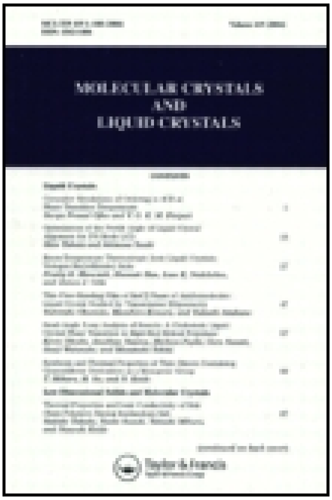

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Monosubstituted Ferrocene-Containing Liquid Crystals

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Monosubstituted Ferrocene-Containing Liquid Crystals

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The synthesis and mesophase characterization of some monosubstituted ferrocene-containing liquid crystals were reported. For a better understanding of the thermal behavior, the LC properties were compared with a series of pattern compounds, possessing similar structures, but without the ferrocenyl unit. The introduction of the ferrocenyl unit in the rigid core induced monotropic or enantiotropic behavior, depending upon the number of carbonyl groups in the structure. Monotropic behavior is a little surprising, since the presence of the bulky ferrocenyl unit is expected to inhibit the ordering process in the solid state (crystallization). The observed behavior is rationalized by the change of the dipole moment in the rigid core, when either one or two ester groups are present.

Keywords: azobenzene; ferrocenomesogens; liquid crystal; nematic phases

1. INTRODUCTION

In recent years, studies focused on the synthesis and mesomorphic properties of monosubstituted ferrocenyl containing liquid crystals

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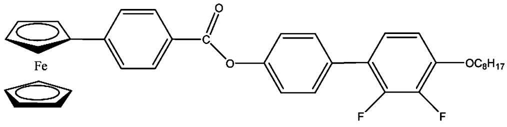
(ferrocenomesogens) have gained increasing importance [1,2]. Malthete and Billard have synthesized the initial series of mesogenic ferrocene derivatives [3]. At the time, their results were surprising, in that it seemed likely that monosubstituted ferrocenes would be poor candidates for stabilizing liquid crystalline phases. Partly, this was attributed to their unfavorable molecular shape (L-shaped geometry) and also to the repulsive steric effects of the ferrocene unit reducing the ability of the molecules to be placed in layers, thus mostly favoring the formation of nematic and smectic A phases. Based on the X-ray analysis, Loubser *et al.* described the structure of a monosubstituted ferrocenomesogen, **I**, containing a terminal ferrocenyl group and laterally substituted fluorine atoms, which exhibited a relatively low melting point and clearing temperature [4].

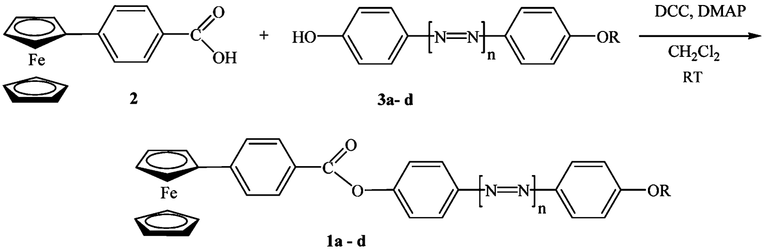


I

Generally, the liquid crystalline behavior was clearly evidenced only for the cases when the mesogenic unit contained conjugated systems incorporating ferrocene and at least three aromatic rings [1]. The core of a mesogen determines the approximate temperature range where mesophases will occur and what types of mesophases are possible. Thus, terminal substituents are needed to balance the rigidity with the flexibility of the molecule. The most frequent terminal substituents contain straight alkyl/alkoxy chain [5].

This paper presents the synthesis and structural characterization of a new series of monosubstituted ferrocenyl-containing liquid crystals **1a–d** (Scheme 1). For evidencing the correlations between structure and mesogenic properties, some analogues containing the same mesogenic core were also synthesized. Some of these compounds contain in the structure an azobenzene unit which may give rise to configurational photocontrol.

We have reported previously the isomerization capacity of azobenzene groups, even in condensed state [6]. This behavior was distinguished to the polymers with azo group in the main or side chain [7–9]. In order to explain the liquid crystalline behavior of the synthesized compounds, molecular simulations were performed using the HYPERCHEM program. Some of the synthesized compounds contain azo group in the molecule, permitting the reversible



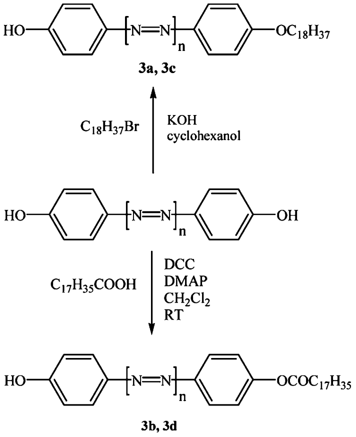
SCHEME 1 The synthesis of 4-ferrocenylbenzoates where: **1a:** n = 1, R = $-C_{18}H_{37}$, **1b:** n = 1, R = $-OC-C_{17}H_{35}$, **1c:** n = 0, R = $-C_{18}H_{37}$, **1d:** n = 0, R = $-OC-C_{17}H_{35}$, **3a:** n = 1, R = $-C_{18}H_{37}$, **3b:** n = 1, R = $-OC-C_{17}H_{35}$, **3c:** n = 0, R = $-C_{18}H_{37}$, **3d:** n = 0, R = $-OC-C_{17}H_{35}$.

trans-cis isomerization under UV irradiation, which may determine the potential use of such compounds.

