Synthesis and Characterization of Liquid Crystalline Compounds based on a Symmetric [1,3,4]oxadiazole Core

ELENA-RALUCA BULAI (CIOANCA)[1,2], IRINA CARLESCU[1], DAN SCUTARU[1]*

[1] Gheorghe Asachi Technical University of Iasi, Faculty of Chemical Engineering and Environmental Protection, Department of Natural and Synthetic Polymers, 71 Dimitrie Mangeron Blv., 700050, Iasi, Romania,

[2] Stefan cel Mare University of Suceava, Faculty of Mechanical Engineering, Mechatronics and Management, Department of Technology & Management, 13 Universităţii Str., 720229, Suceava, Romania

This paper presents the synthesis and liquid crystalline properties of some new bent core liquid crystalline compounds based on a symmetric [1,3,4]oxadiazole core and containing azo and esteric linking groups. Compounds were prepared by the esterification reaction of 2,5-bis-(4-(4'-hydroxy)azobenzene)-[1,3,4]oxadiazole with aliphatic carboxylic acids containing 5÷10 and 18 carbon atoms and structurally characterized by means of NMR, FT-IR and mass spectroscopy. Their mesomorphic properties were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy. Seven compounds presented liquid crystalline properties, mainly enantiotropic, the identified mesophases being of nematic, smectic and of B type, characteristic to biaxial compounds.

Keywords: liquid crystals, bent core molecules, 2,5-disubstituted-[1,3,4]oxadiazole

Liquid crystalline condition was discovered by Friedrich Reinitzer, over 100 years ago in some cholesterol esters which are natural products found in plants and animals (1888) [1].

In recent years, the liquid crystals of banana-shaped molecules have attracted interest of both theorists and experimentalists, mainly for its ability to generate liquid crystalline mesophases in which spontaneous polarization (SP) in the absence of chiral groups chiral in their molecular structures appears. In 1970, Freiser theoretically predicted the biaxial nematic mesophases [2].

These findings were the beginning of numerous researches related to the structure and properties of these new mesophases, which differs appreciably from the conventional mesophases generated by calamitic mesogens. Different studies have led to the discovery of new banana-shape liquid crystals containing oxadiazolic rings as central units and aromatic mesogens connected *via* azo, imino or esteric groups. The presence of azo groups will permit *trans/cis* isomerization under UV light irradiation, with significant modification of liquid crystalline properties, and with potential application in microelectronics [3,4].

More classes of liquid crystals based on different cores as 1,3-disubstituted benzene, 2,5-disubstituted-[1,3,4]oxadiazole, 2,7-dihydroxynaphtalene, 2,5-disubstituted-thiophene, 1,3-bis-(4-hydroxyphenylazo) benzene have been synthesized and characterized [5-9]. The unique properties of these compounds have led to studies which permitted a detailed understanding of the structure-properties relationship in the bent-shaped liquid crystals [10-15].

In this paper we have synthesized and investigated a new series of symmetric derivatives of [1,3,4] oxadiazole containing azo and esteric groups into structure with liquid crystalline properties. Their mesomorphic properties were investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM).

The differential scanning calorimetry and the polarizing microscope observations indicated for seven compounds the presence of liquid crystalline properties mainly of enantiotropic type.

Experimental part

Materials and methods

All chemicals were used as purchased unless mentioned otherwise. All reactions involving DCC and DMAP (Aldrich) were performed under a dry atmosphere of nitrogen. 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 are reported in ppm relative to tetramethylsilane (TMS) as internal standard. FT-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). Transition temperatures were determined using a Linkam heating stage and Linksys 32 temperature control unit in conjunction with a Axioscop 40 Zeiss polarizing optical microscope and Qimaging/ Retiga – 4000R camera for image capture, the transitions being confirmed by DSC analysis (Mettler Toledo DSC1). Heating and cooling cycles were run at rates of 10^0C/min under nitrogen atmosphere, with samples measured in closed lid aluminum pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase standards. All thermal analyses were performed on a Mettler-Toledo TGA SDTA851^e derivatograph in an N_2 atmosphere, with a flow rate of 20mL/min and a heating rate of 10^0C/min from 25^0C to 900^0C. In order to obtain comparable data, constant operational parameters were kept for all samples.

