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ASYMMETRIC BENT-CORE LIQUID CRYSTALS BASED ON A 2,7-DIHYDROXYNAPHTALENE CORE WITH AZO AND ESTERIC CONNECTING GROUPS

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ABSTRACT. Two series of asymmetric bent-core type derivatives containing 2,7-dihydroxynaphtalene as central unit and 4-(4-alkyloxyfenilazo)-benzoyl and 4-methoxy-benzoyl or 3-bromo-4-methoxy-benzoyl side arms as mesogenic groups have been synthesized. The liquid crystalline properties have been investigated by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). All the synthesized compounds presented liquid crystalline properties, mainly monotropic, with smectic or nematic textures.

Keywords: *bent-core compounds, 2,7-dihydroxynaphtalene azo aromatic mesogens*

INTRODUCTION

In the last period, an outstanding development occurs in the field of unconventional liquid crystals, which present very different molecular shapes if compared with the so-called "classic liquid crystals" and that are capable to generate atypical mesophases, with specific textures. Unconventional liquid crystals are organic derivatives with liquid crystalline properties and unusual molecular shape such as: *banana* type mesogens, *bent-core*, *bow shaped* or *boomerang* structures [1-5], *disc-rod* systems [6-9], *butterfly* mesogens [10], dendrimers up to supermolecules [11] and complex supramolecular structures [12]. New types of mesophases were discovered and physical forces permitting the self-assembling of such systems in ordered structured were investigated.

Among the unconventional liquid crystals, the bent core compounds represent a very promising field. Although biaxial nematic phase was predicted by Freiser forty years ago, it remained a hot subject in the literature in the effort to prove the existence of this new mesophase as a physical reality by using the known experimental methods [13]. Now, it is considered that the use of biaxial nematic liquid crystals for LCD will ensure much faster response times at lower costs. In the case of bent core compounds, the reorientation of the molecules does not require much energy when compared to nematics.

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Structure property relations in bent core mesogens are less predictable than those of calamitics. The only criterion need to be applied is that two mesogenic groups should be connected non-linearly. The connection is made through a central unit, which plays a key role in inducing the bent shape of molecules. If the connection between the mesogenic lateral groups is not in tight angle, there is no chance to obtain banana mesogens even if the construction of the molecule in all other buildings stones corresponds to the structure of bananas [14]. The most calamitic molecules can play the mesogenic groups role in *bent core* systems, being constituted from two aromatic rings connected through different connection groups and a terminal chain, linked in *para* position of the aromatic rings. These calamitic molecules are preferentially connected to an aromatic rigid core of five or six atoms, in the way that the angle between the two wings (bending angle) to be between 120 and 140°. Generally, the majority of bent core compounds are 1,3-disubstituted benzenes, 2,7-disubstituted naphthalene ring [15-17], 1,3,4-oxadiazol or 2,5-disubstituted-tiophene [18], 2,6-disubstituted pyridine [19] etc.

An important role on transition temperature controlling, interval and type of forming mesophase has the length, rigidity and the polarity of lateral structures and the length and the chemical nature of terminal chains. The nature, position and direction of connecting groups between rings play an important role on banana mesophases.

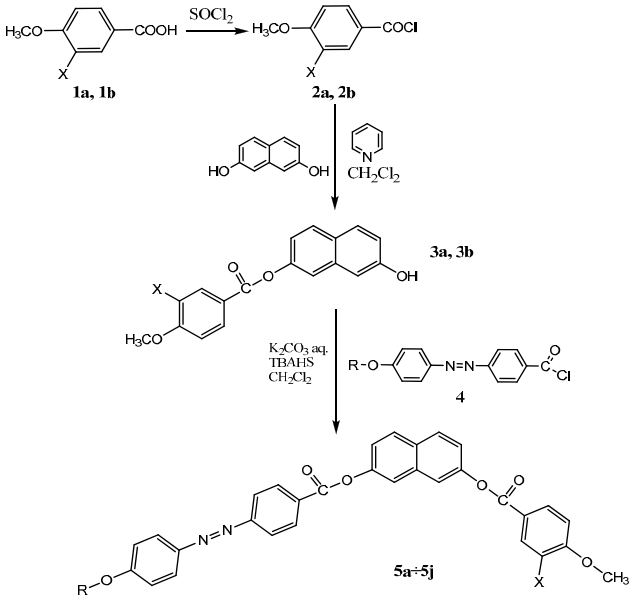
The most successful bent core mesogenic materials exhibiting several (switchable) mesophases contain the sensitive azomethine group. But this group is thermally instable and sensitive to proton and metal surfaces. The *bent-core* molecules containing azo linkage have been little studied, although there are numerous examples for other classes of liquid crystalline compounds in which the presence of this connecting group offered very interesting properties to the synthesized structures [20].

Study of *bent-core* units based on biaxial liquid crystals represents a very actual subject not only from theoretically point of view but practically too. The existence of a stable biaxial nematic mesophase might produce a whole class of liquid crystals based on devices that will considerably improve the switching properties or as optical compensation films etc [21].

This paper presents the synthesis, structural characterization and mesomorphic properties of two new series of asymmetric bent core compounds, containing azo-aromatic and esteric linkages as connecting groups, based on a 2,7-dihydroxynaphthalene core and 4-(4-alcoxifenilazo)-benzoyl and 4-methoxy-benzoyl or 3-bromo-4-methoxy-benzoyl units as mesogenic groups. The liquid crystalline properties were evaluated by means of polarized optical microscopy and differential scanning calorimetry. All the synthesized compounds presented liquid crystalline properties, mainly of monotropic type, with nematic or smectic textures.

