Synthesis and Characterization of Some Liquid Crystalline Compounds based on a 2,7-dihydroxynaphthalene Core

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The paper presents the synthesis and structural characterization of some liquid crystalline compounds derived from 2,7-dihydroxynaphthalene and containing azo-aromatic and esteric connecting groups. Two classes of compounds were obtained by reacting 2,7-dihydroxynaphthalene with the corresponding 4-(4-alkoxyphenylazo)-benzoic acid chlorides, in the presence of K₂CO₃ and THBAS as phase transfer catalyst, in dichloromethane / water. Two classes of compounds have been isolated through mono- or di-esterification of 2,7-dihydroxynaphthalene. Polarized optical microscopy and DSC investigations evidenced that only the mono-esters of 2,7-dihydroxynaphthalene presented enantiotropic liquid crystalline properties, mainly of nematic type.

Keywords: liquid crystals, 2,7-dihydroxynaphthalene, azo-aromatic compounds

In the recent years, a considerable interest focused on the liquid crystalline properties of banana shaped molecules [1]. The design and synthesis of novel achiral banana shaped mesogens forming ferro- and/or antiferroelectric smectic or columnar mesophases is one of the most exciting research activities in the area of thermotropic liquid crystals. Banana-shaped liquid crystalline compounds broadly require two units: (i) a central unit, which provides the bending angle, and (ii) two rodlike units with a terminal aliphatic chain which could be attached to the central unit [2-10]. Literature data reported several central core aromatic molecules which are able to ensure the necessary bending angle between 120-140° and central core aromatic molecules which are able to ensure the central unit [2-10]. The design and synthesis of novel achiral banana shaped mesogens forming ferro- and/or antiferroelectric smectic or columnar mesophases is one of the most exciting research activities in the area of thermotropic liquid crystals. Banana-shaped liquid crystalline compounds broadly require two units: (i) a central unit, which provides the bending angle, and (ii) two rodlike units with a terminal aliphatic chain which could be attached to the central unit [2-10]. Literature data reported several central core aromatic molecules which are able to ensure the necessary bending angle between 120-140° and central core aromatic molecules which are able to ensure the central unit [2-10].

Most of the bent-core mesogens reported so far are monomorphic and many of them exhibit an antiferroelectric switching behaviour. In addition, depending on the molecular structure of these compounds, smectic A, smectic C, or nematic phases have been obtained either individually or in combination with B-phases. A direct transition from an antiferroelectric B2 phase to a nematic phase and a columnar B1 phase to a nematic phase have also been observed[14-15]. Pelzl have observed the spontaneous chiral ordering of molecules in the nematic phase. On application of an electric field to this texture, a fan-shaped texture with equidistant stripes (chiral nature) can be induced, which is very unusual. Although the nematic phase has been observed in many bent-core compounds, its occurrence in combination with B-phases is very limited. Hence, there is a need to synthesize more compounds with varying molecular structure in order to have a clear understanding of the occurrence of this type of transition. In general, the relationship between molecular structure and the mesomorphic behavior involves different aspects: for example, the position and magnitude of the bending angle, the number of phenyl rings present in the bent-core, the type and influence of lateral substituents, the nature and orientation of linking groups, and length of the terminal chains[1-4].

This paper presents the synthesis, structural characterization and mesomorphic properties of two new series of bent core compounds that have as central unit 2,7-dihydroxynaphthalene and as mesogenic groups 4-(4-alkoxyphenylazo)-benzoyl moieties. The liquid crystalline properties were evaluated by means of polarized optical microscopy and differential scanning calorimetry.

Experimental part

Materials and methods

4-(4-Alkoxynaphthalazo)-benzoic acid chlorides have been prepared according to literature data [16]. All other materials used in the present work have been purchased from Sigma Aldrich and were used as received. For column chromatography Silica gel 60 (Merck) was used, while for thin layer chromatography Silica gel plates (Merck Silica gel F_{254}) were used.

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 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 an Axioskop 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. 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 N\textsubscript{2} atmosphere, with a flow rate of 20 ml/min and a heating rate of 10 °C/min from 25 to 900°C.

**Synthesis**

The preparation of 7-hydroxy-naphthalene-2-yl-4-(4-(alkoxy)phenyl)azo benzoxides (3a+e) and naphthalene-2,7-diyd-bis(4-(4-(alkoxy)phenyl)azo)benzoates (4a+e) was carried out by adapting literature methods [17]. A mixture of naphthalene-2,7-diol (1) (0.3 g, 1.875 mmol), 4-(4-alkoxyphenylazo)-benzoyl chloride (2.06 mmol) (2a+e), potassium carbonate (0.345g, 2.5 mmol), tetrabutylammonium hydrogensulfate (0.016 g, 0.046 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 sulfate and concentrated on rotaevaporator. Compounds 3 and 4 were separated by column chromatography on silica gel using a mixture of methylene chloride : ethyl acetate 20:1 as eluent. Orange products. Yields: 10.75±21.11 % for compounds 3a+3e and 8.81±17.93 % for compounds 4a+4e.