Synthesis

2,5-Bis-(p-aminophenyl)-[1,3,4] oxadiazole (1) has been prepared by the reaction of *p*-aminobenzoic acid with hydrazine sulphate in polyphosphoric acid (PPA), according to a published method (m.p. = 259–262°C) [16].

* *dscutaru@ch.tuiasi.ro; Tel.: 0040 232 278683*

2,5-Bis-(4-(4'-hydroxy)azobenzene)-[1,3,4]oxadiazole (2) has been obtained by diazotization of (**1**) and coupling of the diazonium salt to phenol.

Diazotization: (**1**) (5 g, 19.8 mmol), was dissolved in 75 mL of water and HCl 32% (4.17 mL). The mixture was heated for half an hour at 50°C until complete dissolution and then cooled to 0° C. $NaNO_2$ (3 g, 43.47 mmol) dissolved in 25 mL of water was then slowly added and the solution was maintained under stirring for one additional hour.

Coupling: the solution of the diazonium salt thus obtained was added dropwise to a solution containing phenol (4.8 g, 51.06 mmol), NaOH (2.4 g, 60 mmol) and 150 mL of water. The mixture was maintained at 0-5°C for 6 h under stirring. The obtained fine precipitate was centrifuged, washed with water and then dried. Purification by column chromatography: silicagel/ethyl acetate: dichloromethane = 10:1, η = 14.3% (1 g), m.p.= 312°C. *^{1}H-NMR* δ_H ppm (DMSO-d6): 10.47 (s, 2H, -OH), 8.35 (d, 4H, Ar), 8.04 (d, 4H, Ar), 7.88 (d, 4H, Ar), 6.98 (d, 4H, Ar). *^{13}C-NMR* δ_C ppm (DMSO-d6): 163.46, 161.28, 153.47, 144.94, 127.58, 124.96, 123.99, 122.60, 115.59 (9C, aromatic).

General procedure of esterification

A mixture of 1 equiv. of (**2**), 2.2 equiv. of the aliphatic acid and a catalytic amount of DMAP, dissolved in dry CH_2Cl_2, was stirred for few minutes and 2.2 equiv. of DCC dissolved in dry dichloromethane was added dropwise. The reaction mixture was stirred for 24 h at room temperature under an inert atmosphere of nitrogen. After removal of the DCC by filtration, the solvent was concentrated and the product was purified by column chromatography on silica gel using dichloromethane as eluent.

2,5-Bis-[(4-pentanoyloxyphenylazo)-4-phenyl]-[1,3,4]oxadiazole (3a)

Quantities: bisphenol (**2**) (0.5 g, 1.08 mmol), pentanoic acid (0.257 mL, 2.37 mmol), DCC (0.49 g, 2.37 mmol), DMAP (catalytic), 100 ml dichloromethane, η = 29.4% (0.20 g), m.p. (enantiotropic liquid crystal): 264°C (K/LC), 289°C (LC/I), 275°C (I/LC), 161°C (LC/K). *^{1}H-NMR* δ_H ppm ($CDCl_3$): 8.32 (d, 4H, Ar), 8.06 (d, 4H, Ar), 8.00 (d, 4H, Ar), 7.28 (d, 4H, Ar), 2.60 (t, 4H, OCO-CH_2-), 1.78 (cv, 4H, -CH_2-), 1.26 (m, 4H, aliphatic), 1.00 (t, 6H,- CH_3). *^{13}C-NMR* δ_C ppm ($CDCl_3$): 171.77 (>C=O), 164.57, 154.54, 153.66, 150.33, 128.04, 125.79, 124.45, 123.65, 122.40 (9C aromatic), 34.26, 27.06, 22.31, 13.66 (4C aliphatic). *FT-IR* (KBr, cm^{-1}): 1755.22 (ν OCO). *m/z* ($CHCl_3$): 629.06 [M-1].