RESULTS AND DISCUSSION

The synthesis of the target compounds is depicted in **Scheme 1**. The final compounds were obtained in a two step reaction. In the first step, 2,7-dihydroxynaftalene was reacted with 4-methoxy- or 3-bromo-4-methoxy benzoylchlorides [22] in the presence of pyridine, in anhydrous dichloromethane to form the monoesters **3a**, **3b**. In the second step, monoesters **3a**, **3b** were reacted with 4-(4-alkyloxyphenylazo)-benzoyl chloride, in aqueous K_2CO_3 / dichloromethane, using tetrabutylammonium hydrogen sulfate (*TBAHS*) as phase transfer catalyst. All the obtained compounds were purified by column chromatography (silicagel, methylene chloride : ethyl acetate = 20:1) and characterized by ^{1}H- and ^{13}C-NMR and mass spectrometry. Yields were between 39.4-82.3%.



Scheme 1.

The presence of liquid crystalline properties was investigated by means of differential scanning calorimetry (DSC) and polarized light optical microscopy (POM). All the synthesized **5a ÷ 5j** compounds presented liquid crystalline properties, mainly of monotropic type (only compound **5j** presented enantiotropic liquid crystalline properties).

For a better confirmation of the intervals of mesophases, the DSC runs for compounds **5i** and **5j** were repeated several times with heating-cooling cycles of 10, 20 and 40^0C per minute but no significant changes could be observed. The observed textures were assigned by visual comparison (under the microscope) with literature data [23].

Table 1. Transition temperatures [°C] and transition enthalpies [$J \cdot g^{-1}$] of compounds **5a÷5j**

Comp.	n	*T / °C [ΔH / Jg^{-1}]*						T_{onset}
		Heating (^oC)		*Cooling (^oC)*				
		Cr/N	N/I	I/Sch.	I/Sm_x	N	Cr	
5a	6	-	140 [-48.72]	137*	-	130 [0.24]	96 [46.29]	349
5b	7	-	133 [-36.87]	130*	-	124 [0.22]	104 [42.56]	350
5c	8	-	140 [-47.85]	135*	-	127 [0.20]	108 [29.37]	353
5d	9	-	150 [-59.04]	146*	-	131 [8.47]	107 [2.81]	339
5e	10	-	146 [-55.36]	142*	-	112 [0.21]	92 [39.33]	337
5f	6	-	149 [-48,27]	-	-	99*	86 [21,85]	295
5g	7	-	159 [-45,83]	-	-	108*	103 [19,32]	329
5h	8	-	147 [-45,25]	-	-	109*	98 [27,35]	333
5i	9	-	129 [-32,03]	-	106 [0,35]	-	91 [11,72]	323
5j	10	130 [0,28]	146 [-0,28]	-	135 [0,94]	-	107 [32,51]	319

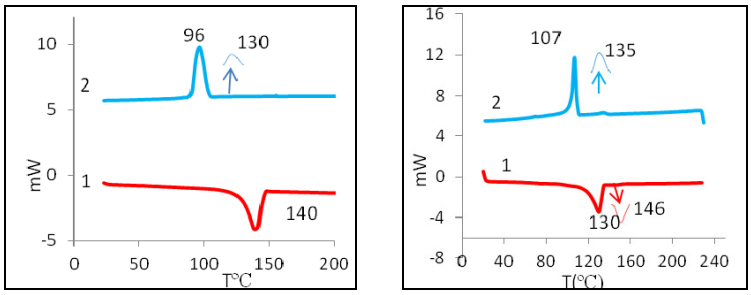
Abbreviation: Cr-crystalline, Sm_x-smectic, I-isotropic, N-nematic, Sch. – Schlieren * Data obtained from POM investigations T_{onset} - the initial temperature at which the degradations processes begin

For all the investigated compounds, the isotropisation temperatures and the isotropic – liquid crystal transitions are relatively low (between 129 – 159^0C on heating and 106 – 146^0C on cooling).

For the **5a ÷ 5e** compounds, the stability range of the mesophases on cooling is reasonable large (between 26 – 50^0C) while for **5f÷5j** brominated compounds is relatively small (between 5 – 28^0C). In the case of compound **5j**, when heated, the stability range of the mesophase is only 16^0C. Taking into consideration the structural differences between the two series of compounds, it may be concluded that the presence of bromine atom in the structure of **5f÷5j** compounds has a negative influence upon the stability of the mesophases.

Due to the very small transition enthalpies, the temperatures of entering into mesophase for **5a÷5h** compounds could be evidenced only by means of polarized optical microscopy.

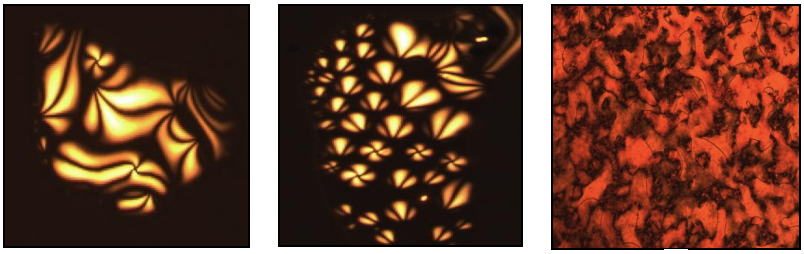
As examples, Figure 1 exemplifies the DSC curves for compounds **5a** and **5j**.



a) **b)**

Figure 1. DSC curves: (a) **5a**: 1 – second heating, 2 – first cooling, (b) **5j**: 1 – second heating, 2 – first cooling