2. RESULTS AND DISCUSSION

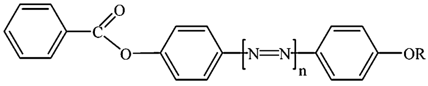
The design and synthesis of ferrocene-containing mesogens presented in this paper was carried out in accordance to the initial guidelines of Loubser and Imrie [4]. Hence, a benzene ring was inserted as a spacer between the ferrocenyl group and the linker, while the core of the molecule contains other two benzene rings connected directly or through an azo group. It was previously shown that the insertion of a benzene ring as a spacer between the ferrocene and the carbonyloxy linker results in a lowering of clearing temperature and increases both the thermal and photochemical stabilities by attenuating the withdrawal of electron density from the ferrocenyl group. The presence of the azo group in the molecule, permitting the reversible trans-cis isomerization under UV irradiation, may determine the use of such compounds as light modulators for micro-displays. The synthesis of ferrocene derivatives involved the esterification of 4-ferrocenyl-benzoic acid with a series of phenylazo- and biphenyl-phenols bearing alkoxy/acyloxy chains as terminal substituents, as presented in Scheme I.

4-Ferrocenyl-benzoic acid **2** was synthesized using the diazonium method [10]; alkylated/acylated phenols **3a–d** were prepared by the reaction of the corresponding bis-phenols with 1 equiv. of stearyl bromide, in the presence of potassium hydroxide [11] and with 1 equiv. of stearic acid in the presence of DCC and DMAP, as presented in Scheme 2.



SCHEME 2 The synthesis of the acylated/alkylated phenols: 3a, 3b: n = 1, 3c, 3d: n = 0.

In order to investigate the influence of ferrocene unit upon mesomorphic properties, analogues **4a–d** were prepared, by reacting benzoic acid with the **3a–d** phenols. The reactions were carried out in a similar manner as presented in Scheme 1.

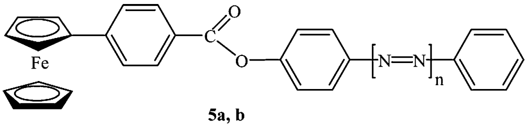


4a - d

4a: n=1, R= -$C_{18}H_{37}$, **4b**: n=1, R= -OC-$C_{17}H_{35}$

4c: n=0, R= -$C_{18}H_{37}$, **4d**: n=0, R= -OC-$C_{17}H_{35}$

Compounds **5a**, **b**, obtained by reaction of 4-ferrocenyl-benzoic acid with 4-phenylazo-phenol and, respectively, biphenyl-4-ol, in the presence of DCC and DMAP, were synthesized in order to investigate the influence of the flexible chain over the mesomorphic properties.



5a, b

5a: n=1, **5b**: n=0

The results showed that, by removal of the alkoxy/acyloxy terminal chain, the mesogenic behavior disappeared. This is a consequence of

TABLE 1 Geometric Parameters of the Synthesized Products

Compound code	Rigid core length (Å)	Rigid core diameter (Å)	Flexible segment length (Å)	Flexible/rigid ratio
1a	20.5	6	21.7	1.06
1b	21.4	6	20.5	0.96
1c	18.5	6	21.8	1.18
1d	19.5	6	20.4	1.05
4a	17.6	6	21.8	1.24
4b	18.3	6	20.5	1.12
4c	15.4	6	21.7	1.41
4d	16.6	5.0	20.5	1.23

the fact that a *rod-like* rigid core rarely produces mesophases because of the crystalline behavior being favored. Generally, flexible terminal substituents are necessary for establishing an equilibrium between rigidity and flexibility. Optical microscopy and DSC analysis indicated that compounds **1a–d** presented liquid crystalline properties.

In order to explain the liquid crystalline behavior of the synthesized compounds, some conformational theoretical studies were performed. The geometric characteristics of the compounds are presented in Table 1.

The liquid crystalline behavior of the synthesized compounds is summarized in Table 2.

TABLE 2 Phase-Transition temperatures (°C) and Enthalpy Changes (J/g) of Compounds

		Transition T (ΔH)			
Compound	n	K/LC	LC/I	I/LC	LC/K
R = $-C_{18}H_{37}$					
1a	1	135.7 (29.84)	–	134.6 (–1.59)	118.5 (–50.01)
1c	0	136.3 (52.44)	–	131.9 (–2.80)	127.2 (–40.72)
4a	1	119.1(159.83)	123.8(2.58)	121.7 (–3.28)	103.1 (–159.81)
4c	0	–	–	–	–
R = $-OC-C_{17}H_{35}$					
1b	1	128.4 (45.62)	145.3 (3.86)	143.8 (–2.27)	116.0 (–47.83)
1d	0	128.6 (46.41)	137.5 (2.74)	136.3 (–2.75)	117.5 (–46.81)
4b	1	123.8 (89.064)	127.1 (1.24)	126.7 (–1.88)	108.0 (–91.82)
4d	0	122.9 (75.89)	125.7 (3.21)	124.9 (–4.27)	105.9 (–75.62)

K = crystalline phase.
LC = liquid crystalline phase.
I = isotropic phase.

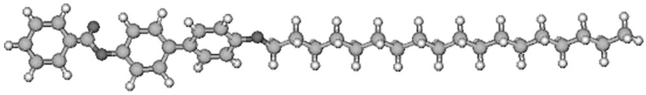


FIGURE 1 Geometry of the compound **4c**.

Compound **4c** proved to be non-mesogenic; it presents just a crystalline phase, which melted at 129°C. The absence of the liquid crystalline properties may be explained by the fact that flexible/rigid ratio, with a value of 1.41, is too large (Fig. 1).