2,5-Bis-[(4-hexanoyloxyphenylazo)-4-phenyl]-[1,3,4]oxadiazole (3b)

Quantities: bisphenol (**2**) (0.5 g, 1.08 mmol), hexanoic acid (0.266 mL, 2.37 mmol), DCC (0.49 g, 2.37 mmol), DMAP (catalytic), 100 mL dichloromethane, η = 26.68% (0.19 g), m.p. (enantiotropic liquid crystal): 256°C (K/LC), 284°C (LC/I), 253°C (I/LC), 194°C (LC/K). *^{1}H-NMR* δ_H ppm ($CDCl_3$): 8.31 (d, 4H, Ar), 8.06 (d, 4H, Ar), 8.00 (d, 4H, Ar), 7.28 (d, 4H, Ar), 2.59 (t, 4H, -OCO-CH_2-), 1.79 (cv, 4H, -CH_2-), 1.26 (m, 8H, aliphatic), 0.90 (t, 6H,- CH_3). *^{13}C-NMR* δ_C ppm ($CDCl_3$): 171.77 (>C=O), 164.57, 154.53, 153.65, 150.33, 128.04, 125.77, 124.45, 123.65, 122.39 (9C aromatic), 34.26 - 13.66 (5C aliphatic). *FT-IR* (KBr, cm^{-1}): 1755.22 (ν OCO). *m/z* ($CHCl_3$): 657.12 [M-1].

2,5-Bis-[(4-heptanoyloxyphenylazo)-4-phenyl]-[1,3,4]oxadiazole (3c)

Quantities: bisphenol (**2**) (0.5 g, 1.08 mmol), heptanoic acid (0.235 mL, 2.37 mmol), DCC (0.49 g, 2.37 mmol), DMAP (catalytic), 100 mL dichloromethane, η = 24.25% (0.18 g), m.p. (enantiotropic liquid crystal): 253°C (K/LC), 276°C (LC/I), 265°C (I/LC), 154°C (LC/K). *^{1}H-NMR* δ_H ppm ($CDCl_3$): 8.31 (d, 4H, Ar), 8.06 (d, 4H, Ar), 7.99 (d, 4H, Ar), 7.27 (d, 4H, Ar), 2.59 (t, 4H, -OCO-CH_2-), 1.79 (cv, 4H, -CH_2-), 1.26 (m, 12H, aliphatic), 0.93(t, 6H,- CH_3). *^{13}C-NMR* δ_C ppm ($CDCl_3$): 171.77 (>C=O), 164.56, 154.53, 153.66, 150.32, 128.03, 125.78, 124.45, 123.65, 122.39 (9C aromatic), 34.56, 29.73, 28.84, 24.95, 22.50, 13.96 (6C aliphatic). *FT-IR* (KBr, cm^{-1}): 1755.22 (ν OCO). *m/z* ($CHCl_3$): 685.41 [M-1].

2,5-Bis-[(4-octanoyloxyphenylazo)-4-phenyl]-[1,3,4]oxadiazole (3d)

