mixture of dichloromethane : hexanes as eluent. Yields between 50 and 63 %.

The liquid crystals properties of compounds **4a÷4e** and **5a÷5e** were investigated by combination of differential scanning calorimetry (DSC) and polarized optical microscopy (POM). All the investigated compounds presented liquid crystalline properties, mainly monotropic. Table 1 contains the transition temperatures and transition enthalpies of the studied esters. Figure 1 presents as examples the DSC curves for compounds **4a** and **5e**.

The types of liquid crystalline textures were assigned using with literature data by visual comparison [17]. The



Scheme 1. Synthesis of bent-core liquid crystals compounds
 compounds of **4a**÷**4e** series present liquid crystalline behaviour only on the cooling cycle. The first compound with six atoms in the flexible chain shows an unidentified texture in the form of long leaves which grow from isotropic

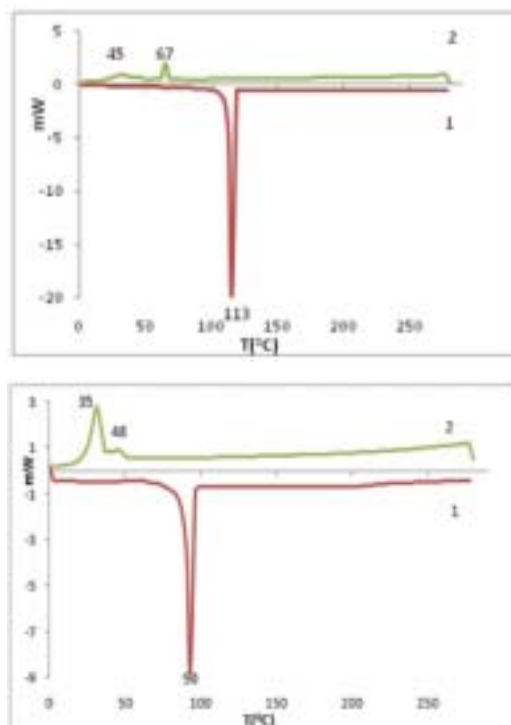


Fig. 1. DSC curves: (a) **4a**: 1- first heating, 2- first cooling and (b) **5e**: 1- second heating, 2- second cooling

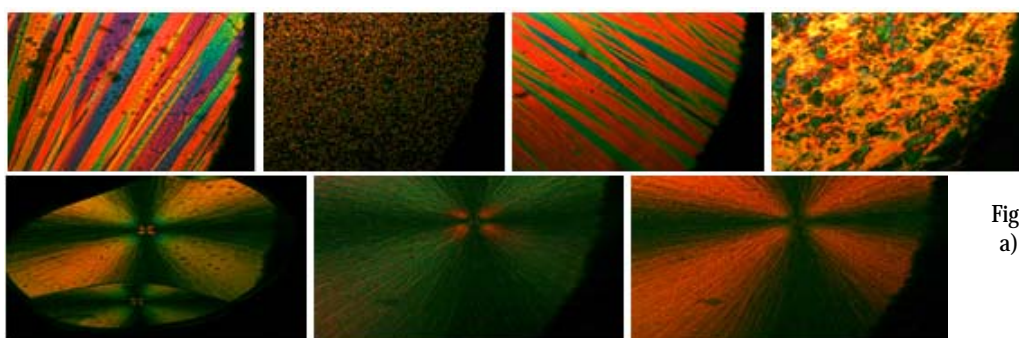


Fig. 2. Textures of **4a**÷**4e** series compounds: a) **4a**, first cooling, 90 °C; b) **4b**, second cooling, 64 °C, c) **4c**, second cooling, 49 °C, d) **4e**, first cooling, 65 °C

Fig. 3. Textures of **5a** compound: a) first cooling, 42 °C; b) second heating, 72 °C, c) second heating, 87 °C

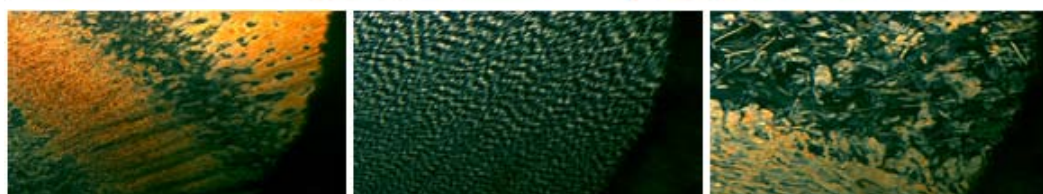


Fig. 4. Textures of **5a**÷**5e** compounds: a) **5c**, second heating, 81 °C; b) **5d**, second cooling, 45 °C, c) **5e**, third heating, 89 °C

melt on cooling, clearly evidenced from POM studies, starting at 95 °C (fig. 2a). The range of the stability of mesophase covers a range of about 50 °C, much higher than the second compound, **4b**, which exhibits however focal conic texture that grows on cooling from the isotropic melt (fig. 2b).

