Symmetric Bent-core Liquid Crystals Based on a 1,3-bis-(4‘-hydroxyphenylazo) Benzene Core

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The paper presents the synthesis and structural characterization of some new symmetric bent-core compounds with liquid crystalline properties. They were obtained by esterification of a 1,3-bis-(4‘-hydroxyphenylazo)-benzene central core with a series of 4-alkoxybenzoic and aliphatic acids, in presence of N,N’-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). Four compounds presented liquid crystalline properties evidenced by polarizing optical microscopy and differential scanning calorimetry.

Keywords: liquid crystals, symmetric bent-core compounds, 1,3-bis-(4‘-hydroxyphenylazo)benzene

The field of liquid crystals has been vigorously investigated for about half a century and numerous important applications have been developed for them in modern technologies [1]. For example, LC display panels and LC-based organic light emitters are widely used in the information display industry. Liquid crystals formed by bent-shaped molecules represent a growing topic in liquid crystal research.

Liquid crystals (LCs) are a state of matter that have intermediate properties between those of a conventional liquid and a solid crystal [2].

Being a new member in the LC family, banana-shaped LCs have attracted intense attention because of their electro-optically switchable ferro- and antiferroelectricity although the individual molecules are achiral [3–7]. The relationship between the molecular structures and their mesomorphic properties is one of the most intensively studied topic for banana shaped LCs.

Since the beginning of research on the *bent-core* liquid crystals many banana-shaped mesogens have been synthesized, most of them contain four to eight benzene rings [8].

This paper presents the synthesis, characterization and liquid crystalline properties of new symmetric banana shaped compounds, which have as central core 1,3-bis-(4‘- hydroxyphenylazo)benzene. The obtained compounds contain three or five benzene-rings connected through azo and esteric linkage and aliphatic chain at the end. The mesomorphic properties were investigated by differential scanning calorimetry and polarized optical microscopy.

Experimental part

Materials and methods

Analytical reagents such as m-phenylenediamine, aliphatic acids, 4-hydroxybenzoic acid, DCC (N,N‘-dicyclohexylcarbodiimide), DMAP (4-dimethylamino-pyridine) were provided either by Aldrich (Germany) or by Merck (Germany) and were used without further purification. Silica gel 60 (Merck) was used for column chromatography (CC). Thin-layer chromatography (TLC) was performed on silica gel plates (Merck, silica gel F_{254}).

Confirmation of the structures of the intermediates and final products was obtained by ^{1}H-NMR and ^{13}C-NMR, using a Bruker Avance DRX 400 MHz spectrometer (Rheinstein, Germany) with tetramethylsilane 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 (Santa Clara, CA,USA)).

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-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 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 to 900^0C. In order to obtain comparable data, constant operational parameters were kept for all samples.

Synthesis

Synthesis of the central core

1,3-bis-(4‘-hydroxyphenylazo)benzene (2): 1.5g (0.008 mol) m-phenylenediamine dihydrochloride was dissolved in a solution containing 24.11 mL (0.76 mol) hydrochloric acid 32% and 10.4 mL water. The mixture was cooled to -5^0C, and then a solution of $NaNO_2$ (0.018 mol) and 9 mL water was added under stirring to the mixture above. After the addition was finished, the mixture was stirred for 1h. A solution containing 0.93g (0.0098 mol) phenol and 3 mL diethyl ether was added, and the mixture was stirred for another 4 h at 0-5^0C. The precipitated 3-((4-hydroxyphenyl)azo)benzenediazonium salt was filtered off and added slowly over a solution containing 1.24g (0.013 mol) phenol, 1.24g (0.0089 mol) K_2CO_3 and 2.32g (0.041 mol) KOH in 110 mL water, cooled at 0^0C. After 10 h of stirring, the precipitate was filtered off and washed with 400 mL water. The product was purified by CC, m.p.= 216^0C. ***^{1}H-NMR δ_H (DMSO):*** 10.42 (s, 2H, -OH), 8.18 (m, 1H, Ar, J=1.97 Hz), 7.97 (dd, 2H, Ar, J_1=8.76 Hz, J_2=1.97 Hz), 7.885 (d, 4H, Ar, J=8.77 Hz), 7.75 (m, 1H, Ar, J=7.67 Hz), 7.00 (d, 4H, Ar, J=8.77 Hz).***^{13}C-NMR δ_C (DMSO):*** 161.34, 152.91, 145.18, 130.26, 125.16, 124.54, 116.02,

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113.71 (8C aromatic). *FT-IR* (KBr, cm^{-1}): 3244 (ν -OH), *m/z* ($CHCl_3$): 319.03 $[M+1]^+$.