Quantities: bisphenol (**2**) (0.5 g, 1.08 mmol), octanoic acid (0.376 ml, 2.37 mmol), DCC (0.49 g, 2.37 mmol), DMAP (catalytic), 100 mL dichloromethane, η = 31.08% (0.24 g), m.p. (enantiotropic liquid crystal): 249°C (K/LC), 273°C (LC/I), 271°C (I/LC), 121°C (LC/K). *^{1}H-NMR* δ_H ppm ($CDCl_3$): 8.31 (d, 4H, Ar), 8.06 (d, 4H, Ar), 7.99 (d, 4H, Ar), 7.27 (d, 4H, Ar), 2.59 (t, 4H, -OCO-CH_2-), 1.79 (cv, 4H, -CH_2-), 1.26 (m, 16H, aliphatic), 0.91 (t, 6H,- CH_3). *^{13}C-NMR* δ_C ppm ($CDCl_3$): 171.67 (>C=O), 164.45, 154.42, 153.55, 150.21, 127.92, 125.66, 124.34, 123.54, 122.29 (9C aromatic), 34.45, 31.61, 29.63, 28.83, 24.88, 22.52, 13.89 (7C aliphatic,). *FT-IR* (KBr, cm^{-1}): 1759.08 (ν OCO). *m/z* ($CHCl_3$): 713.68 [M-1].

2,5-Bis-[(4-nonanoyloxyphenylazo)-4-phenyl]-[1,3,4]oxadiazole (3e)

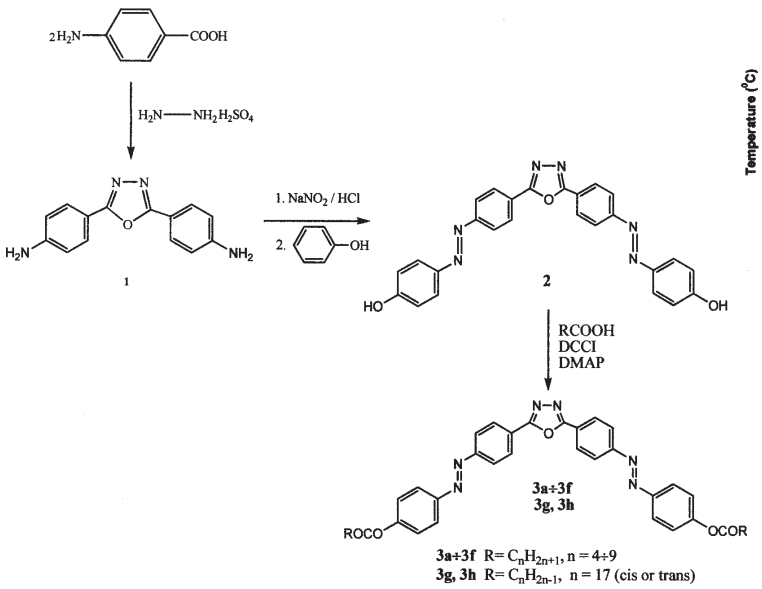
Quantities: bisphenol (**2**) (0.5 g, 1.08 mmol), nonanoic acid (0.413 ml, 2.37 mmol), DCC (0.49 g, 2.37 mmol), DMAP (catalytic), 100 mL dichloromethane, η = 51% (0.51 g), m.p. (enantiotropic liquid crystal): 244°C (K/LC), 274°C (LC/I), 271°C (I/LC), 121°C (LC/K). *^{1}H-NMR* δ_H ppm ($CDCl_3$): 8.30 (d, 4H, Ar), 8.05 (d, 4H, Ar), 7.98 (d, 4H, Ar), 7.27 (d, 4H, Ar), 2.58 (t, 4H, -OCO-CH_2-), 1.79 (cv, 4H, -CH_2-), 1.31 (m, 20H, aliphatic), 0.90 (t, 6H,- CH_3). *^{13}C-NMR* δ_C ppm ($CDCl_3$): 171.73 (>C=O), 164.57, 154.58, 153.71, 150.37, 128.04, 125.82, 124.46, 123.65, 122.39 (9C aromatic), 34.58, 31.87, 29.27, 29.21, 29.15, 25.02, 22.66, 14.01 (8C aliphatic). *FT-IR* (KBr, cm^{-1}): 1751.36 (ν OCO). *m/z* ($CHCl_3$): 742.05 [M-1].