The introduction of a second ester group in the rigid core within compound **4d** has a dual effect: on one side, a slight increase of the length of the rigid unit, if we consider the ester group a part of it, and, on the other side, an intensification of physical interactions. Furthermore, the flexible chain, having one methylene group less, is shorter with about 1 Å. The consequence of the combination of these two effects is the appearance of the liquid crystalline behavior. Compound **4d** shows a very narrow and unstable

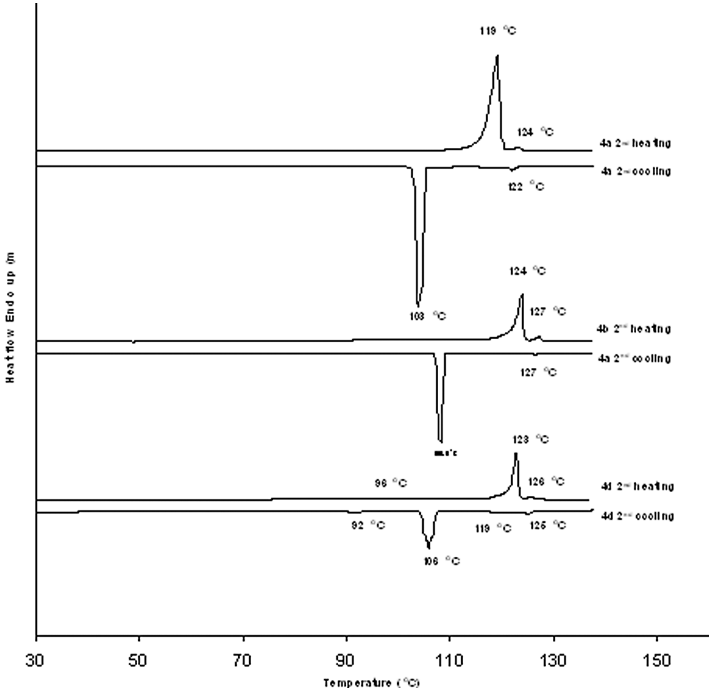


FIGURE 2 DSC thermograms of compounds **4a**, **4b** and **4d**.

mesophase between 123–126°C, on heating (Fig. 2, **4d** heating). On cooling from the isotropic melt, the mesophase is stable over a wider temperature range (125–106°C). Generally, compounds with the ferrocenyl unit in the rigid core increases the stability of the mesophase on cooling [5]. On cooling, Compound 4d exhibited a smectic mesophase between 119–106°C, confirmed by optical microscopy in polarized light (Fig. 3).

In order to increase the intermolecular interactions, the length of the rigid core has been modified for compound **4a**, by replacing the diphenyl moiety with an azobenzene unit (Fig. 4). The liquid crystalline behavior was maintained with a slight increase of the mesomorphic domain on heating (119–124°C). On cooling, the liquid crystalline behavior is similar to that of Compound **4d**.

The introduction of a second ester group in the rigid core (**4b**) led to a slight increase of the isotropisation temperature, but did not increase the stability of mesophase on heating. The nematic phase of compounds **4a** and **4b** was observed by polarized optical microscopy and confirmed by the DSC analysis and the ratio between the crystalline melting and isotropisation enthalpies.

The presence of the ferrocenyl unit in the rigid core leads to significant changes on the mesomorphic behavior. For example, in the case of compounds **1a–d**, the introduction of the ferrocene increases the range

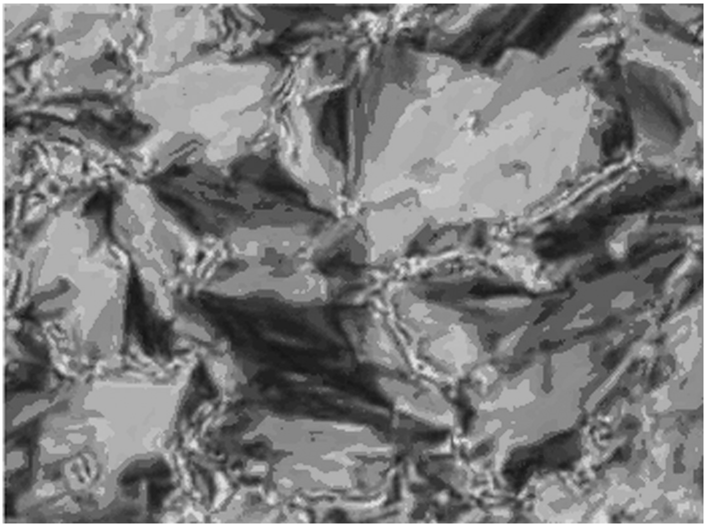


FIGURE 3 Photomicrograph of compound **4d**, 116°C, first cooling.

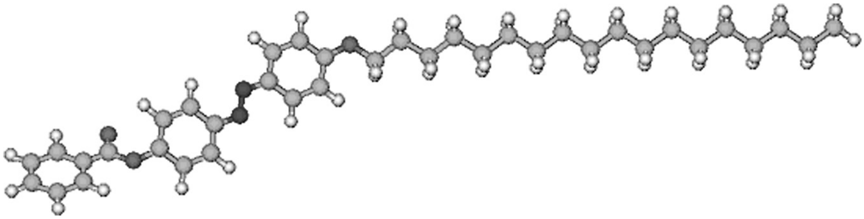
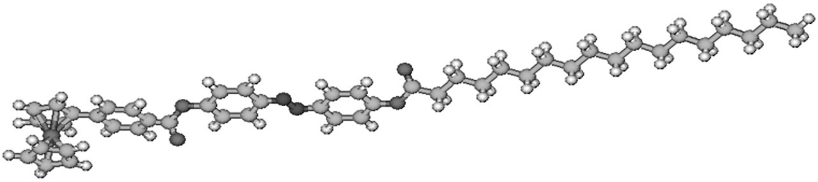


FIGURE 4 Geometry of the compound **4a**.