7-hydroxynaphthalene-2-yl 4-((4-(hexyloxy)phenyl)azo) benzene (3a)

Yield 11.50 % (0.1 g). \textsuperscript{1}H-NMR δ ppm (CDCl\textsubscript{3}): 8.41 (d, 2H, Ar, J=8.55 Hz), 8.03 (d, 2H, Ar, J=8.55 Hz), 8.01 (d, 2H, Ar, J=8.7 Hz), 7.86 (d, 1H, Ar, J=8.8 Hz), 7.80 (d, 1H, Ar, J=8.8 Hz), 7.89 (d, 1H, Ar, J=1.9 Hz), 7.27 (dd, 1H, Ar, J=2.2 Hz, J=8.9 Hz), 7.16 (d, 1H, Ar, J=2.0 Hz), 7.12 (dd, 1H, Ar, J=2.4 Hz, J=8.8 Hz), 7.08 (d, 2H, Ar, J=8.9 Hz), 5.06 (s, 1H, -OH), 4.06 (t, 2H, -O-CH\textsubscript{2}-), 1.83 (q, 2H, -CH\textsubscript{2}-CH\textsubscript{3}), 1.49 (q, 2H, -CH\textsubscript{2}-CH\textsubscript{3}), 1.37 (m, 6H, -CH\textsubscript{2}-CH\textsubscript{3}), 0.91 (t, 3H, -CH\textsubscript{3}). \textsuperscript{13}C-NMR δ ppm (CDCl\textsubscript{3}): 164.98, 162.64, 156.19, 154.25, 149.53, 145.53, 142.14, 135.36, 131.30, 130.67, 129.81, 129.40, 127.19, 125.36, 126.61, 118.88, 117.79, 117.32, 115.02, 109.60 (1*>C=O esteric + 14 C, aromatic), 68.64, 31.61, 29.23, 25.74, 22.61, 13.97 (1*-O-CH\textsubscript{2} + 5 C, aliphatic). FT-IR (KBr cm\textsuperscript{-1}): 3419.23 (vOH), 3068.74 (vCH), 2929.86, 2858.85 (vCH, aliphatic), 1718.57 (vCO); m/z (CHCl\textsubscript{3}): 469.31 [M+1].

7-Hydroxynaphthalene-2-yl 4-((4-(hexyloxy)phenyl)azo)benzoate (3b)

Yield 21.11 % (0.19 g). \textsuperscript{1}H-NMR δ ppm (CDCl\textsubscript{3}): 8.35 (d, 2H, Ar, J=8.55 Hz), 7.967 (d, 2H, Ar, J=8.55 Hz), 7.945 (d, 2H, Ar, J=8.77 Hz), 7.80 (d, 1H, Ar, J=8.8 Hz), 7.73 (d, 1H, Ar, J=8.8 Hz), 7.53 (d, 1H, Ar, J=1.9 Hz), 7.21 (dd, 1H, Ar, J=2.2 Hz, J=8.9 Hz), 7.09 (d, 1H, Ar, J=2.0 Hz), 7.06 (dd, 1H, Ar, J=2.4 Hz, J=8.8 Hz), 7.02 (d, 2H, Ar, J=8.9 Hz), 5.06 (s, 1H, -OH), 4.06 (t, 2H, -O-CH\textsubscript{2}-), 1.83 (q, 2H, -CH\textsubscript{2}-CH\textsubscript{3}), 1.49 (q, 2H, -CH\textsubscript{2}-CH\textsubscript{3}), 1.37 (m, 6H, -CH\textsubscript{2}-CH\textsubscript{3}), 0.91 (t, 3H, -CH\textsubscript{3}). \textsuperscript{13}C-NMR δ ppm (CDCl\textsubscript{3}): 164.99, 162.67, 156.14, 154.31, 149.59, 147.20, 135.39, 131.30, 127.90, 129.40, 127.22, 125.36, 126.62, 118.87, 117.82, 117.32, 115.06, 109.63 (1*>C=O esteric + 18 C, aromatic), 68.68, 31.30, 29.30, 29.07, 26.06, 22.62, 14.01 (1*-O-CH\textsubscript{2} + 6 C, aliphatic). FT-IR (KBr cm\textsuperscript{-1}): 3419.93 (vOH), 3068.74 (vCH), 2922.15, 2854.64 (vCH, aliphatic), 1722.43 (vCO); m/z (CHCl\textsubscript{3}): 483.33 [M+1].

