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Synthesis and Liquid Crystalline Properties of some Esters of 4-Ferrocenyl-4'-hydroxyazobenzene

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Abstract

The paper describes synthesis and mesogenic behavior of a new class of ferrocenomesogens obtained by esterification of 4-ferrocenyl-4'-hydroxyazobenzene with some 4-*n*-alkyloxybenzoic acids / 4-*n*-alkanoyloxy or 4-*n*-alkenoyloxybenzoic acids in the presence of N,N'-dicyclohexylcarbodiimide and 4-dimethylaminopyridine. Based on differential scanning calorimetry and polarized optical microscopy investigations, it was established that 12 from the 15 synthesized compounds presented liquid crystalline properties, mainly monotropic nematic. All the investigated compounds were thermally stable in the existence range of the mesophases. Molecular modeling studies have been performed in order to establish correlations between structure and liquid crystalline properties. Parameters as lengths, diameters, dipole moments and molecular asymmetry coefficients and geometries of minimum energy have been obtained. A model of a cell of minimum energy for systems containing eight molecules of type 4-((4-ferrocenyl-phenylazo)phenyl) 4-alkyloxybenzoate has been proposed.

Keywords: Liquid crystals, azo ferrocenomesogens, nematic phases

1. Introduction

In the field of liquid crystals with metal atoms, ferrocene-containing liquid crystals have been frequently studied. This is understandable, because the bulky ferrocenyl unit can be used to increase thermal stability and to bring physical properties such as color, polarisability, magnetism and offers many synthetic possibilities.[1–12] Due to its high reactivity towards electrophiles, a lot of interesting ferrocene containing liquid-crystalline compounds, such as mono-, di- or trisubstituted ferrocene derivatives, ferrocenophanes, ferrocene containing polymers, ferrocene containing dendrimers, ferrocene-fullerene dyads, hydrogen – bonded ferrocene have been synthesized.[6–15] These materials display nematic, smectic, TGBA, blue phases, columnar or cubic mesophases. Such compounds may have possible applications in nanotechnology, solar cell technology, electro-optic devices, switches and rewritable color recording devices.[4–11] New applications of these materials are still waiting to be discovered.

A large number of ferrocene derivatives with liquid crystalline properties are monosubstituted. Molecular simulations have showed that the molecular shape of such monosubstituted ferrocene derivatives is of L-profile, with a high length/diameter ratio. This shape allows interactions between molecules and favors the appearance of mesophases.[2] Studies based on synthesis and mesogenic investigations of monosubstituted ferrocene derivatives have demonstrated that ferrocenomesogens have to contain minimum three benzene rings and that mesogenic properties and thermal stability can be modified by varying the nature of groups attached to the ferrocenyl unit.[1–4]

The goal of the paper is to extend the classes of monosubstituted ferrocenomesogens obtained in our research group, which mainly incorporated azobenzene units in different regions of the molecules. The paper presents the synthesis and liquid crystalline properties of two classes of compounds obtained by the esterification of 4-ferrocenyl-4'-hydroxyazobenzene with some 4-*n*-alkyloxybenzoic acids / 4-*n*-alkanoyloxy or 4-*n*-alkenoyloxybenzoic acids. Both two classes contain the azobenzene unit directly connected to the ferrocene.

2. Experimental

2. 1. Materials and Instrumentations

All chemicals such as *n*-alkyl bromides, 4-hydroxybenzoic acid, elaidic and oleic acids, ferrocene, TBAHS, DCC, DMAP etc, were purchased from Aldrich 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 or Al_2O_3 plates (Merck, silica gel F_{254}, aluminum oxide F_{254}). Dichloromethane was dried over K_2CO_3 and freshly distilled before use. 4-Nitro–4'-hydroxyazobenzene was obtained according to the literature data.[16]