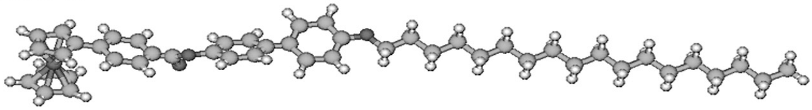
and stability of the mesophases. These materials exhibit the monotropic and enantiotropic phases.

For compounds similar with **1c** and **1d**, literature data have mentioned the appearance of smectic and nematic phases, as a function of the length of the flexible spacer. Thus, the nematic phase appears for compound with the lengths of flexible chain smaller than 9 Å (5–8 methylene groups). An increase of the flexible chain (from 9 to 16.5 Å, corresponding to 8–14 methylene groups) leads to the appearance of the smectic phase next to the nematic one. It should be mention that, while increasing the length of flexible chain, the stability of the smectic range increases gradually and, in sequence, the nematic phase narrows rapidly [5]. For the length of the flexible chain more than 16.5 Å, the thermal behavior of such compounds was not yet studied.

The presence of the ferrocenyl unit in the rigid core of Compound **1c** led to the appearance of a monotropic LC, with a higher clearing temperature as compared with compounds **4a–d**. Although the ferrocenyl unit is a bulky substituent, asymmetrically connected to the axis of the rigid core (Fig. 5 – Compound **1c**), the system shows a highly compact packing of the molecules in the crystalline state, leading to the appearance of a



Compound **1b**



Compound **1c**

FIGURE 5 Geometry of the LC ferrocene-containing compounds.

monotropic behavior. On cooling, the appearance of the mesophase takes place 4°C below the clearing temperature (Fig. 6 – **1c**).

The introduction of a second ester group in the rigid core (Compound **1d**) led to an enantiotropic behavior, but the clearing temperature has about the same value with **1c** ($T_i = 137°C$). On heating, the stability of the mesophase is wider (129–137°C), as compared with the first series of compounds (Compounds **4a–d**). The increase of the mesophase stability, in the presence of the ferrocenyl unit, may be explained by the gradual decrease of the flexible/rigid ratio (close to 1 value, in the case of Compound **1d**).

The replacement of the diphenyl unit with the azobenzene one (Compound **1a**) will have as a result a monotropic behavior. The clearing temperatures of the Compounds **1a** and **1d** are almost the same, confirming that the physical intermolecular interactions are very similar. Because the flexible/rigid ratio is almost the same for these two compounds, it indicates that the change from monotropic to enantiotropic behavior is induced by the electronic delocalization in the aromatic conjugate system. In the case of Compound **1d**, the presence of two ester groups, at both ends of the diphenyl unit,

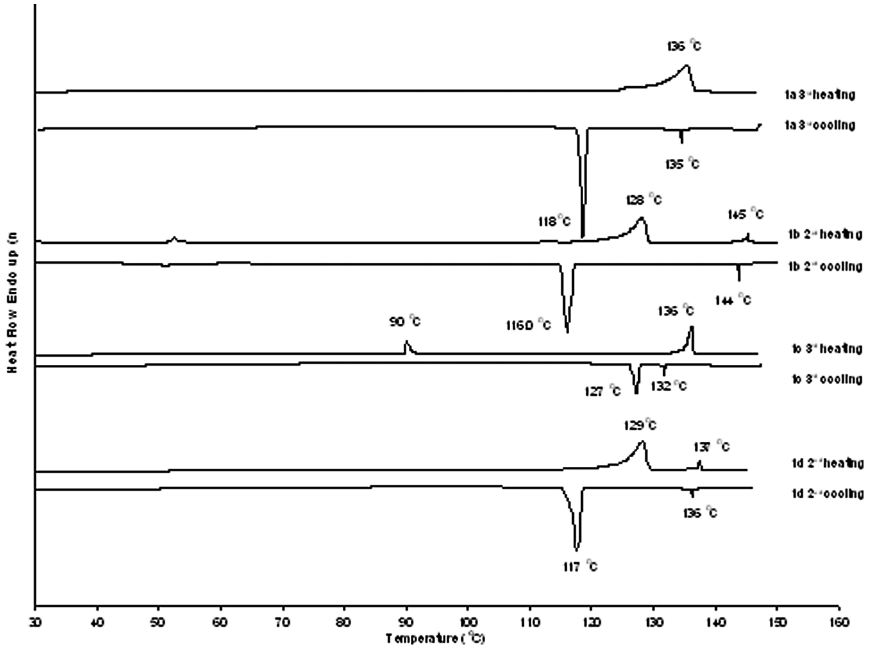
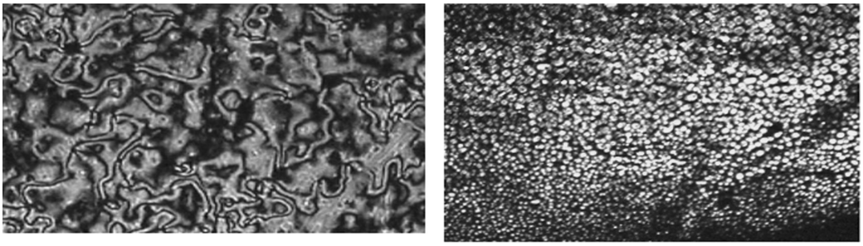