2,5-Bis-[(4-dodecanoyloxyphenylazo)-4-phenyl]-[1,3,4] (3f)

Quantities: bisphenol (**2**) (0.5 g, 1.08 mmol), decanoic acid (0.408 g, 2.37 mmol), DCC (0.49 g, 2.37 mmol), DMAP (catalytic), 100 mL dichloromethane, η= 18.66% (0.19 g), m.p. (enantiotropic liquid crystal): 244°C (K/LC), 275°C (LC/I), 272°C (I/LC), 141°C (LC/K). *^{1}H-NMR* δ_H ppm ($CDCl_3$): 8.33 (d, 4H, Ar), 8.08 (d, 4H, Ar), 8.02 (d, 4H, Ar), 7.28 (d, 4H, Ar), 2.60 (t, 4H, -OCO-CH_2-), 1.79 (cv, 4H, -CH_2-), 1.29 (m, 24H, aliphatic), 0.90 (t, 6H,- CH_3). *^{13}C-NMR* δ_C ppm ($CDCl_3$): 171.74 (>C=O), 164.56, 154.28, 153.43, 150.11, 127.97, 125.57, 124.44, 123.62, 122.41 (9C aromatic), 34.46, 31.87, 29.70, 29.42, 29.27, 29.11, 24.90, 22.68, 14.11 (9C aliphatic). *FT-IR* (KBr, cm^{-1}): 1751.36 (ν OCO). *m/z* ($CHCl_3$): 770.41 [M-1].

2,5-Bis-[(4-oleatoyloxyphenylazo)-4-phenyl]-[1,3,4]oxadiazole (3g)

Quantities: bisphenol (**2**) (0.5 g, 1.08 mmol), oleic acid (0.749 mL, 2.37 mmol), DCC (0.49 g, 2.37 mmol), DMAP (catalytic), 100 mL dichloromethane, η = 20.56% (0.20 g), m.p. (monotrop liquid crystal): 210°C (K/CL), 210°C (I/CL), 165°C (CL/K). *^{1}H-NMR* δ_H ppm ($CDCl_3$): 8.32 (d, 4H, Ar), 8.07 (d, 4H, Ar), 8.01 (d, 4H, Ar), 7.28 (d, 4H, Ar), 5.36 (m, 4H, -HC=CH-), 2.60 (t, 4H, -OCO-CH_2-), 1.78 (cv, 4H, -CH_2-), 1.31 (m, 52H, aliphatic), 0.88 (t, 6H,-CH_3). *^{13}C-NMR* δ_C ppm ($CDCl_3$): 171.87 (>C=O), 164.45, 154.28, 153.44, 150.11, 127.95, 125.57, 124.44, 123.62, 122.39, 130.10, 129.71 (9C aromatic and 2C >C=C<), 34.44, 30.95, 29.79, 29.70, 29.55, 29.48, 29.33, 29.28, 29.18, 27.26, 27.18, 26.45,



Scheme 1. Synthesis of the symmetric [1,3,4] oxadiazole derivatives

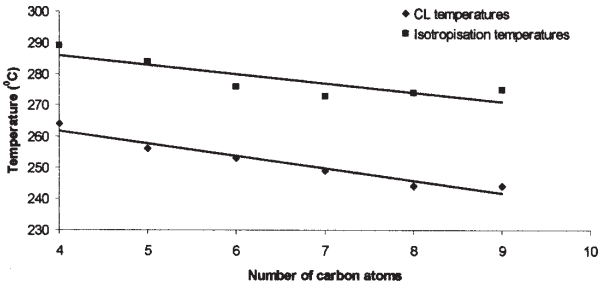


Fig. 1. Variation of transition temperatures as a function of the number of carbon atoms, first heating

24.89, 22.70, 14.12 (15C alifatic). *FT-IR* (KBr, cm^{-1}): 1751.36 (ν OCO). *m/z* ($CHCl_3$): 990.11 [M-1].