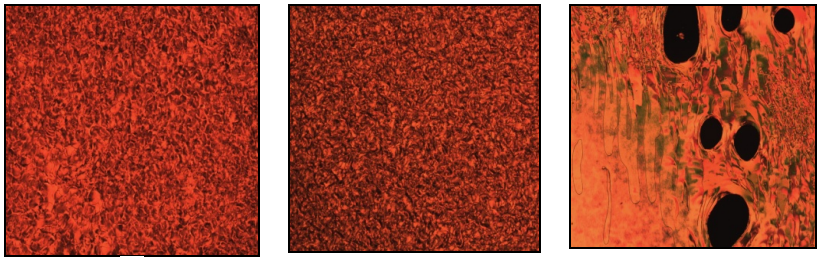
According to POM, on cooling, compound **5a** presents two liquid crystalline transitions: the first one, with Schlieren textures, begins at 137 ^{0}C and ends at 130^{0}C (Figure 2a and 2b); the second one, of nematic type, starts at 130^{0}C and holds until crystallization (96^{0}C) (Figure 2c).



a) **b)** **c)**

Figure. 2. Optical textures for compound **5a**: Schlieren textures, a) 135^{0}C and b) 131^{0}C; nematic texture, c) 127^{0}C

Figure 3 presents some other example of nematic textures of compounds 5b ÷ 5d.



a) **b)** **c)**

Figure 3. Nematic optical textures (cooling): a) **5b**, 118^{0}C, b) **5c**, 115^{0}C, c) **5d**, 120^{0}C.

In the case of brominated compounds **5f÷5j** polarized optical microscopy evidenced both nematic and smectic textures.

Compounds **5f÷5h** have a monotropic behavior, with nematic textures when cooling, while compound **5i** revealed a smectic one (Figure 4).

For compound **5j**, during the heating process polarized optical microscopy showed a nematic texture between 130 – 146^{0}C (Figure 5a). On cooling, between 135 – 107, SmA *bâtonnets* texture appeared (Figure 5b).

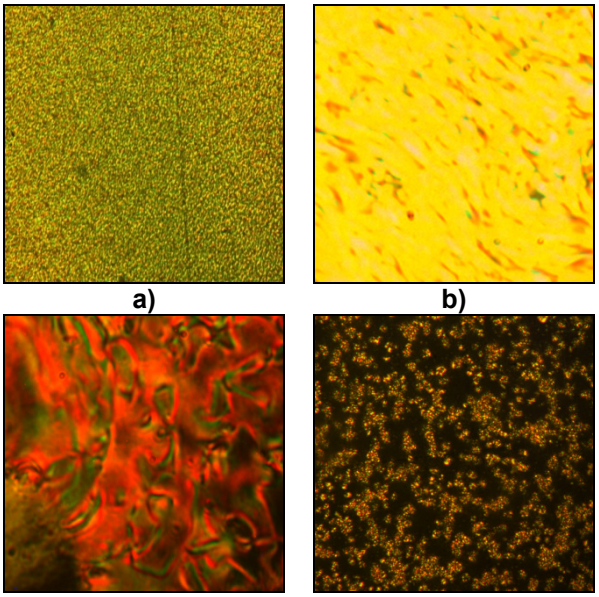


Figure 4. Optical textures, second cooling: nematic:
a) **5f**, 90^{0}C, b) **5g**, 104^{0}C, c) **5h**, 97^{0}C; smectic: d) **5i**, 98^{0}C.

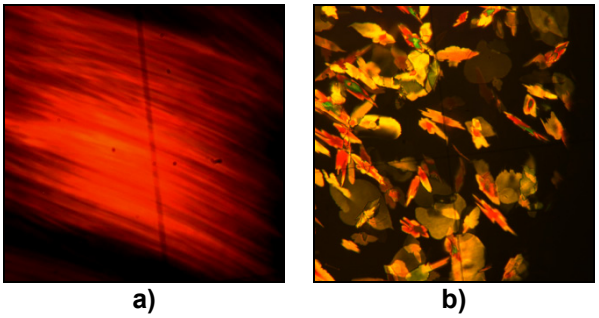


Figure 5. Optical textures for compound **5j**:
a) second heating, 135^{0}C, nematic; b) second cooling, 120^{0}C, smectic A, bâtonnets

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 200^0C higher than the isotropisation temperatures (**Table 1)**. For all **5a ÷ 5j** compounds, thermal degradation took place in only one stage, with a weight loss of about 70%. In all the cases, a residue of about 30% has been left. Such a thermal behavior, with T_{onset} values between 300 and 350^0 is similar with other classes of bent core compounds containing azo-aromatic and esteric linking groups [24,25].

CONCLUSIONS

Two series of asymmetric bent-core derivatives based on 2,7-dihydroxynaphtalene core and with 4-(4-alcoxifenilazo)-benzoyl and 4-methoxy-benzoyl or 3-bromo-4-methoxy-benzoyl wings as mesogenic groups have been synthesized and investigated by DSC and POM from the point of view of liquid crystalline properties. All the synthesized compounds presented liquid crystalline properties, mainly monotropic, with nematic or smectic textures. Thermogravimetric studies evidenced a very good thermal stability for all the investigated compounds.

EXPERIMENTAL SECTION

MATERIALS

3-Bromo-4-metoxy-benzoic acid (**1b**), 4-metoxy-benzoyl chloride (**2a**), 3-bromo-4-metoxy-benzoyl chloride (**2b**) and 4-(4-alkoxyphenylazo)-benzoyl chloride (**4**) have been prepared accordingly to literature data [22, 26]. All other materials used in the present work have been purchased from Sigma Aldrich and used as received. For column chromatography Silica gel 60 (Merck) was used, while for thin layer chromatography Silica gel plates (Merck Silica gel F254) were used.

TECHNIQUES

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 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 10^0C/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_2 atmosphere, with a flow rate of 20 ml/min and a heating rate of 10 ^{0}C/min from 25 to 900°C.