The NMR spectra were recorded using a Bruker Avance DRX 400 MHz spectrometer with tetramethylsilane as internal standard. The IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrometer (NaCl crystal window). The mass spectra were recorded with a quadrupole-time of flight mass spectrometer equipped with an electrospray ion source (Agilent 6520 Accurate Mass Q-ToF LC/MS). The optical textures were observed using a Linkam heating stage and Linksys 32 temperature control unit in conjunction with a Axioscop 40 Zeiss polarizing optical microscope and Qimaging / Retiga-4000R camera for image capture. Transition temperatures were confirmed by DSC analysis (Mettler Toledo TGA-SDTA 851e). Heating and cooling cycles were run at rates of 10 °C/min under nitrogen atmosphere. All thermal analyses were performed on a Mettler-Toledo TGA SDTA851^e derivatograph in an N_2 atmosphere, with a flow rate of 20 mL/min and a heating rate of 10 °C/min from 25 °C to 900 °C. In order to obtain comparable data, constant operational parameters were kept for all samples. The melting points were recorded using a melting point meter Krüss Optotronic KSPI – N.

The minimization of the individual molecules was performed with the quantum DMol 3 module. The systems consisting from several molecules were optimized with molecular mechanic Forcite module (Materials Studio 4.0).[17]

2. 2. Synthesis

Synthesis of 4-ferrocenyl-4'-hydroxyazobenzene (3)

Step I: reduction of 4-nitro–4'-hydroxyazobenzene

4-Nitro–4'-hydroxyazobenzene (17.98 g, 73.99 mmol) was dissolved under reflux in 650 ml of ethanol and a hot solution containing 53.3 g (222.08 mmol) sodium sulfide nonahydrated salt, 100 ml of water and 100 ml of ethanol was added over. The mixture was heated under reflux for 6 hours. After cooling, the mixture was progressively neutralized using concentrated hydrochloric acid to pH = 7. The yellow solid was collected by filtration and washed several times with water. 4-Amino–4'-hydroxyazobenzene was further used without prior purification. Yellow crystals, Yield: 12 g (76.1%). ^{1}H-NMR (DMSO, 400 MHz): δ 8.83 (s, 1H, OH), 7.76 (d, 2H, ArH), 7.71 (d, 2H, ArH), 6.98 (d, 2H, ArH), 6.79 (d, 2H, ArH), 5.30 (s, 2H, NH_2). ^{13}C-NMR (DMSO, 100 MHz): δ 160.27, 152.55, 147.70, 145.38, 125.60, 124.98, 116.72, 114.96 (8C, aromatic).

Step II: diazotization and arylation

A mixture of 4-amino-4'-hydroxyazobenzene (12 g, 56 mmol), 25 ml water and 18 ml hydrochloric acid 32% was cooled to –5 ~ 0 °C with an ice-salt bath. $NaNO_2$ (3.9 g, 56 mmol) was dissolved in 9 ml water and the aqueous solution was added dropwise, under stirring, to the mixture above. After the addition was finished, the mixture was stirred for 30 min at 0 °C. Ferrocene (5.3 g, 28 mmol), was dissolved in 200 ml diethyl ether and 0.21 g tetrabutylammonium hydrogen sulfate was added as phase transfer catalyst. The mixture was stirred at 5°C for 30 min and then the diazonium salt solution was added dropwise under stirring. After the addition was finished, the reaction mixture was further stirred for 72 h at room temperature. The deep red organic layer was collected, washed several times with water, dried over anhydrous $MgSO_4$ and evaporated to give a red solid. 4-Ferrocenyl-4'-hydroxyazobenzene (**3**) was purified by column chromatography on silica gel with n-hexane: diethyl ether = 1:1 as eluent to give red crystals. M.p. = 176 °C, Yield: 3 g (23%). IR (KBr, cm^{-1}) 3270 (ν OH), 3092, 3053 (ν CH aromatic), 1584, 1500 (ν C-C aromatic), 1134 (ν C-O), 847 (ν CH aromatic, p-disubstituted). ^{1}H-NMR (DMSO, 400 MHz): δ 10.27 (s, 1H, OH), 7.8 (d, 2H, ArH), 7.75 (d, 2H, ArH), 7.65 (d, 2H, ArH), 6.96 (d, 2H, ArH), 4.89 (t, 2H, C_5H_4), 4.43 (t, 2H, C_5H_4) 4.06 (s, 5H, C_5H_5). ^{13}CNMR (DMSO, 100 MHz): δ 161.11, 150.51, 145.95, 142.76, 126.84, 125.07, 122.82, 116.41 (8C, ArH), 83.83, 70.04, 67.12, 65.04, (4C, $C_5H_{5,}$ C_5H_4).