General method for synthesis of compounds 4a-e

To a mixture of 1 equiv. compound **(2)** and 2 equiv. of **(3a-e)** 4-alkyloxybenzoic acids in 100 mL anhydrous dichloromethane, 3.6 equiv. of DCC and 3 equiv. of DMAP were added. The reaction mixture was stirred for 72 h at room temperature and then the precipitated N,N'-dicyclohexylurea (DCCU) was filtered off. The solvent was evaporated in vacuum and the solid was chromatographed on silicagel using a 20/1 mixture of dichloromethane/ethyl acetate as eluent.

1,3-bis-(4-(4-hexyloxybenzoil)phenylazo)-benzene (4a)

Quantities: 1,3-bis-(4-hydroxyphenylazo)-benzene ***(2)*** (0.3 g; 0.94 mmol), 4-hexyloxybenzoic acid ***(3a)*** (0.419 g; 1.89 mmol), DCC (0.700 g; 3.39 mmol), DMAP (0.345 g; 2.82 mmol), 100 mL dry dichloromethane. Orange product, η= 21% (0.150 g), liquid crystal: 141^0C (K/LC), 171^0C (LC/I), 168^0C (I/LC), 129^0C (LC/K) .***^1H-NMR δ_H ppm ($CDCl_3$):*** 8.45 (m, 1H, Ar), 8.17 (d, 4H, Ar, J=8.76 Hz), 8.05 (m, 6H, Ar), 7.68 (m, 1H, Ar), 7.40 (d, 4H, Ar, J=8.77 Hz), 6.99 (d, 4H, Ar, J=8.99 Hz), 4.05 (t, 4H, $-O-CH_2$), 1.83 (cv, 4H, $-CH_2$), 1.49 (cv, 4H, $-CH_2$), 1.36 (m, 8H, aliphatic), 0.92 (t, 6H, $-CH_3$). ***^{13}C-NMR δ_C ppm ($CDCl_3$):*** 164.55 (>C=O esteric), 163.69, 153.42, 153.32, 150.04, 132.34, 129.62, 125.32, 124.27, 122.49, 121.15, 116.42, 114.35 (12C, aromatic); 68.33, 31.50, 29.01, 25.61, 22.54, 13.98 (6C, aliphatic). *m/z* ($CHCl_3$): 727.23 $[M+1]^+$.

1,3-bis-(4-(4-heptyloxybenzoil)phenylazo)-benzene (4b)

Quantities:1,3-bis-(4-hydroxyphenylazo)-benzene ***(2)*** (0.3 g; 0.94 mmol), 4-heptyloxybenzoic acid ***(3b)*** (0.445 g; 1.89 mmol), DCC (0.700g; 3.39 mmol), DMAP (0.345g; 2.82 mmol), 100 mL dry dichloromethane. Orange product, η = 21% (0.150 g), liquid crystal: 148^0C (K/LC), 158^0C (LC/I), 152^0C (I/LC), 128^0C (LC/K) .***^1H-NMR δ_H ppm ($CDCl_3$):*** 8.45 (m, 1H, Ar), 8.16 (d, 4H, Ar, J=8.77 Hz), 8.05 (m, 6H, Ar), 7.68 (m, 1H, Ar), 7.40 (d, 4H, Ar, J=8.77 Hz), 6.98 (d, 4H, Ar, J=8.77 Hz), 4.05 (t, 4H, $-O-CH_2$), 1.83 (cv, 4H, $-CH_2$), 1.48 (cv, 4H, $-CH_2$), 1.33 (m, 12H, aliphatic), 0.91 (t, 6H, $-CH_3$). ***^{13}C-NMR δ_C ppm ($CDCl_3$):*** 164.61 (>C=O estheric), 163.75, 153.48, 153.38, 150.10, 132.39, 129.64, 125.37, 124.32, 122.54, 121.20, 116.47, 114.40 (12C, aromatic); 68.38, 31.76, 29.11, 29.04, 22.96, 22.60, 14.08 (7C, aliphatic). *m/z* ($CHCl_3$): 755.59 $[M+1]^+$.