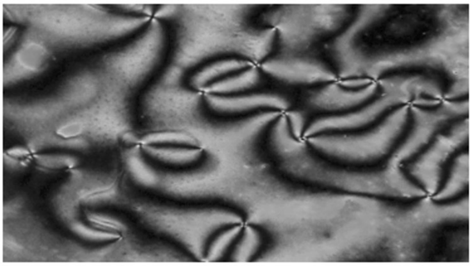
FIGURE 6 DSC thermograms of compounds **1a–1d**.

combined with the partial interruption of the extended conjugate system (because of the rotation of the two diphenyl aromatic rings) was because of a uniform distribution of the electronic density in the two aromatic rings of the diphenyl unit. In the case of Compound **1a**, in conjunction with the presence of an extended aromatic system due to the azo group, a delocalization of the electronic cloud towards the ester group will appear. The result will be an increase of the dipolmoment of the rigid core of Compound **1a** and probably, leading to a better packing in the crystalline phase, and thus, to a monotropic behavior. These presumptions are confirmed by the enantiotropic behavior of the Compound **1b**, where the introduction of a second ester group in the rigid core will impose the return to an enantiotropic behavior. The decrease of the flexible/rigid ratio to a sub-unit value, combined with a strengthening of the lateral interactions due to the presence of the second ester group will have as result an important increase of the isotropisation temperature ($T_i = 145°C$). In the same time, a stabilization of the mesophase takes place, Compound **1b** showing a 17°C mesophase range on heating (128–145°C).

As expected for systems with a *rod-like* rigid core, the pattern compounds **5a**, **5b**, in which the alkoxy/acyloxy chains were removed, did not exhibit liquid crystalline properties. All synthesized ferrocene



Compound **1a**, 134 °C, first cooling   Compound **1b**, 145 °C, first cooling



Compound **1c**, 137 °C, fourth cooling

FIGURE 7 Photomicrograph of some ferrocene containing liquid crystals.

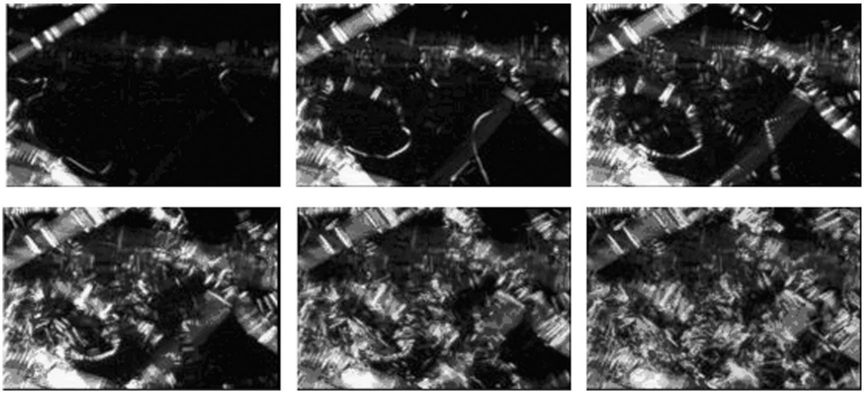


FIGURE 8 Optical photomicrographs of compound **1c**, 139.5–139.2°C, fifth cooling, 0.2°C/min, 500× magnification.

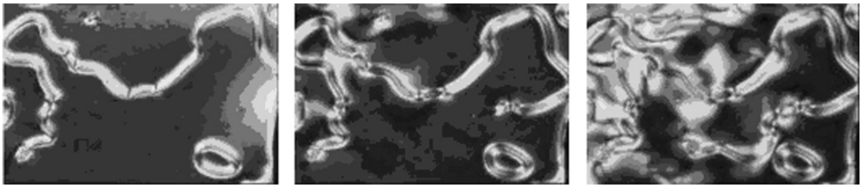


FIGURE 9 Compound **1d**, 135.5–125.2°C, third cooling at 1°C/min, 200 × magnification.

derivatives displayed nematic mesophases confirmed by optical microscopy in polarized light and ratios between the crystalline melting and isotropisation enthalpies. Representative examples of images of the mesophases are shown in Figure 7.

An interesting observation was that if Compound **1c** was heated and cooled at a very slow rate, a ribbon structure was formed (Fig. 8). This process is extremely fast (ends in just a few seconds) and because of that the images are not very clear. Changes in the texture of the mesophase was also observed in the case of Compound **1d** (Fig. 9), but not as dramatic as in the case of Compound **1c**, although the difference between these two samples is that **1c** has an alkoxy group as end chain group, while **1d** has an ester end group.

3. CONCLUSIONS

A series of monosubstituted ferrocene-containing liquid crystals have been synthesized and characterized. The liquid crystalline compounds without ferrocene group presented a very short stability of the mesophase on heating, all of them exhibiting an enantiotropic behavior. The introduction of the ferrocenyl unit in the rigid core induced a monotropic or enantiotropic behavior, although the appearance of a monotropic behavior is a little surprising, because the bulkiness ferrocenyl unit is asymmetrically connected in respect to the rigid core axis. These behaviors have been explained by the change of the dipolmoment in the rigid core, when one or two ester groups are present. Compound **1b**, presenting the smallest value of the flexible/rigid ratio, showed the largest stability of the mesophase, on heating. Compound 1c shows an interesting behavior if heated/cooled very slowly ($\leq 1^\circ$C/min). A ribbon type structure is formed within few seconds.