SYNTHESIS

General method for the preparation of 2-(4- methoxyphenylcarbonyloxy) -2-hydroxynaphtalene (3a) and 2-(3-bromo-4-methoxyphenylcarbonyloxy)-2-hydroxynaphtalene (3b). Compounds were prepared by adapting literature data [27]. To a mixture of 2,7-dihydroxynaphtalene (14.18 mmol) and pyridine (86,77 mmol) in dry dichloromethane (80 ml), a solution of acyl chloride **2** (3.53 mmol) in dichloromethane (10 ml) was added dropwise at 0^0C. The solution was stirred at 0^0C for 24 h, diluted with water (100 ml), extracted with dichloromethane, dried over $MgSO_4$ and evaporated. A viscous residue was obtained which was purified by column chromatography on Silica Gel using a mixture of methylene chloride: ethyl acetate 20:1 as eluent and giving the purified products as white powder.

2-(4-Methoxyphenylcarbonyloxy)-2-hydroxynaphtalene (3a). Quantities: 2.27 g (14.18 mmol) 2,7-dihydroxynaphtalene, 7 ml (86.77 mmol) pyridine, 0.60 g (3.53 mmol) 4-methoxybenzoyl chloride. Yield 40.76 % (1.7 g), m.p.= 203^0C. ^{1}H-NMR δ_C ppm (DMSO-d6): 9.86 (s, 1H, -OH), 8.13 (d, 2H, Ar, J= 8.8 Hz), 7.83 (dd, 2H, Ar, J_1= 8.8 Hz, J_2= 15.3 Hz), 7.57 (d, 1H, Ar, J= 2.0 Hz), 7.16 (m, 4H, Ar), 7.10 (dd, 1H, Ar, J_1= 2.3 Hz, J_2= 8.8 Hz), 3.89 (s, 3H, -O-CH_3). ^{13}C-NMR δ_C ppm (DMSO-d6): 164.40, 163.71, 155.95, 148.82, 135.13, 131.97, 129.29, 129.01, 125.66, 121.05, 118.42, 118.22, 116.96, 114.26, 108.48 (1 * >C=O esteric + 14 C, aromatic), 55.61(-O-CH_3). *FT-IR* (KBr, cm^{-1}): 3435.21 (vOH, aromatic), 3068.74 (vCH, aromatic), 2929.86, 2858.5 (vCH, aliphatic), 1718.57 (v O-C=O); m/z (DMSO): 317.16 $[M+Na]^+$.

2-(3-Bromo-4-methoxyphenylcarbonyloxy)-2-hydroxynaphtalene (3b). Quantities: 2.27 g (14.18 mmol) 2,7-dihydroxynaphtalene, 7 mL (86.77 mmol) pyridine, 0.87 g (3.53 mmol) 3-bromo-4-methoxybenzoyl chloride. Yield 31.25 % (1.65 g), m.p.= 185^0C. ^{1}H-NMR δ_C ppm (DMSO-d6): 9.98 (s, 1H, -OH), 8.55 (dd, 1H, Ar, J_1= 2.19, Hz, J_2= 8.55 Hz), 8.295 (d, 1H, Ar, J= 2.19 Hz), 7.86 (1H, d, Ar, J= 8.98 Hz), 7.82 (1H, d, Ar, J= 8.77 Hz), 7.585 (1 H, d, Ar, J= 1.97 Hz), 7.33 (1 H, d, Ar, J= 8.77 Hz), 7.18 (1 H, dd, Ar, J_1= 2.19 Hz, J_2= 8.77 Hz), 7.14 (1H, d, Ar, J= 2.19), 7.10 (1 H, dd, Ar, J_1= 2.41 Hz, J_2= 8.77 Hz), 3.99 (s, 3H, -CH_3).^{13}C-NMR δ_C ppm (DMSO-d6): 163.27, 159.68, 155.92, 148.60, 135.02, 134.12, 131.36, 129.25, 128.99, 125.66, 122.33, 118.43, 118.00, 116.87, 112.58, 110.71, 108.42 (1 * >C=O esteric + 16 C, aromatic), 56.77 (-O-CH_3). *FT-IR* (KBr, cm^{-1}): 3431.36 (v OH, aromatic), 3058.09 (vCH, aromatic), 2962.65, 2941.44 (vCH, aliphatic), 1712.78 (v O-C=O); m/z (DMSO): 395.08 $[M+Na]^+$.

General method for the preparation of 2-((4-alkyloxyphenyl)-4-azophenylcarbonyloxy)-7-(4-methoxyphenylcarbonyloxy)naphtalen (5a÷5e) and 2-((4-alkyloxyphenyl)-4-azophenylcarbonyloxy)-7-(3-bromo-4-methoxy-phenylcarbonyloxy)naphtalen (5f÷5j). Compounds were prepared by adapting literature data [28]. Acyl chlorides were prepared and introduced immediately into synthesis. A mixture of compound **3**, 4-(4-alkyloxyphenylazo)-benzoyl chloride **4**, potassium carbonate, tetrabutylammonium hydrogensulfate (TBAHS) in dichloromethane (150 mL) and water (40 mL) were vigorously stirred for 24 h at room temperature. For a good solubility of the compound **3** in methylene chloride a few drops of tetrahydrofuran (THF) were added. The organic layer was separated, washed several times with distilled water, dried on anhydrous magnesium sulfate and concentrated on rotary evaporator. Compounds (**5a÷5j**) were purified by column chromatography on Silica Gel using a mixture of methylene chloride: ethyl acetate 20:1 as eluent. Orange products were obtained.