1,3-bis-(4-(4-octyloxybenzoil)phenylazo)-benzene (4c)

Quantities: 1,3-bis-(4-hydroxyphenylazo)-benzene ***(2)*** (0.3 g; 0.94 mmol), 4-octyloxybenzoic acid ***(3c)*** (0.471 g; 1.88 mmol), DCC (0.700 g; 3.39 mmol), DMAP (0.345g; 2.82 mmol), 100 mL dry dichloromethane. Orange product, η= 44% (0,327 g), liquid crystal: 135^0C (K/LC), 155^0C (LC/I), 151^0C (I/LC), 116^0C (LC/K).***^1H-NMR δ_H ppm ($CDCl_3$):*** 8.45 (m, 1H, Ar), 8.16 (d, 4H, Ar, J=8.77 Hz), 8.04 (m, 6H, Ar), 7.67 (m, 1H, Ar), 7.39 (d, 4H, Ar, J=8.77 Hz), 6.98 (d, 4H, Ar, J=8.98 Hz), 4.05 (t, 4H, $-O-CH_2$), 1.82 (cv, 4H, $-CH_2$), 1.47 (cv, 4H, $-CH_2$), 1.30 (m, 16H, aliphatic), 0.90 (t, 6H, $-CH_3$). ***^{13}C-NMR δ_C ppm ($CDCl_3$):*** 164.55 (>C=O esteric), 163.72, 153.45, 153.33, 150.06, 132.35, 129.63, 125.33, 124.29, 122.50, 121.18, 116.48, 114.37 (12C, aromatic); 68.35, 31.78, 29.30, 29.18, 29.08, 25.97, 22.62, 14.07 (8C, aliphatic). *m/z* ($CHCl_3$): 783.28 $[M+1]^+$.

1,3-bis-(4-(4-nonyloxybenzoil)phenylazo)-benzene (4d)

Quantities:1,3-bis-(4-hydroxyphenylazo)-benzene ***(2)*** (0.4 g; 1.26 mmol), 4-nonyloxybenzoic acid ***(3d)*** (0.664 g; 2.52 mmol), DCC (0.934g; 4.53 mmol), DMAP (0.461g; 3.77 mmol), 100 mL dry dichloromethane. Orange product, η= 40% (0.410 g), liquid crystal: 140^0C (K/LC), 148^0C (LC/I), 145^0C (I/LC), 118^0C (LC/K) .***^1H-NMR δ_H ppm ($CDCl_3$):*** 8.45 (m, 1H, Ar), 8.16 (d, 4H, Ar, J=8.77 Hz), 8.05 (m, 6H, Ar), 7.67 (m, 1H, Ar), 7.40 (d, 4H, Ar, J=8.77 Hz), 6.98 (d, 4H, Ar, J=8.77 Hz), 4.05 (t, 4H, $-O-CH_2$), 1.82 (cv, 4H, $-CH_2$), 1.48 (cv, 4H, $-CH_2$), 1.30 (m, 20H, aliphatic), 0.89 (t, 6H, $-CH_3$). ***^{13}C-NMR δ_C ppm ($CDCl_3$):*** 164.60 (>C=O estheric), 163.76, 153.49, 153.37, 150.10, 132.39, 129.67, 125.37, 124.32, 122.54, 121.21, 116.50, 114.40 (12C, aromatic); 68.39, 31.88, 29.52, 29.38, 29.26, 29.11, 25.99, 22.67 14.11 (9C, aliphatic). *m/z* ($CHCl_3$): 811.66 $[M+1]^+$.

1,3-bis-(4-(4-decyloxybenzoil)phenylazo)-benzene (4e)

Quantities: 1,3-bis-(4-hydroxyphenylazo)-benzene ***(2)*** (0.3 g; 0.94 mmol), 4-decyloxybenzoic acid ***(3e)*** (0.525 g; 1.89 mmol), DCC (0.700 g; 3.39 mmol), DMAP (0.345g; 2.82 mmol), 100 mL dry dichloromethane. Orange product, η = 21% (0.150 g), m.p = 141^0C. ***^1H-NMR δ_H ppm ($CDCl_3$):*** 8.45 (m, 1H, Ar), 8.16 (d, 4H, Ar, J=8.55 Hz), 8.055 (m, 6H, Ar), 7.67 (m, 1H, Ar), 7.395 (d, 4H, Ar, J=8.55 Hz), 6.98 (d, 4H, Ar, J=8.77 Hz), 4.04 (t, 4H, $-O-CH_2$), 1.82 (cv, 4H, $-CH_2$), 1.48 (cv, 4H, $-CH_2$), 1.28 (m, 24H, aliphatic), 0.89 (t, 6H, $-CH_3$). ***^{13}C-NMR δ_C ppm ($CDCl_3$):*** 164.56 (>C=O esteric), 163.72, 153.46, 153.34, 150.06, 132.37, 129.65, 125.35, 124.29, 122.51, 121.27, 116.48, 114.37 (12C, aromatic); 68.35, 31.68, 29.54, 29.35, 29.30, 29.14, 29.08, 25.96, 22.67, 14.10 (10C, aliphatic). *m/z* ($CHCl_3$): 839.69 $[M+1]^+$.