4. EXPERIMENTAL

Materials

All reactions were performed under an atmosphere of dry nitrogen. Silica gel 60 (Merck) or Al_2O_3 (active, neutral, Merck) were used for column chromatography. Plate chromatography was performed on Silica gel or Al_2O_3 plates (Merck, Silicagel F_{254}, Alluminium oxide F_{254}). Ethyl ether and dichloromethane were distilled over $CaCl_2$ and P_2O_5 prior to use. Ferrocene (Aldrich), dicyclohexylcarbodiimide (Aldrich), 4-N,N-dimethylamino-pyridine (Aldrich), 4,4-dihydroxydiphenyl (Aldrich) were used as received. 4-Ferrocenyl-benzoic acid and 4,4-dihydroxyazobenzene (DHAB) were prepared following literature procedures [10,11].

Techniques

Confirmation of the structures of the intermediates and the final products was obtained by ^{1}H-NMR and ^{13}C-NMR spectroscopy using a Varian Gemini 200 MHz spectrometer with tetramethylsilane as internal standard. IR spectra were recorded using a Nicolet Magna 550 FT-IR spectrometer (NaCl crystal window). Transition temperatures and enthalpies were determined using a Mettler FP52 heating stage and FP5 temperature control unit in conjunction with a Nikon polarizing optical microscope, the transitions being confirmed by DSC analysis (Perkin Elmer Pyris 1, Perkin Elmer TAC 7/DX, Perkin Elmer Intracooler 2P). Heating and cooling cycles were run at rate of 2°C/min, under nitrogen atmosphere, with Compounds measured in closed lid aluminum pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase standards.

The molecular simulations were performed using the HYPERCHEM program [12]. The initial molecular conformation of the simulated products was optimized using a MM+ field force and the value of the total potential energy of the single molecule was obtained. In order to search the real value for minimum energy (not a local minimum) the obtained conformation was followed by a molecular dynamic cycle and re-minimized. The criterion of energy convergence was to obtain a residual root-mean-square force in the simulated system of less than 0.05 kJ/mol $*$ Å. Minimization was performed using the steepest-descent and conjugate-gradient algorithm described by Fletcher and Reeves.

Synthesis

General Procedures for Preparing Phenol Intermediates 3a–d

General procedure for preparing octadecyloxy derivatives 3a, 3c. A solution containing 21.85 mmol 4,4′dihydroxyazobenzene or 4,4′dihydroxybiphenyl and 1.728 g (30.857 mmol) KOH in 25 ml cyclohexanol was heated at 100°C, under stirring, until the complete dissolution of KOH. To the stirred solution, 7.276 g (21.85 mmol) stearyl bromide in 10 ml cyclohexanol was added and the reaction mixture was refluxed for 3 hours. The reaction mixture was poured into 100 ml 10% HCl in water and than filtered. The crude product was dried, suspended in ethyl acetate, refluxed for two hours and filtered out. The **3a** solid was further purified by passing through a column of silica gel (chloroform:ethyl acetate), while the insoluble **3c** one was used without further purification.

4-(4′-Octadecyloxy-phenylazo)-phenol, 3a. $\eta = 84.5\%$. Mp = 106–110°C. IR (KBr pellets): 3435, 2918, 2848, 1604, 1473, 1251, 844 cm^{-1}. ^{1}H-NMR (CDCl$_3$): δ (ppm): 7.95–7.03 (8H, aromatic protons), 4.9 (1H, $-$OH), 4.05, (t, 2H, $-O-CH_2-$), 1.92–0.92 (35 H, methylene and methyl protons). ^{13}C-NMR (CDCl$_3$): δ (ppm): 161.0, 159.5, 145.1, 144.3, 124.0, 123.3, 116.0, 114.5 (8C, aromatic), 68.9 ($-O-CH_2-$), 32.0–14.3 (17 aliphatic carbons).

4′-Octadecyloxy-biphenyl-4-ol, 3c. $\eta = 47.9\%$. Mp = 132°C. IR (KBr Pellets): 3408, 2918, 2850, 1608, 1500, 1467, 817 cm^{-1}.

General procedure for preparing octadecanoyloxy derivatives 3b, 3d. Dicyclohexylcarbodiimide (0.53 g, 2.57 mmol) and N, N-dimethylaminopyridine (catalytic amount), were added to a stirred solution of

4,4′dihydroxyazobenzene or 4,4′dihydroxybiphenyl (2.336 mmol) and stearic acid (0.66 g, 2.336 mmol) in 50 ml anhydrous ethyl ether. The reaction mixture was stirred overnight at room temperature. The dicyclohexylurea was filtered off and the solvent was removed under reduced pressure. The crude products were used without further purification.

Octadecanoic acid 4-(4-hydroxy-phenylazo)-phenyl ester, 3b. $\eta =$ 34.77%. Mp = 130–133°C. IR (KBr pellets): 3444, 2916, 2848, 1743, 1600, 1469, 1273, 844 cm^{-1}.

Octadecanoic acid 4′-hydroxy-biphenyl–4-yl ester, 3d. $\eta = 24.69\%$. Mp = 117–120°C. IR (KBr pellets): 3332, 2916, 2848, 1743, 1612, 1500, 1236, 827 cm^{-1}.

General Procedure For Preparing Ferrocenyl Derivatives 1a-1d

To a solution containing 0.4 g (1.306 mmol) 4-ferrocenyl-benzoic acid and 1.306 mmol **3a** ÷ **3d** phenols in 50 ml anhydrous CH_2Cl_2, a solution containing 0.296 g (1.436 mmol) DCC and a catalytic amount of DMAP in 10 ml anhydrous CH_2Cl_2 was added. The reaction mixture was stirred for 4 hours at room temperature. The dicyclohexylurea was filtered off and the solvent was removed under reduced pressure. The obtained solids were purified by passing through a column of silica gel (chloroform:hexanes = 1:1). Yields 17.8 ÷ 52.0%.