7-hydroxynaphthalene-2-yl 4-((4-(octyloxy)phenyl)azo)benzoate (3c)

Yield 10.75 % (0.1 g). \textsuperscript{1}H-NMR δ ppm (CDCl\textsubscript{3}): 8.36 (d, 2H, Ar, J=8.5 Hz), 7.968 (d, 2H, Ar, J=8.55 Hz), 7.945 (d, 2H, Ar, J=8.77 Hz), 7.80 (d, 1H, Ar, J=8.8 Hz), 7.74 (d, 1H, Ar, J=8.8 Hz), 7.53 (d, 1H, Ar, J=1.7 Hz), 7.22 (dd, 1H, Ar, J=2.2 Hz, J=8.9 Hz), 7.09 (d, 1H, Ar, J=5.3 Hz), 7.06 (dd, 1H, Ar, J=2.3 Hz, J=8.8 Hz), 7.02 (d, 2H, Ar, J=8.9 Hz), 5.08 (s, 1H, -OH), 4.06 (t, 2H, -O-CH\textsubscript{2}-), 1.93 (q, 2H, -CH\textsubscript{2}CH\textsubscript{3}), 1.48 (q, 2H, -CH\textsubscript{2}-), 1.34 (m, 6H, -CH\textsubscript{2}-CH\textsubscript{3}), 0.90 (t, 3H, -CH\textsubscript{3}). \textsuperscript{13}C-NMR δ ppm (CDCl\textsubscript{3}): 165.00, 152.63, 156.09, 154.25, 149.53, 147.13, 135.34, 131.29, 125.69, 129.79, 129.39, 127.17, 125.36, 122.60, 118.85, 117.79, 117.31, 115.01, 109.59 (1*>C=O esteric + 18 C, aromatic), 68.64, 31.85, 29.37, 29.26, 29.05, 26.22, 21.64, 14.04 (1*-O-CH\textsubscript{2} + 7 C, aliphatic). FT-IR (KBr cm\textsuperscript{-1}): 3421.71 (vOH), 3068.74 (vCH), 2922.15, 2852.71 (vCH, aliphatic), 1720.50 (vCO); m/z (CHCl\textsubscript{3}): 497.35 [M+1].
The reactions were performed in the presence of aqueous potassium carbonate / dichloromethane, using TBHAS as phase transfer catalyst. Several other attempts to obtain the esters of 2,7-dihydroxynaphthalene failed (DCCI / DMAP method, working in homogeneous media with pyridine or TFA as bases etc).

Not unexpectedly, thin layer chromatography evidenced a quite complex composition of the reaction mixture. Column chromatography separation afforded the mono- and di-esters of 2,7-dihydroxynaphthalene in an approximate 1:1 molar ratio (scheme 1). The obtained yields were between 10.75+21.11 % for compounds 3a+3e and 8.81+17.93 % for compounds 4a+4e.

Liquid crystalline properties

The investigations through polarized optical microscopy (POM) and differential scanning calorimetry (DSC) indicated the existence of the mesomorphic properties only for the mono-esters 3a+3e. Compounds 4a+4e do not present liquid crystalline properties, which is quite unexpected taking into consideration that literature data present several classes of symmetric bent core liquid crystalline compounds, with similar structures and with a rich polymorphism.

For all the compounds 3a+3e, polarized optical microscopy indicated that the liquid crystalline properties are of enantiotropic type, the ordering into mesophases being evidenced both on heating and cooling cycles.

Table 1 synthetically presents the mesomorphic properties and transition enthalpies of compounds 3a+3e and 4a+4e. Taking into consideration the importance of thermal stability in the existing range of mesophases, table 1 also presents, based on thermal stability studies, the T_{net} temperatures, the initial temperature at which the degradation processes begin.

Graphic representation of temperature variation of isotropisation and crystallization depending on the number of carbon atoms of the terminal alky chain highlights the appearance of the even/odd effect, meaning that derivatives with an odd number of carbon atoms present isotropisation and crystallization temperatures inferior to their superior and inferior homologues.

Compounds 3a+3e present mesomorphic properties with ordering in nematic mesophases, with ribbon and Schlieren like textures. For compounds 3d and 3e differential calorimetric data evidenced also the existence of crystalline-crystalline transitions both on cooling and heating cycles. In the case of compounds 3a-3c, no crystalline-crystalline transitions, both on cooling and heating cycles could be observed (fig.2).

When heated, compound 3a presents Schlieren characteristic textures, the mesophase starting at 190°C and lasting up to isotropic temperature at 214°C (fig. 3a).

On cooling, nematic droplets come into view at 218°C (fig. 3b), which maintain down to 210°C, when a Schlieren-like textures. For compounds 3d and 3e differential calorimetric data evidenced also the existence of crystalline-crystalline transitions both on cooling and heating cycles. In the case of compounds 3a-3c, no crystalline-crystalline transitions, both on cooling and heating cycles could be observed (fig.2).