General procedure for the synthesis of monosubstituted ferrocenyl derivatives (7a÷7f)

A mixture of 4-alkyloxybenzoic acid (2.6 mmol), DCC (2.86 mmol) and DMAP (catalytic amount) in dry dichloromethane was stirred at room temperature for 2h. Then a solution of 4-ferrocenyl-4'-hydroxyazobenzene (2.6 mmol) in dry dichloromethane was added. The reaction mixture was stirred at room temperature for about 2 days. The precipitated N,N'-dicyclohexyl urea was filtered off and the filtrate was rotary evaporated. The products were purified by column chromatography on silica gel/n-hexane : CH_2Cl_2 = 1:1.

4-((4-ferrocenyl-phenylazo)phenyl) 4-hexyloxybenzoate (7a)

Quantities: 4-hexyloxybenzoic acid (0.577 g, 2.6 mmol), DCC (0.59 g, 2.86 mmol), DMAP (catalytic amount), 4-ferrocenyl-4'-hydroxyazobenzene (1g, 2.6 mmol). Orange crystals. Yield: 0.25 g (16.7%). IR (KBr, cm^{-1}) 3099, 3084 (ν CH aromatic), 2947, 2924 (ν CH aliphatic), 1720 (ν C=O), 1604, 1510 (ν C=C aromatic), 1279 (ν C-O), 845 (ν CH aromatic p-disubstituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): ä 8.17 (d, 2H, ArH), 8.01 (d, 2H, ArH), 7.87 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.38 (d, 2H, ArH), 6.99 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 4.05 (t, 2H, CH_2O), 1.82 (cv, 2H, CH_2), 1.48 (cv, 2H, CH_2), 1.35 (m, 4H, CH_2), 0.92 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 164.66 (esteric), 163.70, 152.89, 150.69, 150.47, 143.35, 132.37, 126.36, 123.92, 123.12, 122.45, 121.28, 114.37 (12C aromatic), 83.81, 69.84, 69.73, 68.36, 66.82, 31.55, 29.06, 25.66, 22.59, 14.03 (4C ferrocene + 6C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 587 [M+1]$^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-heptyloxybenzoate (7b)

Quantities: 0.613g (2.6 mmol) 4-heptyloxybenzoic acid; 0.59 g (2.86 mmol) DCC, DMAP (catalytic amount), 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield: 0.45 g (28.6%).

IR (KBr, cm^{-1}) 3101, 3084 (ν CH aromatic), 2951, 2920 (ν CH aliphatic), 1718 (ν C=O), 1604, 1512 (ν C=C aromatic), 1278 (ν C-O), 846 (ν CH aromatic p-disubstituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.15 (d, 2H, ArH), 7.99 (d, 2H, ArH), 7.85 (d, 2H, ArH), 7.59 (d, 2H, ArH), 7.35 (d, 2H, ArH), 6.99 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.05 (s, 5H, C_5H_5), 4.03 (t, 2H, CH_2O), 1.83 (cv, 2H, CH_2), 1.32~1.48 (m, 8H, 4XCH_2), 0.90 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100MHz): δ 164.66 (esteric), 163.70, 152.89, 150.70, 150.47, 143.34, 132.37, 126.37, 123.91, 123.11, 122.45, 121.2, 114.37 (12 C aromatic), 83.82, 69.83, 69.72, 68.37, 66.82, 31.76, 29.10, 29.03, 25.95, 22.6, 14.08 (4C ferrocene + 7C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 601 [M+1]$^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-octyloxybenzoate (7c)