General method for synthesis of compounds 6a-f

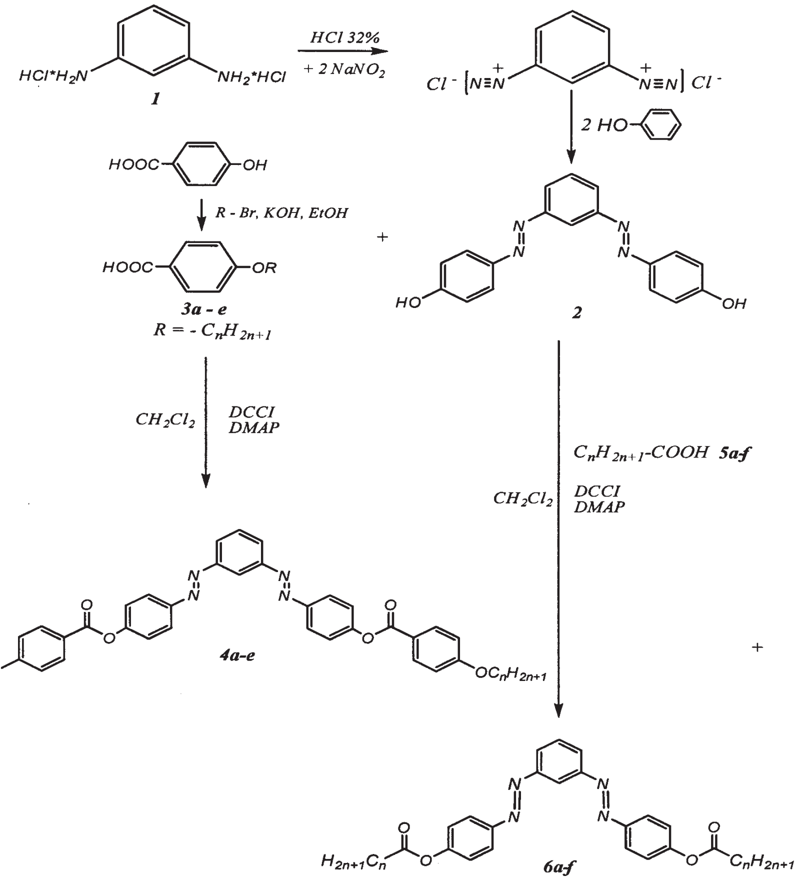
To a mixture of 1 equiv. of 1,3-bis-(4-hydroxyphenylazo)-benzene **(2)** and 2.2 equiv. of **(5a-f)** aliphatic acids in about 100 ml anhydrous dichloromethane, 3.6 equiv. of DCC and 3 equiv. of DMAP were added dropwise. The reaction mixture was stirred for 48 h at room temperature and then the precipitated N,N'- dicyclohexylurea was filtered off. The solvent was evaporated and the product was purified by column chromatography on silica gel using a mixture of dichloromethane/ethyl acetate = 20:1 as eluent.

1,3-bis-(4'-pentanoyloxy-4-benzeneazo)-benzene (6a)

Quantities: 1,3-bis-(4hydroxyphenylazo)-benzene (**2**) (0.4 g, 1.26 mmol), pentanoic acid (**5a**) (0.303 mL, 2.76 mmol), DCC (0.934 g, 4.53 mmol), DMAP (0.461 g, 3.78 mmol), 100 mL dichloromethane. Orange product, η = 44% (0.266 g), m.p = 89^0C.***^1H-NMR δ_H ppm*** ($CDCl_3$): 8.42 (m, 1H, Ar), 8.01 (m, 6H, -Ar), 7.66 (m, 1H, Ar), 7.265 (d, 4H, Ar, J=8.99 Hz), 2.60 (t, 4H, $-OCO-CH_2$), 1.77 (cv, 4H, $-CH_2$), 1.46 (cv, 4H, aliphatic), 0.99 (t, 6H, $-CH_3$). ***^{13}C-NMR δ_C ppm ($CDCl_3$):*** 171.94 (>C=O esteric), 153.33, 153.09, 150.08, 129.67, 125.38, 124.27, 122.31, 116.44 (8C, aromatic), 34.16, 26.95, 22.26, 13.74 (4C, aliphatic). *m/z* ($CHCl_3$): 487.14 $[M+1]^+$.