2,5-Bis-[(4-elaidicoyloxyphenylazo)-4-phenyl]-[1,3,4]oxadiazole (3h)

Quantities: bisphenol (**2**) (0.5 g, 1.08 mmol), elaidic acid (0.671 g, 2.37 mmol), DCC (0.49 g, 2.37 mmol), DMAP (catalytic), 100 mL dichloromethane, η = 18.7% (0.20 g), m.p. = 220°C. *^{1}H-NMR* δ_H ppm ($CDCl_3$): 8.33 (d, 4H, Ar), 8.08 (d, 4H, Ar), 8.01 (d, 4H, Ar), 7.28 (d, 4H, Ar), 5.40 (m, 4H, HC=CH), 2.60 (t, 4H, -OCO-CH_2-), 1.78 (cv, 4H, -CH_2-), 1.26 (m, 52H, aliphatic), 0.88 (t, 6H,-CH_3). *^{13}C-NMR* δ_C ppm ($CDCl_3$): 171.91 (>C=O), 164.46, 154.29, 153.44, 150.11, 130.57, 127.96, 125.58, 124.45, 122.41 130.57, 130.19 (9C aromatic and 2C >C=C<), 34.45, 30.95, 29.67, 29.57, 29.32, 29.28, 29.20, 29.12, 29.08, 28.99, 28.95, 26.44, 24.89, 22.69, 14.12 (15C alifatic). *FT-IR* (KBr, cm^{-1}): 1751.36 (ν OCO). *m/z* ($CHCl_3$): 990.08 [M-1].

Results and discussions

Synthesis of the [1,3,4]oxadiazole derivatives

The symmetric derivatives of [1,3,4]oxadiazole were prepared by using the synthetic route presented in scheme 1. The synthesis of final compounds **3a÷ 3h** involved three stages: the first one involved the synthesis of *2,5-bis-(p-aminophenyl)-[1,3,4]oxadiazole* by the condensation of *p*-aminobenzoic acid with hydrazine sulphate in the presence of polyphosphoric acid [16], in the second stage compound **2** was obtained by *bis*-diazotation of **1** followed by bis-phenol coupling [16] and the last one involved the bis-esterification of compound **2** with aliphatic carboxylic acids in the presence of N,N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as catalyst (η = 20 ÷ 51%). All the synthesized products were purified by column chromatography and were structurally characterized by means on ^{1}H- and ^{13}C-NMR, mass and FT-IR spectroscopy.

Liquid crystalline properties

The presence of [1,3,4]oxadiazole bent-shaped core induces liquid crystalline properties. The DSC and polarized optical microscopy observations indicated for the six compounds **3a÷3f** the presence of enantiotropic liquid crystalline properties. Compound **3h** (containing oleic acid as terminal chains) exhibited only a monotropic behaviour while for compound **3g** (containing elaidic acid in terminal chains) no liquid crystalline properties could be evidenced.

The liquid crystalline properties of the synthesized symmetric [1,3,4]oxadiazole derivatives, based on DSC data, are schematically presented in table 1.

On heating, transition temperatures are high: the liquid crystalline domains begin between 244-264^{0}C while the isotropisation temperatures are ranged between 273-289^{0}C. The thermal stability of all the synthesized compounds was very good, the initial temperature at which thermal degradation begins (T_{onset} values in table 1) being with around 50^{0}C higher than the isotropisation ones.

For **3a÷3f** compounds, data presented in table 1 clearly evidence the linear decrease of the temperatures at which the liquid crystalline properties appeared and of the isotropisation temperatures when the number of carbon atoms of the terminal chains increase (fig. 1).

For all compounds presenting an enantiotropic behavior, the existence range of the mesophases on cooling are considerable wider (between 131 – 150^{0}C) if compared with the heating cycles (between 24 and 31^{0}C).