2-((4-Hexyloxyphenyl)-4-azophenylcarbonyloxy)-7-(4-methoxyphenyl-carbonyloxy)naphtalen (5a). Quantities: 0.22 g (0.8297 mmol) 2-(4-methoxyphenylcarbonyloxy)-2-hydroxynaphtalene, 0.28 g (0.8297 mmol) 4-(4-hexyloxyphenylazo)-benzoyl chloride, 0.14 g (1.005 mmol) K_2CO_3, 6.4 mg (0.019 mmol) TBAHS. Yield 70.48 % (0.32 g), orange product, liquid crystal: 140^0C (K/I), 137^0C (I/CL), 130^0C (CL/CL), 96^0C (CL/K). ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.37 (d, 2H, Ar, J= 8.4 Hz), 8.20 (d, 2H, Ar, J= 8.8 Hz), 7.99 (d, 2H, J= 7.4 Hz), 7.97(d, 2H, Ar, J= 8.6 Hz), 7.93(dd, 2H, Ar, J_1= 3.7 Hz, J_2=8.9 Hz), 7.69 (dd, 2H, Ar, J_1= 1.7 Hz, J_2= 9.9 Hz), 7.39 (dd, 1H, Ar, J_1= 2.2 Hz, J_2= 6.8 Hz), 7.36 (dd, 1H, Ar, J_1= 2.2 Hz, J_2= 6.58 Hz), 7.01 (m, 4H, Ar), 4.05 (t, 2H, -O-CH_2-), 3.90 (s, 3H, -O-CH_3), 1.83 (qv, 2H, -CH_2-), 1.49 (qv, 2H, -CH_2-), 1.32 (m, 4H, -CH_2-), 0.92 (t, 3H, -CH_3).^{13}C-NMR δ_C ppm ($CDCl_3$): 164.95, 164.79, 163.99, 162.49, 155.86, 149.48, 149.24, 146.86, 134.43, 132.38, 131.28, 130.34, 129.54, 129.42, 129.32, 125.33, 122.56, 121.73, 121.44, 121.06, 118.62, 118.54, 114.83, 113.89 (2*>C=O esteric + 22 C, aromatic), 68.46, 55.53, 31.56, 29.13, 25.68, 22.60, 14.04 (1*-O-CH_2- + 1*-O-CH_3 + 5 C, aliphatic); m/z($CHCl_3$): 603.36 [M+1].

2-((4-Heptyloxyphenyl)-4-azophenylcarbonyloxy)-7-(4-methoxy-phenyl- carbonyloxy)naphtalen (5b). Quantities: 0.22 g (0.8297 mmol) 2-(4-methoxyphenylcarbonyloxy)-2-hydroxynaphtalene, 0.29 g (0.8297 mmol) 4-(4-heptyloxyphenylazo)-benzoyl chloride, 0.14 g (1.005 mmol) K_2CO_3, 6.4 mg (0.019 mmol) TBAHS. Yield 68.81 % (0.32 g), orange product, liquid crystal: 133^0C (K/I), 130^0C (I/CL), 124^0C (CL/CL), 104^0C (CL/K). ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.37 (d, 2H, Ar, J= 8.5 Hz), 8.20 (d, 2H, Ar, J= 8.9 Hz), 7.99 (d, 2H, Ar, J= 7.24 Hz), 7.965 (d, 2H, Ar, J= 7.46 Hz), 7.925 (dd, 2H, Ar, J_1= 3.6 Hz, J_2= 8.99 Hz), 7.69 (dd, 2H, Ar, J_1= 2.0 Hz, J_2= 9.86 Hz), 7.385 (dd, 1H, Ar, J_1= 2.2 Hz, J_2= 6.8 Hz), 7.365 (dd, 1H, Ar, J_1= 2.2 Hz, J_2= 6.58 Hz), 7.01 (m, 4H, Ar), 4.05 (t, 2H, -O-CH_2-), 3.89 (s, 3H, -O-CH_3), 1.83 (qv, 2H, -CH_2-), 1.48 (qv, 2H, -CH_2-), 1.32 (m,

6H, -CH_2-), 0.91 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.94, 164.79, 163.98, 162.48, 155.84, 149.46, 149.23, 146.85, 134.42, 132.38, 131.27, 130.32, 129.53, 129.42, 129.33, 125.32, 122.55, 121.71, 121.44, 121.05, 118.62, 118.53, 114.82, 113.88 (2*>C=O esteric + 22 C, aromatic), 68.45, 55.52, 31.77, 29.16, 29.04, 25.96, 22.61, 14.10 (1*-O-CH_2- + 1*-O-CH_3 + 6 C, aliphatic); m/z($CHCl_3$): 617.38 [M+1].

2-((4-Octyloxyphenyl)-4-azophenylcarbonyloxy)-7-(4-methoxyphenyl-carbonyloxy)naphtalen (5c). Quantities: 0.22 g (0.8297 mmol) 2-(4-methoxy-phenylcarbonyloxy)-2-hydroxynaphtalene, 0.31 g (0.8297 mmol) 4-(4-octyloxy-phenylazo)-benzoyl chloride, 0.14 g (1.005 mmol) K_2CO_3, 6.4 mg (0.019 mmol) TBAHS. Yield 42.10 % (0.20 g), orange product, liquid crystal: 140^{0}C (K/I), 135^{0}C (I/CL), 127^{0}C (CL/CL), 108^{0}C (CL/K). ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.38 (d, 2H, Ar, J= 8.5 Hz), 8.21 (d, 2H, Ar, J= 8.7 Hz), 7.99 (d, 2H, Ar, J= 7.7 Hz), 7.97 (d, 2H, Ar, J= 8.7 Hz), 7.93 (dd, 2H, Ar, J_1= 4.0 Hz, J_2= 8.9 Hz), 7.69 (dd, 2H, Ar, J_1= 2.0 Hz, J_2= 10.1 Hz), 7.39 (dd, 1H, Ar, J_1= 2.0 Hz, J_2= 7.1 Hz), 7.37 (dd, 1H, Ar, J_1= 2.0 Hz, J_2= 7.1 Hz), 7.02 (m, 4H, Ar), 4.06 (t, 2H, -O-CH_2-), 3.90 (s, 3H, -O-CH_3), 1.83 (qv, 2H, -CH_2-), 1.49 (qv, 2H, -CH_2-), 1.33 (m, 8H, -CH_2-), 0.90 (t, 3H, -CH_3).^{13}C-NMR δ_C ppm ($CDCl_3$): 164.96, 164.81, 164.00, 162.50, 155.87, 149.48, 149.24, 146.87, 134.44, 132.39, 131.29, 130.34, 129.55, 129.43, 129.34, 125.33, 122.56, 121.74, 121.45, 121.07, 118.63, 118.55, 114.84, 113.90 (2*>C=O esteric + 22 C, aromatic), 68.47, 55.54, 31.82, 29.35, 29.24, 29.17, 26.01, 22.67, 14.12 (1*-O-CH_2- + 1*-O-CH_3 + 7 C, aliphatic); m/z($CHCl_3$): 631.39 [M+1].