1,3-bis-(4'-hexanoyloxy-4-benzeneazo)-benzene (6b)

Quantities: 1,3-bis-(4hydroxyphenylazo)-benzene (**2**) (0.4 g, 1.26 mmol), hexanoic acid (**5b**) (0.349 mL, 2.78 mmol), DCC (0.934 g, 4.53 mmol), DMAP (0.461 g, 3.78 mmol), 100 mL dichloromethane. Orange product, η = 45% (0.290 g), m.p = 91^0C. ***^1H-NMR δ_H ppm ($CDCl_3$):***



Scheme 1. Synthesis of symmetric bent-core type compounds based on a 1,3-bis (4'-hydroxybenzeneazo)benzene core (**4a**, n= 6; **4b**, n= 7; **4c**, n= 8; **4d**, n= 9; **4e**, n= 10; **6a**, n= 4; **6b**, n= 5; **6c**, n= 6; **6d**, n= 7; **6e**, n= 8; **6f**, n= 9)

8.42 (m, 1H, Ar), 8.02 (m, 6H, Ar), 7.66 (m, 1H, Ar), 7.265 (d, 4H, Ar, J=8.99 Hz), 2.60 (t, 4H, -OCO-CH$_2$), 1.79 (cv, 4H, -CH$_2$), 1.41 (m, 8H, aliphatic), 0.94 (t, 6H, -CH$_3$). ***^{13}C-NMR δ$_C$ ppm (CDCl$_3$):*** 171.95 (>C=O esteric), 153.33, 153.09, 150.08, 129.67, 125.37, 124.27, 122.31, 116.45 (8C, aromatic), 34.41, 31.27, 24.58, 22.33, 13.93 (5C, aliphatic). *m/z* (CHCl$_3$): 515.17 [M+1]$^+$.

1,3-bis-(4'-heptanoyloxy-4-benzeneazo)-benzene (6c)

Quantities: 1,3-bis-(4hydroxyphenylazo)-benzene (**2**) (0.4 g, 1.26 mmol), heptanoic acid (**5c**) (0.391 mL, 2.76 mmol), DCC (0.934 g, 4.53 mmol), DMAP (0.461 g, 3.78 mmol), 100 mL dichloromethane. Orange product, η = 30% (0.203 g), m.p = 91^{0}C. ***^{1}H-NMR δ$_H$ ppm (CDCl$_3$):*** 8.42 (m, 1H, Ar), 8.02 (m, 6H, Ar), 7.66 (m, 1H, Ar), 7.265 (d, 4H, Ar, J=8.99 Hz), 2.59 (t, 4H, -OCO-CH$_2$), 1.78 (cv, 4H, -CH$_2$), 1.35 (m, 12H, alipahtic), 0.92 (t, 6H, -CH$_3$). ***^{13}C-NMR δ$_C$ ppm (CDCl$_3$):*** 171.95 (>C=O estheric), 153.33, 153.09, 150.08, 129.67, 125.37, 124.27, 122.31, 116.45 (8C, aromatic), 34.45, 31.44, 28.78, 24.87, 22.49, 14.04 (6C, aliphatic). *m/z* (CHCl$_3$): 543.20 [M+1]$^+$.

1,3-bis-(4'-octanoyloxy-4-benzeneazo)-benzene *(6d)*

Quantities: 1,3-bis-(4hydroxyphenylazo)-benzene (**2**) (0.4 g, 1.26 mmol), octanoic acid (**5d**) (0.437 mL, 2.76 mmol), DCC (0.934 g, 4.53 mmol), DMAP (0.461 g, 3.78 mmol), 100 mL dichloromethane. Orange product, η = 51% (0.366 g), m.p = 95^{0}C. ***^{1}H-NMR δ$_H$ ppm (CDCl$_3$):*** 8.42 (m, 1H, Ar), 8.02 (m, 6H, -Ar), 7.66 (m, 1H, Ar), 7.265 (d, 4H, Ar, J=8.55 Hz), 2.59 (t, 4H, -OCO-CH$_2$), 1.78 (cv, 4H, -CH$_2$), 1.32 (m, 16H, aliphatic), 0.91 (t, 6H, -CH$_3$). ***^{13}C-NMR δ$_C$ ppm (CDCl$_3$):*** 171.94 (>C=O esteric), 153.31, 153.07, 150.06, 129.67, 125.35, 124.25, 122.29, 116.42 (8C, aromatic), 34.43, 31.65, 29.06, 28.91, 24.88, 22.59, 14.05 (7C, aliphatic). *m/z* (CHCl$_3$): 571.22 [M+1]$^+$.