Compound	K/LC	LC/I	I/LC	LC/K	T_{onset} (^{0}C)
3a	264 [-40]	289 [-32]	275 [23]	161 [7]	324
3b	256 [-36]	284 [-31]	253 [7]	194 [1]	323
3c	253 [-32]	276 [-23]	265 [19]	154 [2]	316
3d	249 [-94]	273 [-56]	271 [55]	121[24]	327
3e	244 [-38]	274 [-24]	271 [23]	121 [9]	335
3f	244 [-36]	275 [-25]	272 [22]	141 [14]	329
3g (cis)	-	212 [-40]	210 [7]	165 [8]	300
3h (trans)	-	169 [-8]	-	67 [5]	208

Abbreviation: K-crystalline, LC-liquid crystal, I-isotropic, T_{onset} - initial temperature at which thermal degradation begins

Table 1
TRANSITION TEMPERATURES (°C) AND TRANSITION ENTHALPIES (J/G, BETWEEN SQUARE BRACKETS) OF COMPOUNDS 3a ÷ 3h

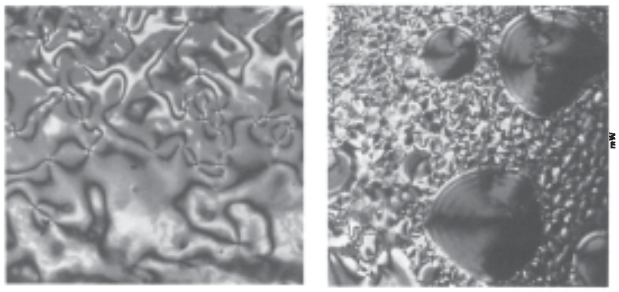


Fig. 2. Optical textures of compound 3a: a) first heating, 286°C and b) second cooling, 250°C

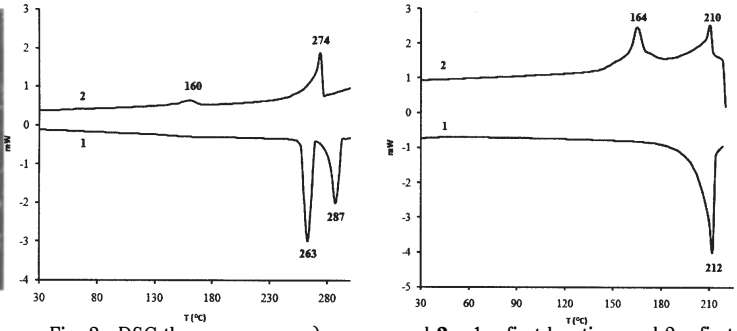


Fig. 3. DSC thermograms: a) compound **3a**: 1 – first heating and 2 – first cooling; b) compound **3g**: 1 – first heating and 2 – first cooling

The first two compounds of the series, **3a** and **3b**, presented nematic phase, with characteristic Schlieren textures (fig. 2a). On cooling, the microscopy observations evidenced different textures, especially in the case of compound **3a**, that presented some toric like domains around 250°C (fig. 2b).

Figure 3a presents, as a typical example, the DSC thermogram of compound **3a**, which evidences the existence of a very large range of stability of the mesophase on cooling. Similar thermograms were obtained for compounds **3b** - **3f.**

Starting with the third compound of the series, the polarized optical microscopy evidenced that the mesophase behaviour changed substantially. The microscopy investigations for compound **3c** showed firstly the appearance of some non-specific textures followed by the transition to a nematic texture. On cooling, the behavior was more complex, some non-specific *leaves like* textures, corresponding probably to a B type mesophases, whose nature could not be established (fig. 4a).

For **3d** compound, a mosaic like texture has been identified at 250°C on heating, similar to the B_1 mesophase, characteristic to bent-core compounds (fig. 4b). On cooling, some *leaves like* textures appears, similar to compound **3c**. More complex mesophases have been observed for compounds **3e** and **3f**, on cooling (fig. 5a, 5b). By using the decrossing of polarizers (5-10°), some domains appear bright or dark at the same temperature, indicating the presence of chiral separated domains (fig. 5c and 5f). Such behaviour is similar to B_4 mesophases.