2-((4-Nonyloxyphenyl)-4-azophenylcarbonyloxy)-7-(4-methoxyphenyl-carbonyloxy)naphtalen (5d). Quantities: 0.22 g (0.8297 mmol) 2-(4-methoxyphenylcarbonyloxy)-2-hydroxynaphtalene, 0.32 g (0.8297 mmol) 4-(4-nonyloxyphenylazo)-benzoyl chloride, 0.14 g (1.005 mmol) K_2CO_3, 6.4 mg (0.019 mmol) TBAHS, yield 82.30 % (0.32 g), orange product, liquid crystal: 150^{0}C (K/I), 146^{0}C (I/CL), 131^{0}C (CL/CL), 107^{0}C (CL/K) ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.36 (d, 2H, Ar, J= 8.4 Hz), 8.20 (d, 2H, Ar, J= 8.7 Hz), 7.98 (d, 2H, Ar, J= 7.0 Hz), 7.96 (d, 2H, Ar, J= 8.5Hz), 7.92 (dd, 2H, Ar, J_1= 3.4 Hz, J_2= 8.8 Hz), 7.68 (dd, 2H, Ar, J_1= 1.4 Hz, J_2= 9.6 Hz), 7.38 (dd, 1H, Ar, J_1= 2.1 Hz, J_2= 7.3 Hz), 7.36 (dd, 1H, Ar, J_1= 2.2 Hz, J_2= 7.3 Hz), 7.00 (m, 4H, Ar), 4.04 (t, 2H, -O-CH_2-), 3.88 (s, 3H, -CH_3), 1.82 (qv, 2H, -CH_2-), 1.47 (qv, 2H, -CH_2-), 1.29 (m, 10 H, -CH_2-), 0.89 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.93, 164.77, 163.98, 162.49, 155.84, 149.47, 149.23, 146.85, 134.43, 132.37, 131.27, 130.33, 129.52, 129.41, 129.31, 125.33, 122.55, 121.72, 121.43, 121.05, 118.61, 118.53, 114.82, 113.89 (2*>C=O esteric + 22 C, aromatic), 68.45, 55.51, 31.87, 29.53, 29.38, 29.26, 29.16, 26.00, 22.68, 14.12 (1*-O-CH_2- + 1*-O-CH_3 + 8 C, aliphatic); m/z($CHCl_3$): 645.41 [M+1].

2-((4-Decyloxyphenyl)-4-azophenylcarbonyloxy)-7-(4-methoxy phenyl- carbonyloxy)naphtalen (5e). Quantities: 0.22 g (0.8297 mmol) 2-(4-methoxyphenylcarbonyloxy)-2-hydroxynaphtalene, 0.33 g (0.8297 mmol) 4-(4-decyloxyphenylazo)-benzoyl chloride, 0.14 g (1.005 mmol) K_2CO_3, 6.4 mg (0.019 mmol) TBAHS. Yield 44.33 % (0.32 g), orange product, liquid crystal: 146^{0}C (K/I), 142^{0}C (I/CL), 112^{0}C (CL/CL), 92^{0}C (CL/K). ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.37 (d, 2H, Ar, J=8.1 Hz), 8.20 (d, 2H, Ar, J= 8.5 Hz), 7.97 (d, 2H, Ar, J= 7.1 Hz), 7.96 (d, 2H, Ar, J= 8.4 Hz), 7.93 (dd, 2H, Ar, J_1= 3.3 Hz, J_2= 8.7 Hz), 7.67 (dd, 2H, Ar, J_1= 1.3 Hz, J_2= 9.5 Hz), 7.38 (dd, 1H, Ar, J_1= 2.1 Hz, J_2= 7.3 Hz), 7.35 (dd, 1H, Ar, J_1= 2.3 Hz, J_2= 7.4 Hz), 7.01 (m, 4H, Ar), 4.04 (t, 2H, -O-CH_2-), 3.89 (s, 3H, -CH_3), 1.82 (qv, 2H, -CH_2-), 1.47 (qv, 2H, -CH_2-), 1.32 (m, 12H, -CH_2-), 0.89 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.94, 164.78, 163.98, 162.48, 155.84, 149.47, 149.23, 146.85, 134.42, 132.38, 131.27, 130.32, 129.53, 129.42, 129.31, 125.33, 122.55, 121.71, 121.44, 121.05, 118.62, 118.53, 114.82, 113.88 (2*>C=O esteric + 22 C, aromatic), 68.45, 55.52, 31.89, 29.56, 29.56, 29.38, 29.32, 29.16, 26.00, 22.69, 14.13 (1*-O-CH_2- + 1*-O-CH_3 + 9 C, aliphatic); m/z($CHCl_3$): 659.43 [M+1].