1,3-bis-(4'-nonanoyloxy-4-benzeneazo)-benzene (6e)

Quantities: 1,3-bis-(4hydroxyphenylazo)-benzene (**2**) (0.4 g, 1.26 mmol), nonanoic acid (**5e**) (0.485 mL, 2.77 mmol), DCC (0.934 g, 4.53 mmol), DMAP (0.461 g, 3.78 mmol), 100 mL dichloromethane. Orange product, η = 75% (0.565 g), m.p = 96^{0}C. ***^{1}H-NMR δ$_H$ ppm (CDCl$_3$):*** 8.42 (m, 1H, Ar), 8.02 (m, 6H, -Ar), 7.66 (m, 1H, Ar), 7.27 (d, 4H, Ar, J=8,55 Hz), 2.59 (t, 4H, -OCO-CH$_2$), 1.78 (cv, 4H, -CH$_2$), 1.30 (m, 20H, aliphatic), 0.90 (t, 6H, -CH$_3$). ***^{13}C-NMR δ$_C$ ppm (CDCl$_3$):*** 171.96 (>C=O esteric), 153.34, 153.10, 150.09, 129.68, 125.38, 124.28, 122.32, 116.45 (8C, aromatic), 34.46, 31.82, 29.41, 29.23, 29.13, 24.91, 22.66, 14.11 (8C, aliphatic). *m/z* (CHCl3): 599.25 [M+1]$^+$.

1,3-bis-(4'-decanoyloxy-4-benzeneazo)-benzene (6f)

Quantities: 1,3-bis-(4hydroxyphenylazo)-benzene (**2**) (0.450 g, 1.42 mmol), decanoic acid (**5f**) (0.535 g; 3.11 mmol), DCC (1.05 g, 5.09 mmol), DMAP (0.518 g; 4.24 mmol), 100 mL dichloromethane. Orange product, η = 42% (0.473 g), m.p = 99^{0}C. ***^{1}H-NMR δ$_H$ ppm (CDCl$_3$):*** 8.42 (m, 1H, Ar), 8.00 (m, 6H, -Ar), 7.66 (m, 1H, Ar), 7.265 (d, 4H, Ar, J=8,91 Hz), 2.60 (t, 4H, -OCO-CH$_2$), 1.78 (cv, 4H, -CH$_2$), 1.29 (m, 24H, aliphatic), 0.89 (t, 6H, -CH$_3$). ***^{13}C-NMR δ$_C$ ppm (CDCl$_3$):*** 171.97 (>C=O esteric), 153.31, 153.08, 150.06, 129.67, 125.39, 124.26, 122.32, 116.43 (8C, aromatic), 34.44, 31.87, 30.93, 29.43, 29.27, 29.12, 24.91, 22.69, 14.13 (9C, aliphatic). *m/z* (CHCl3): 627.28 [M+1]$^+$.

Results and discussions

Scheme 1 depicts the synthetic route for obtaining the two new classes of symmetric *bent-core* type compounds.

The central core, 1,3-bis-(4 hydroxyphenylazo)-benzene, (**2**) was synthesized by adapting the literature data, using diazotization and coupling reactions [9]. The 4-alkyloxybenzoic acids (**3a÷e**), have been synthesized by Williamson etherification of 4-hydroxybenzoic acid with

Table 1
RANGE OF MESOPHASES FOR THE SYMMETRIC
BENT-CORE COMPOUNDS **4a–d**

Compounds	*Range of mesophases (^{0}C)*	
	On heating	*On cooling*
4a	141-171^{0}C	168-129^{0}C
4b	148-158 ^{0}C	152-128^{0}C
4c	135-155^{0}C	151-116^{0}C
4d	140-148^{0}C	145-118^{0}C

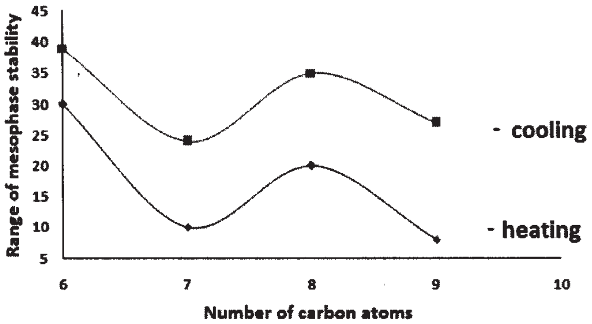


Fig. 1. Variation intervals of the mesophases stabilities

Table 2
TRANSITION TEMPERATURES (°C) AND TRANSITION ENTHALPIES (ΔH / Jg^{-1}) FOR THE BENT-CORE COMPOUNDS **4a-e**

Compounds		*T / ^{0}C* *[ΔH / Jg^{-1}]*				
		Heating (^{o}C)		*Cooling (^{o}C)*		*T_{onset} (^{o}C)*
		K / Sm	**Sm / I**	**I / Sm**	**Sm / K**	
4a	n= 6	141 [-26]	171 [-23]	168 [24]	129 [27]	349
4b	n= 7	148 [-19]	158 [-4]	152 [13]	128 [30]	347
4c	n= 8	135 [-23]	155 [-19]	151 [20]	116 [27]	348
4d	n= 9	140 [-26]	148 [-9]	145 [21]	118 [33]	346
4e	n= 10	-	141 [-48]	-	131 [52]	338