Quantities: 0.65g (2.6 mmol) 4-octyloxybenzoic acid; 0.59 g (2.86 mmol) DCC, DMAP (catalytic amount), 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield: 0.45 g (28.1%). IR (KBr, cm^{-1}) 3099, 3051 (ν CH aromatic), 2945, 2920 (ν CH aliphatic), 1722 (ν C=O), 1606, 1578 (ν C=C aromatic), 1274 (ν C-O), 848 (ν CH aromatic p-disubstituted) ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.15 (d, 2H, ArH), 7.99 (d, 2H, ArH), 7.85 (d, 2H, ArH), 7.59 (d, 2H, ArH), 7.35 (d, 2H, ArH), 6.97 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 4.03 (t, 2H, CH_2O), 1.82 (cv, 2H, CH_2), 1.30~1.48 (m, 10H, 5XCH_2), 0.89 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 164.65 (esteric), 163.69, 152.89, 150.69, 150.47, 143.34, 132.36, 126.37, 123.91, 123.11, 122.44, 121.27, 114.37 (12 C aromatic), 83.82, 69.83, 69.72, 68.37, 66.82, 31.80, 29.33, 29.22, 29.09, 25.99, 22.65, 14.10 (4C ferrocene + 8C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 615 [M+1]$^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-nonyloxybenzoate (7d)

Quantities: 0.686g (2.6 mmol) 4-nonyloxybenzoic acid, 0,59 g (2.86 mmol) DCC, DMAP (catalytic amount), 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield: 0.20 g (12.2%). IR (KBr, cm^{-1}) 3103, 3075 (ν CH aromatic), 2924, 2852 (ν CH aliphatic), 1730 (ν C=O), 1608, 1512 (ν C=C aromatic), 1269 (ν C-O), 846 (ν CH aromatic p-disubstituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.15 (d, 2H, ArH), 7.99 (d, 2H, ArH), 7.85 (d, 2H, ArH), 7.59 (d, 2H, ArH), 7.36 (d, 2H, ArH), 6.97 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 4.04 (t, 2H, CH_2O), 1.82 (cv, 2H, CH_2), 1.30~1.48 (m, 12H, 6XCH_2), 0.89 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 164.66 (esteric),163.69, 152.89, 150.98, 150.46, 143.35, 132.37, 126.37, 123.92, 123.11, 122.45, 121.26, 114.37 (12 C aromatic), 83.80, 69.50, 69.83, 68.36, 66.82, 31.88, 29.52, 29.37, 29.26, 29.10, 25.98, 22.67, 14.12 (4C ferrocene + 9C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 629 [M+1]$^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-decyloxybenzoate (7e)

Quantities: 0.725g (2.6 mmol) 4-decyloxybenzoic acid; 0.59 g (2.86 mmol) DCC, DMAP (catalytic amount), 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield: 0.20 g (12.5%). IR (KBr, cm^{-1}) 3099, 3086 (ν CH aromatic), 2922, 2850 (ν CH aliphatic), 1720 (ν C=O), 1606, 1512 (ν C=C aromatic), 1267 (ν C-O), 848 (ν CH aromatic p-disubstituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.15 (d, 2H, ArH), 7.99 (d, 2H, ArH), 7.85 (d, 2H, ArH), 7.59 (d, 2H, ArH), 7.36 (d, 2H, ArH), 6.97 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 4.05 (t, 2H, CH_2O), 1.83 (cv, 2H, CH_2), 1.28~1.48 (m, 14H, 7XCH_2), 0.89 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 164.66 (esteric), 163.71, 152.90, 150.71, 150.48, 143.36, 132.37, 126.38, 123.92, 123.12, 122.45, 121.28, 114.38 (12 C aromatic), 83.83, 69.84, 69.73, 66.83, 66.38, 31.90, 29.56 ÷ 29.10, 25.99, 22.69, 14.12 (4C ferrocene + 10 C aliphatic). MS: ($CHCl_3$:CH_3OH =3:1): *m/z* 642 [M]$^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-octadecyloxybenzoate (7f)

Quantities: 1.014g (2.6 mmol) 4-octadecyloxybenzoic acid; 0.59 g (2.86 mmol) DCC, DMAP (catalytic amount), 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Red crystals. Yield: 0.45 g (22.8%).