Graphic representation of temperature variation of isotropisation and crystallization depending on the number of carbon atoms of the terminal alky chain highlights the appearance of the even/odd effect, meaning that derivatives with an odd number of carbon atoms present isotropisation and crystallization temperatures inferior to their superior and inferior homologues.

Compounds 3a+3e present mesomorphic properties with ordering in nematic mesophases, with ribbon and Schlieren like textures. For compounds 3d and 3e differential calorimetric data evidenced also the existence of crystalline-crystalline transitions both on cooling and heating cycles. In the case of compounds 3a-3c, no crystalline-crystalline transitions, both on cooling and heating cycles could be observed (fig.2).

When heated, compound 3a presents Schlieren characteristic textures, the mesophase starting at 190°C and lasting up to isotropic temperature at 214°C (fig. 3a).
Nematic texture appears (fig. 3c). In the case of compound 3b, on heating, the same Schlieren texture appears, the mesophase begins at 178°C and isotropisation at 190°C (fig. 4a). On cooling, compound 3b evidenced nematic drops (fig. 4b) which maintained down to 180°C, when a nematic Schlieren texture appeared (fig. 4c) and which transforms to a ribbon type texture at 175°C (fig. 4d).

Differential calorimetric analysis of derivatives 3d and 3e highlights the appearance of crystallin-crystallin transitions. During the first heating of compound 3e it was noted the appearance of a crystallin-crystallin transition at 135°C, while the crystalline - liquid crystalline switch takes place at 175°C (fig. 5). Isotropisation takes place at 196°C. The same polymorphism was observed on the cooling phase.

### Table 1

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Cr/Cr</th>
<th>Cr/N</th>
<th>N/I</th>
<th>I/N</th>
<th>N/Cr</th>
<th>Cr/Gr</th>
<th>T_{onset} [°C]</th>
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<tr>
<td>3a n=6</td>
<td>[190]</td>
<td>[214]</td>
<td></td>
<td>218</td>
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<td>[178]</td>
<td>[190]</td>
<td></td>
<td>185</td>
<td>141</td>
<td></td>
<td>256</td>
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<tr>
<td>3c n=8</td>
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<td>[198]</td>
<td></td>
<td>204</td>
<td>146</td>
<td></td>
<td>266</td>
</tr>
<tr>
<td>3d n=9</td>
<td>[130]</td>
<td>[177]</td>
<td>[197]</td>
<td>197</td>
<td>142</td>
<td>131</td>
<td>270</td>
</tr>
<tr>
<td>3e n=10</td>
<td>[135]</td>
<td>[175]</td>
<td>[196]</td>
<td>197</td>
<td>153</td>
<td>135</td>
<td>282</td>
</tr>
<tr>
<td>4a n=6</td>
<td>[230]</td>
<td>[208]</td>
<td>[213]</td>
<td>208</td>
<td>3143</td>
<td></td>
<td>257</td>
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<tr>
<td>4b n=7</td>
<td>[208]</td>
<td>[213]</td>
<td>[208]</td>
<td>208</td>
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<tr>
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<td>[200]</td>
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<td>4e n=10</td>
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<td>[200]</td>
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<td>3143</td>
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</table>

**Abbreviation:** Cr-crystalline, N-nematic, I-isotropic, T_{onset} – the initial temperature of the beginning of thermal degradation

• Data obtained from POM investigations

Fig. 1. Variation of isotropisation and crystallisation temperatures for 3a+3e compounds as a function of the odd/even number of carbon atoms of the alkyl chain (1. Cr/Liq. Cryst.; 2. Liq. Cryst/Cr)

Fig. 2. DSC curves of compound 3a: 1: first heating; 2: first cooling.

Fig. 3. Optical micrographs of compound 3a: (a) first heating, 212°C; (b) first cooling, 215°C and (c) first cooling, 208°C
The polarized optical microscopy analysis indicates the existence of Schliren textures that are specific for nematic mesophases, starting with 175°C and up to isotropisation at 196°C (Fig. 6).

The presence of a reactive hydroxy group and the existence of liquid crystalline properties of compounds 3a-3e make them very suitable for the synthesis of new classes of asymmetric bent core type compounds, by reacting the hydroxyl group with different mesogenic molecules.

Conclusions

Ten new compounds were synthesized through esterification of 2,7-dihydroxynaphthalene with the corresponding 4-(4-alkoxyphenylazo)-benzoic acid chlorides.

The synthesized compounds have been completely characterized by means of ¹H-NMR, ¹³C-NMR, IR, MS spectra.

After DSC and POM analysis it was found that only the mono-esters of 2,7-dihydroxynaphthalene present liquid crystalline properties of enantiotropic type, with mesophase ordering both on heating and cooling cycles. These compounds may be further used for the synthesis of asymmetric bent core type molecules.

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