Abbreviations : **K** – crystalline ; **Sm** – smectic; **I** – isotropic; T_{onset} –temperature at which thermal degradation begins.

n-alkyl bromides in EtOH and in the presence of KOH [10]. They were purified by recrystallisation from EtOH. Esterification of the central core with the 4-alkyloxybenzoic acids in the presence of DCC and DMAP afforded the new symmetric class of *bent-core* liquid crystals (**4a÷e**), in 20-44 % yields.

The symmetric compounds **6a÷f**, were obtained in 30-75 % yields via esterification of the central core with aliphatic acids **5a÷f,** also in the presence of DCC and DMAP.

Liquid-Crystalline Properties

Investigation of the mesomorphic properties of the symmetric derivatives by polarized optical microscopy and DSC investigations revealed that compounds **6a-6f** do not show liquid-crystalline properties. For compounds **4a-4f** POM and DSC studies evidenced enantiotropic liquid-crystalline properties. The type of mesophases was assigned by visual comparison with known phase standards [11]. For compounds **4a-d** the range of mesophase is wider on cooling (table 1).

The graphical presentation of data presented in table 1 is revealed in figure 1. The variation curves indicate the presence of the odd / even effect, so derivates with the even number of carbon atoms in the terminal chain show a larger range of mesophase.

Table 2 and table 3 present the temperatures of the phase transitions determined by differential scanning calorimetry. Taking into account the importance of thermal stability in the existence range of the mesophases, thermogravimetric studies were performed for all **4a-4f** compounds. All **4a-4f** derivatives showed a very good thermal stability, the initial temperature at which thermal degradation for the first stage begins (T_{onset}) being situated between 338 and 349^{0}C, with about 150^{0}C more than isotropisation temperatures (table 2).

For example, the DSC curves of compound ***4c*** (fig. 2), present on the second heating two endothermic peaks, one at 135^{0}C, and the second at 155^{0}C, this last one corresponding to the isotropisation temperature. Between these two values, on a narrow domain of temperature, the sample presents a smectic type texture. On the second cooling curve, two exothermic peaks are observed, one at 151^{0}C, caused by the transition isotropic-smectic and the second one, at 116^{0}C, corresponding to the transition to the crystalline phase.

Figure 3 presents the liquid crystal textures observed by polarized optical microscopy upon heating and cooling for the symmetric *bent-core* compound ***4c.***

It can be noted that the isotropisation temperatures decrease with the increasing of the number of carbon atoms in the terminal chain (from 171^{0}C for compound

Table 3
TRANSITION TEMPERATURES (°C) AND TRANSITION ENTHALPIES (ΔH / Jg^{-1}) FOR THE COMPOUNDS **6a-f**

Compounds		*T / ^{0}C* *[ΔH / Jg^{-1}]* *Heating (^{0}C)*		*Cooling (^{0}C)*	
		K / K	**K / I**	**I / K**	**K / K**
6a	n= 4	-	102[-37]	-	92 [41]
6b	n= 5	-	102[-44]	-	89 [47]
6c	n= 6	84 [-16]	93 [-40]	84 [53]	55 [20]
6d	n= 7	83 [-17]	95 [-42]	87 [52]	49 [22]
6e	n= 8	89 [-17]	96 [-33]	87 [55]	60 [23]
6f	n= 9	89 [-19]	99 [-46]	90 [60]	57[25]

Abbreviations : K – crystalline ; I – isotropic;