IR (KBr, cm^{-1}) 3097, 3075 (ν CH aromatic), 2920, 2848 (ν CH aliphatic), 1734 (ν C=O), 1600, 1508 (ν C=C aromatic), 1253 (ν C-O), 846 (ν CH aromatic p-disubstituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.15 (d, 2H, ArH), 8.00 (d, 2H, ArH), 7.86 (d, 2H, ArH), 7.60 (d, 2H, ArH), 7.36 (d, 2H, ArH), 6.97 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.41 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 4.05 (t, 2H, CH_2O), 1.83 (cv, 2H, CH_2), 1.26~1.48 (m, 30H, 15XCH_2), 0.88(t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 164.65 (esteric), 163.70, 152.89, 150.70, 150.47, 143.34, 132.36, 126.37, 123.91, 123.11, 122.44, 121.27, 114.37 (12 C aromatic), 83.82, 69.83, 69.72, 66.82, 66.37, 31.93, 29.70 ÷ 29.09, 25.98, 22.69, 14.12 (4C ferrocene + 18C aliphatic). MS: ($CHCl_3$:CH_3OH =3:1): *m/z* 754 $[M]^+$.

General procedure for the synthesis of monosubstituted ferrocenyl derivatives (8a ÷ 8i)

A mixture of 4-(alkanoyloxy)benzoic acids or 4-(alkenoyloxy)benzoic acids (2.6 mmol), DCC (2.86 mmol) in dry dichloromethane was stirred at room temperature for 5 min. Then a solution of 4-ferrocenyl-4'-hydroxyazobenzene (2.6 mmol) in dry dichloromethane was added. The reaction was stirred at room temperature for 24 h. The precipitated N,N'-dicyclohexylurea was filtered off and the filtrate was rotary evaporated. The products were purified by column chromatography on silica gel with n-hexane : CH_2Cl_2 = 1:1 as eluent.

4-((4-ferrocenyl-phenylazo)phenyl) 4-pentanoyloxybenzoate (8a)

Quantities: 0.570 g (2.6 mmol) 4-pentanoyloxy benzoic acid; 0.594 g (2.86 mmol) DCC, 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield 0.35 g (22.81%). IR (KBr, cm^{-1}): 3107, 3078 (ν C-H aromatic) 2924, 2856 (ν C-H aliphatic), 1755 (ν C=O), 1730 (ν C=O), 1600, 1500 (ν C=C aromatic), 1276 (ν C-O, COO), 1211 (ν C-O, COO), 1145 (ν C-O, R-O-Ar), 847 (ν C-H aromatic p-substituted).

^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.27(d, 2H, ArH), 8.02 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.27 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.41 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 2.61 (t, 2H, CH_2COO), 1.77 (cv, 2H, CH_2), 1.47 (m, 2H, CH_2), 0.99 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 171.66, 164.13 (2C, esteric) 155.15, 152.60, 150.69, 150.66, 143.46, 131.86, 126.73, 126.39, 123.97, 123.15, 122.34, 121.95 (12 C aromatic), 83.81, 69.85, 69.75, 66.84 (4C, ferrocene), 34.15, 26.90, 22.24, 13.71 (4C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 586 $[M+1]^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-hexanoyloxybenzoate (8b)

Quantities: 0.607 g (2.6 mmol) 4-hexanoyloxy benzoic acid; 0.594 g (2.86 mmol) DCC, 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield: 0.4 g (25.47%). IR (KBr, cm^{-1}): 3107, 3076 (ν C-H aromatic), 2926, 2855 (ν C-H aliphatic), 1755 (ν C=O), 1732 (ν C=O), 1600, 1500 (ν C=C aromatic), 1277 (ν C-O, COO), 1207 (ν C-O, COO), 1146 (ν C-O, R-O-Ar), 844 (ν C-H aromatic p-substituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.27(d, 2H, ArH), 8.02 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.27 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.41 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 2.60 (t, 2H, CH_2COO), 1.79 (cv, 2H, CH_2), 1.42 (m, 4H, CH_2), 0.95 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 171.68, 164.14 (2C esteric), 155.15, 152.60, 150.69, 150.66, 143.47, 131.86, 126.72, 126.39, 123.97, 123.15, 122.35, 121.95 (12 C aromatic), 83.81, 69.85, 69.75, 66.84 (4C, ferrocene): 34.40, 31.26, 24.53, 22.31, 13.91 (5C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 600 $[M+1]^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-heptanoyloxybenzoate (8c)