Unlike the other compounds of the series, compound **3g** presented only a monotropic behaviour. The phase transition I-LC was observed both on POM and DSC investigations (fig. 3b). The POM investigations evidenced the appearance of non specific *leaves like* textures, on cooling (210 ^{0}C), similar to the B type mesophases.

The last compound of the series, **3h**, did not present liquid crystalline properties, due to the severe modification of the geometry of the molecule in the presence of the *trans* configuration in the terminal alkenoyloxy chains. This change is probably responsible for the inability ordering in liquid crystalline structures as a result of reduced physical interactions between molecules.

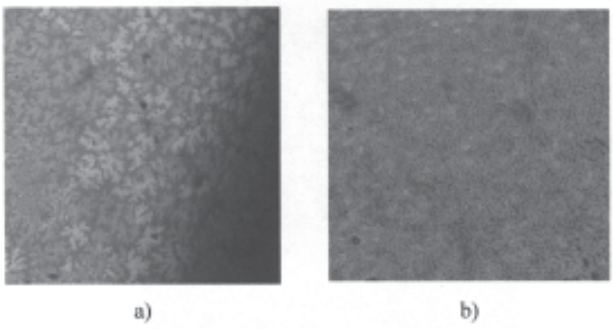


Fig. 4. Optical textures: a) compound **3c**, first cooling, at 235°C; b) compound **3d**, second heating at 250°C

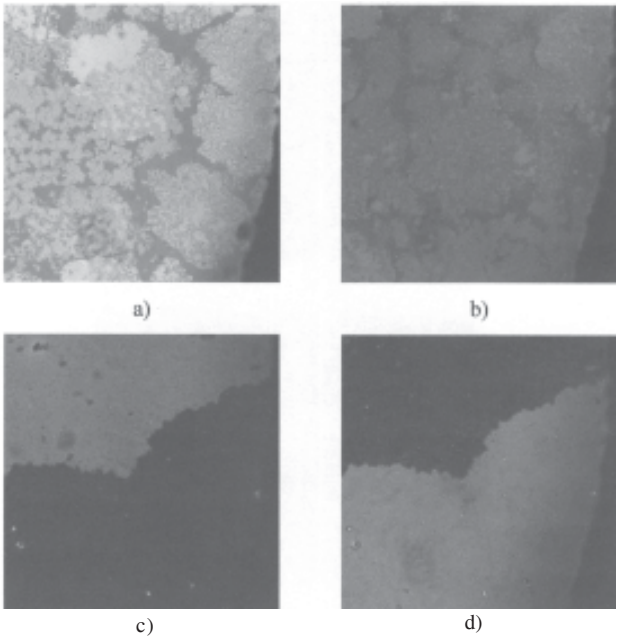


Fig. 5. Optical textures: a) compound **3e**, second cooling at 230°C, b) compound **3f**, second cooling at 225°C, c) and d) compound **3f**, second cooling at 191°C, with decrossing of depolarizers

Conclusions

In this work we have described the synthesis and liquid crystalline properties of a new series of symmetric bent core derivatives based on a 2,5-disubstituted-[1,3,4]oxadiazole core containing azo and ester linking groups. The structure of the compounds has been confirmed by NMR and SM techniques and the mesomorphic properties by DSC and POM analysis. With one exception, all the synthesized compounds presented liquid crystalline properties, mainly enantiotropic. The liquid crystalline behaviour proved to be complex, the identified mesophases being of nematic, smectic and B type, characteristic to biaxial compounds. Generally, the existence ranges of the mesophases on cooling were considerable wider when compared with the heating cycles.

All the synthesized compounds proved to be thermally stable in the existence range of the mesophases.

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