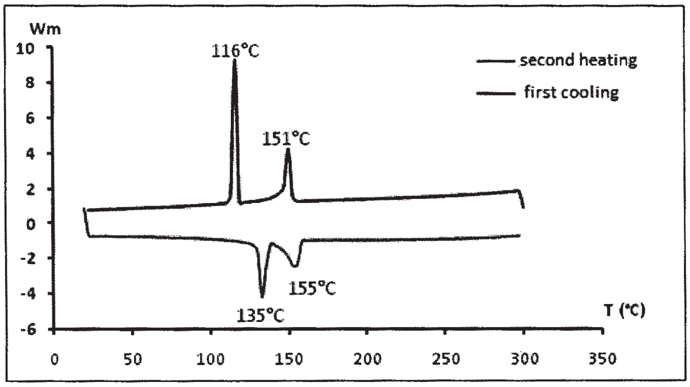
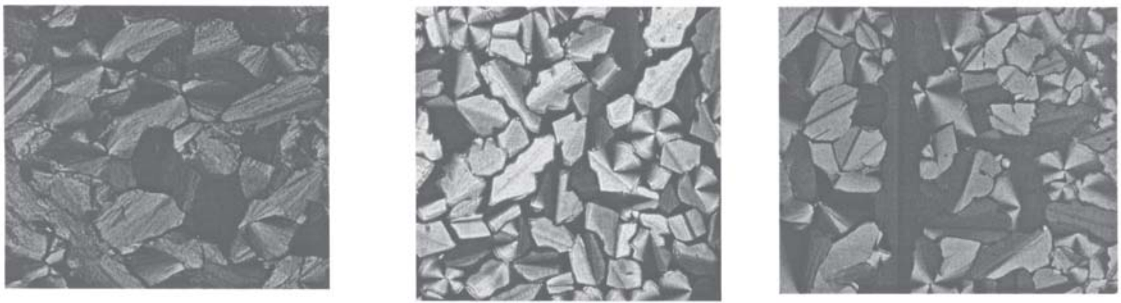


Fig. 2. Differential scanning calorimetric curves of compound **4c**



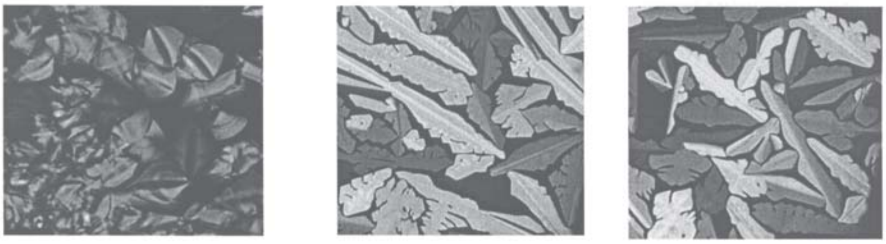
a b c

Fig. 3. Liquid crystal textures observed by polarized optical microscopy for compound **4c**: a) second heating, 150^{0}C; b) second cooling, 130^{0}C; c) first cooling, 133.5^{0}C

4a, to 141^{0}C, for compound ***4e***), phenomenon that appears olso on the cooling cycles.

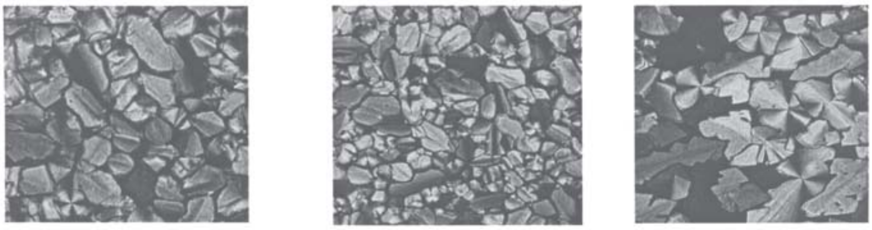
All the DSC curves for the rest of these *bent-core* symmetric compounds are similar to the one presented in figure 2, the differences being the values of the temperatures of phase transitions. Images captured by polarized optical microscope for the rest of the compounds are shown in figure 4. Symmetric derivate ***4a*** has the largest domain of mesophase stability if compared to the other *bent-core* compounds in this new class.

In the case of compounds **6a-6f**, POM and DSC investigations did not evidence the presence of liquid crystalline properties. In the case of compounds **6c-6f**, DSC evidenced only crystalline-crystalline transitions. The lack of liquid crystalline properties for compounds **6a-6f** may be a consequence of a too small number of aromatic rings.



4a: second heating, 149.3°C *4a*: first cooling, 147°C *4a:* second cooling, 132°C

4b: first cooling, 149.3°C *4b*: second heating, 148.8°C



4d: first heating, 145°C *4d*: first cooling, 142.5°C *4d*: second cooling, 128°C

Fig. 4. Optical textures of compounds **4a, 4b, 4d** on heating and cooling cycles

Conclusions

Two new series of symmetric *bent-core* compounds based on a 1,3-bis-(4‘-hydroxyphenylazo) benzene central core have been synthesized and their mesomorphic properties have been investigated. These new compounds were obtained by esterification of the central core with a series of 4-alkoxybenzoic or aliphatic acids. ^{1}H-NMR, ^{13}C-NMR and mass spectroscopy were used for structural characterization. Four of the reported compounds presented enantiotropic liquid-crystalline properties, with smectic type textures. The liquid crystalline behaviour was confirmed by differential scanning calorimetry (DSC) and optical polarizing microscopy (POM). Thermogravimetric studies evidenced that the banana derivates **4a-4f** have a very good thermal stability in the mesophases domain.

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