The mesophase stability on cooling increased again for compound **4c**, which shows a similar behavior as **4a** (fig. 2c). Compound **4d** exhibits the same type of ordering that appears at 86 °C on POM investigations. The last compound of this series, **4e**, having ten atoms into the flexible chain presents a higher fluidity that appears on cooling as nematic domains (fig. 2d).

In the case of **5a**÷**5e** series, the replacing of azo linking group with an esteric one caused the changing of the mesomorphic behaviour, the compounds exhibiting alternatively enantiotropic and monotropic behaviour. The enantiotropic behavior was evidenced only for compounds with an even number of carbon atoms in the flexible tail, respectively for **5a**, **5c** and **5e**. The appearance of mesophase on heating was evidenced only during POM

observations because of the very slow transition process that was difficult to highlight on DSC curves. The mesophase of compound **5a** is illustrated by typical cylindrical focal conic domains that succeed the nematic phase and grows on first cooling (fig. 3a). The brushes in the cylindrical focal conic textures switches to different birefringence colors, from green to high red and gold, which may be seen between crossed polarizers on the second heating (figs. 3b, 3c)

The second compound of this series, **5b**, showed a B type mesophase in the form of thin leaves which grow from isotropic melt on cooling, similar with **4a**÷**4e** compounds. The mesomorphic behaviour of compound **5c** is a bit different if compared with the **5a** and **5b** homologues. From optical photomicrographs (fig. 4a) it can be seen the presence of different textures that changes slowly at 52 °C on the second heating; however, the focal conic domains have been observed on second cooling growing over nematic droplets at 43 °C.

The compound **5d** presents a monotropic behavior, evidenced on cooling by a characteristic B phase that runs

Compd.	T/C[ΔH/J g ⁻¹]								T _{max} °C
	Cooling								
	n	LC	I	LC interval, °C	LC1	LC2	Cr	LC interval, °C	
4a	6	-	113 [-101.64]	-	95*	67 [9.72]	45 [11.66]	50	322
4b	7	-	121 [-112.93]	-	85 [2.33]	83 [28.03]	32 [30.02]	13	328
4c	8	-	117 [-106.49]	-	95*	62 [52.10]	45 [0.67]	50	318
4d	9	-	100 [-58.41]	-	86*	68 [33.69]	64 [0.51]	22	319
4e	10	-	97 [-39.65]	-	87*	58 [0.42]	36 [25.13]	31	318
5a	6	46*	105 [-78.64]	59	69*	58 [28.42]	50 [2.24]	19	318
5b	7	-	106 [-90.86]	-	65*	52 [65.61]	-	13	316
5c	8	75*	94 [-87.70]	19	47*	44 [1.38]	41 [46.92]	6	325
5d	9	-	99 [-87.47]	-	45 [8.63]	40 [1.99]	34 [0.48]	11	343
5e	10	71*	90 [-55.05]	19	76*	48 [3.86]	35 [23.94]	51	339

Abbreviations: Cr, crystalline; LC, liquid crystal; I, isotropic; **max**, the initial temperature at which the degradation process begins; *data obtained from POM

Table 1
TRANSITION TEMPERATURES (°C),
AND TRANSITION ENTHALPIES
[J · g⁻¹] OF COMPOUNDS **4a÷4e** AND
5a÷5e

into an extremely slow process just visible on POM at 47 °C (fig. 4b). The increasing of flexible tail leads to changing in mesomorphic behavior and texture, compound **5e** showing predominantly nematic ordering followed by a B1 ordering on cooling. A B1 mesophase was evidenced also on the third heating appearing from dendritic aggregates near to the isotropic point (fig. 4c).

Conclusions

Two classes of bent core liquid crystalline compounds with a specific architecture and containing resorcinol as central unit were obtained. The final compounds were obtained by reacting 3-(benzyloxy)phenol with some 4-(4-alkyloxyphenylazo)benzoic acids and 4-((4-(alkyloxy)benzoyl)oxy)benzoic acids. All products were purified by column chromatography and characterized using common spectral methods: ¹H-NMR, ¹³C-NMR, FTIR and MS. The liquid crystalline properties were pointed out by DSC and POM analysis. All the investigated compounds exhibited liquid crystalline properties, mainly monotropic, and predominantly with B type optical textures. The transition temperatures for compounds of **4a÷4e** series follow the odd-even effect of the flexible segment, the most stable mesophases on cooling presenting the compounds with an even atom carbons. The replacing of azo linking group with an ester one for the compounds of **5a÷5e** series changed the mesomorphic behaviour, with the appearance enantiotropic behaviour but only for compounds with an even number of carbon atoms in the terminal chain.

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