4-Ferrocenyl-benzoic acid 4-(4-octadecyloxy-phenylazo)-phenyl ester, 1a. $\eta = 17.8\%$. IR (KBr pellets): 2920, 2848, 1728, 1600, 1255, 1141, 1062, 1012, 849 cm^{-1}. ^1H-NMR ($CDCL_3$): δ (ppm): 8.2–7.05 (12H, aromatic protons), 4.75 (s, 2H, ferrocene protons), 4.45, (s, 2H, ferrocene protons), 4.5 (m, 7H, unsubstituted ferrocene ring and $-O-CH_2-$), 1.45–0.95 (35 H, methylene and methyl protons). ^{13}C-NMR ($CDCL_3$): δ (ppm): 165.4 ($>C=O$), 160.5, 158.5, 145.1, 144.3, 141.8, 130.6, 129.4, 127.0, 123.7, 123.1, 119.0, 114.5 (12 aromatic carbons), 82.3, 72, 71.5, 71.0 (4C, C_5H_5 and C_5H_4), 69.0 ($-O-CH_2-$), 31.5–14.4 (17C aliphatic).

4-Ferrocenyl-benzoic acid 4-(4-octadecanoyloxy-phenylazo)-phenyl ester, 1b. $\eta = 35.26\%$. IR (KBr pellets): 2918, 2846, 1761, 1726, 1600, 1490, 1269, 1190, 1139, 1064 cm^{-1}. ^1H-NMR ($CDCL_3$): δ (ppm): 8.2–7.22 (12H, aromatic protons), 4.76 (s, 2H, ferrocene protons), 4.43, (s, 2H, ferrocene protons), 4.064 (s, 5H, unsubstituted ferrocene ring), 2.59 (t, 2H, $-O-CO-CH_2-$protons), 1.78–0.88 (33 H, methylene and methyl protons). ^{13}C-NMR ($CDCL_3$): δ (ppm): 171.5 ($>C=O$), 164.4 ($>C=O$), 152.4, 152.8, 149.75, 146, 129.9, 125.9, 125.3, 123.6, 122.0, 121.8 (aromatic carbons), 82.6, 69.6, 69.5, 66.6 (4C, C_5H_5 and C_5H_4), 34.0–13.7 (17C aliphatic).

4-Ferrocenyl-benzoic acid 4-(4-octadecyloxy-biphenyl) ester,1c. $\eta = 20.3\%$. IR (KBr pellets): 2920, 2848, 1728, 1606, 1496, 1265, 1213, 1166, 1070, 806 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ (ppm): 8.195–6.997 (12H, aromatic protons), 4.8 (t, 2H, ferrocene protons), 4.47, (t, 2H, ferrocene protons), 4.115 (m, 7 H, unsubstituted ferrocene ring and $-O-CH_2-$), 1.88–0.892 (35 H, methylene and methyl protons).^{13}C-NMR ($CDCl_3$): δ (ppm): 165.2 (>C=O), 158.3, 149.5, 145.6, 138.2, 132.3, 129.9, 127.6, 127.2, 126.1, 125.3, 121.5, 114.3 (12 aromatic carbons), 82.6, 70.0, 69.5 67.7, 66.5 (5 C, C_5H_5, $C_5H_4$and $-O-CH_2-$), 31.5–13.7 (17C aliphatic).

4-Ferrocenyl-benzoic acid 4-(4-octadecanoyloxy-biphenyl) ester, 1d. $\eta = 52\%$. IR (KBr pellets): 2922, 2850, 1753, 1726, 1602, 1490, 1265, 1199, 1166, 1138, 819 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ (ppm): 8.149–7.136 (12H, aromatic protons), 4.765 (t, 2H, ferrocene protons), 4.434, (t, 2H, ferrocene protons), 4.122 (m, 5H, unsubstituted ferrocene ring), 2.582 (t, 2H, $-CO-CH_2-$protons), 1.813–0.846 (33 H, methylene and methyl protons). ^{13}C-NMR ($CDCl_3$): δ (ppm): 171.921 (>C=O), 165.0 (>C=O), 150.105, 149.818, 145.751, 137.683, 129.952, 127.750, 127.707, 126.05, 125.34, 121.682, 121.51 (aromatic carbons), 82.65, 69.6, 69.5, 66.6 (4C, C_5H_5 and C_5H_4), 34.05–13.7 (17C aliphatic).

General Procedure For Preparing Phenyl Analogues, 4a-d

To a solution containing 0.2618 g (2.145 mmol) benzoic acid and 2.145 mmol of the corresponding **3a** ÷ **d** phenols in 50 ml anhydrous CH_2Cl_2 a solution containing 0.485 g (2.359 mmol) DCC and a catalytic amount of DMAP in 10 ml anhydrous CH_2Cl_2 was added. The reaction mixture was stirred for 4 hours at room temperature. The dicyclohexylurea was filtered off and the solvent was removed under reduced pressure. The obtained solid was purified by passing through a silica gel column (CH_2Cl_2: hexanes). Yields: 16.5 ÷ 48%.