2-((4-Hexyloxyphenyl)-4-azophenylcarbonyloxy)-7-(3-bromo-4-meth-oxyphenylcarbonyloxy)naphtalen (5f). Quantities: 0.20 g (0.5373 mmol) 2-(3-bromo-4-methoxyphenyl-carbonyloxy)-2-hydroxynaphtalene 0.20 g (0.591 mmol) 4-(4-hexyloxyphenylazo)-benzoyl chloride, 0.10 g (0.7163 mmol) K_2CO_3, 4.52 mg (0.013 mmol) TBAHS. Yield 50 % (0.18 g), orange product, liquid crystal: 149^{0}C (K/I), 99^{0}C (I/CL), 86^{0}C (CL/K). ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.45 (d, 1H, Ar, J= 2.1 Hz), 8.38 (d, 2H, Ar, J= 8.6 Hz), 8.19 (dd, 1H, Ar, J_1= 2.1 Hz, J_2= 8.6 Hz), 7.96 (m, 6H, Ar), 7.71 (d, 1H, Ar, J= 2.0 Hz), 7.68 (d, 1H, Ar, J= 2.0 Hz), 7.40 (dd, 1H, Ar, J_1= 2.3 Hz, J_2= 8.9 Hz), 7.36 (dd, 1H, Ar, J_1= 2.2 Hz, J_2= 8.9 Hz), 7.02 (m, 3H, Ar), 4.06 (t, 2H, -O-CH_2-), 4.01 (s, 3H, -O-CH_3), 1.83 (qv, 2H, -CH_2-), 1.50 (qv, 2H, -CH_2-), 1.37 (m, 4H, -CH_2-), 0.93 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.81, 163.85, 162.54, 160.18, 155.94, 149.37, 149.28, 146.93, 135.44, 134.44, 131.43, 131.31, 130.36, 129.64, 129.46, 125.35, 123.03, 122.58, 121.22, 118.60, 114.87, 111.60, 111.25 (2*>C=O esteric + 21 C, aromatic), 68.51, 56.57, 31.58, 29.15, 25.70, 22.61, 14.03 (1*-O-CH_2- + 1*-O-CH_3 + 5 C, aliphatic). m/z($CHCl_3$): 681.32 [M+1].

2-((4-Heptyloxyphenyl)-4-azophenylcarbonyloxy)-7-(3-bromo-4-meth-oxyphenylcarbonyloxy)naphtalen (5g). Quantities: 0.20 g (0.5373 mmol) 2-(3-bromo-4-methoxyphenyl-carbonyloxy)-2-hydroxynaphtalene 0.21 g (0.591 mmol) 4-(4-heptyloxyphenylazo)-benzoyl chloride, 0.10 g (0.7163 mmol) K_2CO_3, 4.52 mg (0.013 mmol) TBAHS. Yield 40.54 % (0.15 g), orange product, liquid crystal: 159^{0}C (K/I), 108^{0}C (I/CL), 103^{0}C (CL/K). ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.45 (d, 1H, Ar, J= 1.9 Hz), 8.38 (d, 2H, Ar, J= 8.5 Hz), 8.19 (dd, 1H, Ar, J_1= 1.9 Hz, J_2= 8.6 Hz), 7.96 (m, 6H, Ar), 7.71 (d, 1H, Ar, J= 1.6 Hz), 7.68 (d, 1H, Ar, J= 1.6 Hz), 7.40 (dd, 1H, Ar, J_1= 2.1 Hz, J_2= 8.9 Hz), 7.36 (dd, 1H, Ar, J_1= 2.1 Hz, J_2= 8.9 Hz), 7.02 (m, 3H, Ar), 4.06 (t, 2H, -O-CH_2-), 4.00 (s, 3H, -O-CH_3), 1.83

(qv, 2H,-CH_2-), 1.49 (qv, 2H, -CH_2-), 1.36 (m, 6H, -CH_2-), 0.91 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.79, 163.83, 162.53, 160.17, 155.93, 149.36, 149.27, 146.92, 135.43, 134.43, 131.41, 131.29, 130.35, 129.63, 129.44, 125.34, 123.02, 122.58, 121.21, 118.58, 114.86, 111.80, 111.24 (2*>C=O esteric + 21 C, aromatic), 68.50, 56.56, 31.78, 29.19, 29.05, 25.98, 22.61, 14.08 (1*-O-CH_2- + 1*-O-CH_3 + 6 C, aliphatic). m/z($CHCl_3$): 695.19 [M+1].

2-((4-Octyloxyphenyl)-4-azophenylcarbonyloxy)-7-(3-bromo-4-methoxyphenylcarbonyloxy)naphtalen (5h). Quantities: 0.20 g (0.5373 mmol) 2-(3-bromo-4-methoxyphenyl-carbonyloxy)-2-hydroxynaphtalene, 0.22 g (0.591 mmol) 4-(4-octyloxyphenylazo)-benzoyl chloride, 0.10 g (0.7163 mmol) K_2CO_3, 4.52 mg (0.013 mmol) TBAHS. Yield 39.47 % (0.15 g), orange product, liquid crystal: 147^{0}C (K/I), 109^{0}C (I/CL), 98^{0}C (CL/K). ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.45 (d, 1H, Ar, J= 2.1 Hz), 8.37 (d, 2H, Ar, J= 8.3 Hz), 8.19 (dd, 1H, Ar, J_1= 2.1 Hz, J_2= 8.6 Hz), 7.96 (m, 6H, Ar), 7.71 (d, 1H, Ar, J= 2.1 Hz), 7.68 (d, 1H, Ar, J= 2.1Hz), 7.40 (dd, 1H, Ar, J_1= 2.3 Hz, J_2= 8.9 Hz), 7.36 (dd, 1H, Ar, J_1= 2.2 Hz, J_2= 8.8 Hz), 7.02 (m, 3H, Ar), 4.06 (t, 2H, -O-CH_2-), 4.00 (s, 3H, -O-CH_3), 1.83 (qv, 2H, -CH_2-), 1.49 (qv, 2H, -CH_2-), 1.35 (m, 8H, -CH_2-), 0.90 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.80, 163.85, 162.51, 160.13, 155.88, 149.31, 149.23, 146.87, 135.41, 134.39, 131.42, 131.28, 130.31, 129.61, 129.44, 125.32, 122.96, 122.57, 121.21, 118.59, 114.83, 111.75, 111.21 (2*>C=O esteric + 21 C, aromatic), 68.47, 56.55, 31.81, 29.34, 29.24, 29.17, 26.01, 22.67, 14.12 (1*-O-CH_2- + 1*-O-CH_3 + 7 C, aliphatic). m/z($CHCl_3$): 708.14 [M+1].