Benzoic acid 4-(4-octadecyloxy-phenylazo)-phenyl ester, 4a. $\eta =$ 30.0%. IR (KBr pellets): 2916, 2848, 1741, 1604, 1585, 1496, 1253, 1209, 842 cm^{-1}. ^{1}H-NMR ($CDCL_3$): δ (ppm): 8.25–6.96 (12H, aromatic protons), 4.04 (t, 2H, $-OCH_2-$), 1.82–0.84 (35H, methylene and methyl protons). ^{13}C-NMR ($CDCL_3$): δ (ppm): 174.3 (>C=O), 161.8 (>C=O), 152.1, 150.0, 146.2, 133.3, 129.8, 128.1, 124.3, 123.3, 121.8, 114.2 (aromatic carbons), 67.9 ($-o-CH_2-$), 31.5–13.7 (17C aliphatic).

Benzoic acid 4-(4-octadecanoyloxy-phenylazo)-phenyl ester, 4b. $\eta = 48\%$. IR (KBr pellets): 2916, 2848, 1735, 1595, 1492, 1288, 1155, 694 cm^{-1}. ^1H-NMR ($CDCL_3$): δ (ppm): 8.31–7.29 (12H, aromatic protons), 2.66 (t, 2H, $-O-CO-CH_2-$protons), 1.84–0.91 (33H, methylene and methyl protons).^{13}C-NMR ($CDCL_3$): δ (ppm): 171.5 ($>C=O$), 164.3 ($>C=O$), 152.5, 152.4, 149.7, 149.6, 133.3, 129.8, 128.8, 128.2, 123.7, 123.6, 121.9, 121.8 (aromatic carbons), 34.0–13.7 (17C aliphatic).

Benzoic acid 4-(4-octadecyloxy-biphenyl) ester, 4c. $\eta = 33.9\%$. IR (KBr pellets): 2916, 2848, 1732, 1610, 1500, 1294, 806 cm^{-1}. ^1H-NMR ($CDCL_3$): δ (ppm): 8.24–6.948 (12H, aromatic protons), 3.996 (t, 2H, $-OCH_2-$), 1.864–0.846 (35H, methylene and methyl protons). ^{13}C-NMR ($CDCL_3$): δ (ppm): 166.0 ($>C = O$), 158.5, 149.5, 138.4, 133.3, 129.7, 128.1, 127.6, 127.3, 121.4, 114.3 (aromatic carbons), 67.6($-O-CH_2-$), 33.0–13.8 (17C aliphatic).

Benzoic acid 4-(4-octadecanoyloxy-biphenyl) ester, 4d. $\eta = 16.5\%$. IR (KBr pellets): 2916, 2848, 1737, 1606, 1496, 1290, 1161, 696 cm^{-1}. ^1H-NMR ($CDCL_3$): δ (ppm): 8.25–7.13 (12H, aromatic protons), 2.58 (t, 2H, $-O-CO-CH_2-$protons), 1.77–0.84 (33H, methylene and methyl protons). ^{13}C-NMR ($CDCL_3$): δ (ppm): 171.9 ($>C=O$), 164.4 ($>C=O$), 149.9, 149.8, 137.7, 137.5, 133.2, 129.7, 129.0, 128.1, 127.7, 121.6, 121.5 (aromatic carbons), 34.0–13.7 (17C aliphatic).

General Procedure For Preparing Phenyl Analogues, 5a, 5b

To a solution containing 0.25 g (0.816 mmol) 4-ferrocenyl-benzoic acid and 0.816 mmol 4-phenylazo-phenol or biphenyl-4-ol in 25 ml anhydrous CH_2Cl_2, a solution containing 0.185 g (0.897 mmol) DCC and a catalytic amount of DMAP in 6 ml anhydrous CH_2Cl_2 was added. The reaction mixture was stirred for 4 hours at room temperature. The dicyclohexylurea was filtered off and the solvent was removed under reduced pressure. The darkness brick-colored solid was purified by passing through a column of silica gel (CH_2Cl_2, for 5a and CH_2Cl_2: hexanes 1:1 for 5b). Yields: 53.47 ÷ 68.6%.

4-Ferrocenyl-benzoic acid 4-phenylazo-phenyl ester, 5a. $\eta = 68.6\%$. Mp = 194–200°C. IR (KBr pellets): 1726, 1604, 1591, 1269, 1195, 1180, 1087, 819 cm^{-1}. ^1H-NMR ($CDCL_3$): δ (ppm): 8.15–7.24 (12H, aromatic protons), 4.75 (s, 2H, ferrocene protons), 4.428, (s, 2H, ferrocene protons), 4.062 (s, 5H, unsubstituted ferrocene ring). ^{13}C-NMR ($CDCL_3$): δ (ppm): 163.0 ($>C=O$), 152.6, 152.2, 149.8, 146.0, 130.6, 130.0, 128.7, 125.8, 125.4 123.7, 122.5, 122.0 (12 aromatic carbons), 82.5 69.6, 69.5, 66.6 (ferrocene and ferrocenyl carbons).

4-Ferrocenyl-Benzoic Acid 4-Biphenyl Ester, 5b. $\eta = 53.47\%$. Mp = 239–241°C. IR (KBr pellets): 1724, 1606, 1485, 1276, 1199, 1089, 821 cm^{-1}. ^{1}H-NMR ($CDCL_3$): δ (ppm): 8.2–7.25 (12H, aromatic protons), 4.75 (s, 2H, ferrocene protons), 4.42 (s, 2H, ferrocene protons), 4.069 (m, 5H, unsubstituted ferrocene ring). ^{13}C-NMR ($CDCL_3$): δ (ppm): 164.8 (>C=O), 150.0, 145.7, 140.0, 138.5, 129.9, 128.4, 127.8, 126.9, 126.7, 126.0, 125.3, 121.6 (12 aromatic carbons), 82.7, 69.6, 69.5, 66.5 (ferrocene and ferrocenyl carbons).

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