2-((4-Nonyloxyphenyl)-4-azophenylcarbonyloxy)-7-(3-bromo-4-methoxyphenylcarbonyloxy)naphtalene (5i). Quantities: 0.20 g (0.5373 mmol) 2-(3-bromo-4-methoxyphenyl-carbonyloxy)-2-hydroxynaphtalene, 0.23 g (0.591 mmol) 4-(4-nonyloxyphenylazo)-benzoyl chloride, 0.10 g (0.7163 mmol) K_2CO_3, 4.52 mg (0.013 mmol) TBAHS, yield 78.32 % (0.11 g), orange product, liquid crystal: 129^{0}C (K/I), 106^{0}C (I/CL), 91^{0}C (CL/K). ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.44 (d, 1H, Ar, J= 1.6 Hz), 8.37 (d, 2H, Ar, J= 8.4 Hz), 8.18 (dd, 1H, Ar, J_1= 5.7 Hz, J_2= 7.2 Hz), 7.94 (m, 6H, Ar), 7.69 (d, 1H, Ar, J= 2.4 Hz), 7.68 (d, 1H, Ar, J= 2.3Hz), 7.39 (dd, 1H, Ar, J_1=1.7 Hz, J_2=8.9 Hz), 7.36 (dd, 1H, Ar, J_1= 2.2 Hz, J_2= 8.8 Hz), 7.01 (m, 3H, Ar), 4.05 (t, 2H, -O-CH_2-), 3.99 (s, 3H, -O-CH_3), 1.84 (qv, 2H,-CH_2-), 1.47 (qv, 2H, -CH_2-), 1.29 (m, 10H, -CH_2-), 0.88 (t, 3H, -CH_3).^{13}C-NMR δ_C ppm ($CDCl_3$): 164.78, 163.83, 162.50, 160.12, 155.87, 149.31, 149.25, 146.86, 135.39, 134.39, 131.43, 131.29, 130.28, 129.60, 129.43, 125.44, 122.94, 122.56, 121.20, 118.57, 114.83, 111.75, 111.21 (2*>C=O esteric + 21 C, aromatic), 68.46, 56.54, 31.88, 29.53, 29.38, 29.26, 29.16, 26.00, 22.67, 14.12 (1*-O-CH_2- + 1*-O-CH_3 + 8 C, aliphatic). m/z($CHCl_3$): 723.15 [M+1].

2-((4-Decyloxyphenyl)-4-azophenylcarbonyloxy)-7-(3-bromo-4-methoxyphenylcarbonyloxy)naphtalen (5j). Quantities: 0.20 g (0.5373 mmol) 2-(3-bromo-4-methoxyphenyl-carbonyloxy)-2-hydroxynaphtalene, 0.236 g (0.591 mmol) 4-(4-decyloxyphenylazo)-benzoyl chloride, 0.10 g (0.7163 mmol) K_2CO_3,

4.52 mg (0.013 mmol) TBAHS. Yield 70.88 % (0.28 g), orange product, liquid crystal: 130^0C (K/K), 146^0C (CL/I), 135^0C (I/CL), 107^0C (CL/K). ^{1}H-NMR δ_C ppm ($CDCl_3$): 8.44 (d, 1H, Ar, J= 1.5 Hz), 8.37 (d, 2H, Ar, J= 8.3 Hz), 8.18 (dd, 1H, Ar, J_1= 5.6 Hz, J_2= 7.4 Hz), 7.95 (m, 6H, Ar), 7.70 (d, 1H, Ar, J= 2.3 Hz), 7.67 (d, 1H, Ar, J= 2.3Hz), 7.39 (dd, 1H, Ar, J_1= 1.7 Hz, J_2=8.9 Hz), 7.35 (dd, 1H, Ar, J_1= 2.3 Hz, J_2= 8.6 Hz), 7.00 (m, 3H, Ar), 4.05 (t, 2H, -O-CH_2-), 3.99 (s, 3H, -O-CH_3), 1.82 (qv, 2H,-CH_2-), 1.46 (qv, 2H, -CH_2-), 1.31 (m, 12H, -CH_2-), 0.88 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.78, 163.83, 162.50, 160.12, 155.86, 149.30, 149.23, 146.86, 135.39, 134.39, 131.41, 131.28, 130.29, 129.60, 129.44, 125.45, 122.94, 122.56, 121.20, 118.58, 114.84, 111.74, 111.20 (2*>C=O esteric + 21 C, aromatic), 68.47, 56.55, 31.89, 29.58, 29.56, 29.38, 29.32, 29.16, 26.00, 22.69, 14.13 (1*-O-CH_2- + 1*-O-CH_3 + 8 C, aliphatic). m/z($CHCl_3$): 736.21 [M+1].

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