Quantities: 0.644 g (2.6 mmol) 4-heptanoyloxy benzoic acid; 0.594 g (2.86 mmol) DCC, 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield: 0.52 g (32.35%). IR (KBr, cm^{-1}): 3099, 3078 (ν C-H aromatic), 2918, 2850 (ν C-H aliphatic), 1757 (ν C=O), 1734 (ν C=O), 1601, 1504 (ν C=C aromatic), 1275 (ν C-O, COO), 1233 (ν C-O, COO), 1136 (ν C-O, R-O-Ar), 846 (ν C-H aromatic p-substituted).

^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.27(d, 2H, ArH), 8.02 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.27 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.41 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 2.61 (t, 2H, CH_2COO), 1.78 (cv, 2H, CH_2), 1.35 (m, 6H, CH_2), 0.92 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 171.68, 164.15 (2C esteric), 155.15, 152.60, 150.69, 150.66, 143.47, 131.87, 126.39, 123.98, 123.98, 123.16, 122.35, 121.96 (12 C aromatic), 83.81, 69.85, 69.75, 66.84 (4C, ferrocene), 34.44, 31.43, 28.77, 24.82, 22.48, 14.03 (6C aliphatic). MS: ($CHCl_3$: CH_3OH=3:1): *m/z* 614 $[M]^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-octanoyloxybenzoate (8d)

Quantities: 0.680 g (2.6 mmol) 4-octanoyloxy benzoic acid; 0.594 g (2.86 mmol) DCC, 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield: 0.48 g (29.19%). IR (KBr, cm^{-1}): 3090, 3053 (ν C-H aromatic), 2928, 2851 (ν C-H aliphatic), 1750 (ν C=O), 1736 (ν C=O), 1597, 1500 (ν C=C aromatic), 1269 (ν C-O, COO), 1207 (ν C-O, COO), 1144 (ν C-O, R-O-Ar), 822 (ν C-H aromatic p-substituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.27(d, 2H, ArH), 8 .02 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.27 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 2.60 (t, 2H, CH_2COO), 1.78 (cv, 2H, CH_2), 1.32 (m, 8H, CH_2), 0.90 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 171.65, 164.12 (2C esteric), 155.13, 152.58, 150.67, 150.64, 143.46, 131.85, 126.70, 126.38, 123.97, 123.15, 122.34, 121.94 (12 C aromatic), 83.79, 69.84, 69.75, 66.83 (4C, ferrocene), 34.42, 31.64, 29.05, 28.91, 24.84, 22.60, 14.07 (7C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 628 $[M]^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-nonanoyloxy-benzoate (8e)

Quantities: 0.716 g (2.6 mmol) 4-nonanoyloxy benzoic acid; 0.594 g (2.86 mmol) DCC, 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield: 0.45 g (26.78%). IR (KBr, cm^{-1}): 3088, 3055 (ν C-H aromatic), 2926, 2857 (ν C-H aliphatic), 1755 (ν C=O), 1734 (ν C=O), 1600, 1500 (ν C=C aromatic), 1269 (ν C-O, COO), 1206 (ν C-O, COO), 1165 (ν C-O, R-O-Ar), 847 (ν C-H aromatic p-substituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.27(d, 2H, ArH), 8.02 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.27 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 2.60 (t, 2H, CH_2COO), 1.77 (cv, 2H, CH_2), 1.30 (m, 10H, CH_2), 0.90 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 171.65, 164.12 (2C esteric), 155.13, 152.58, 150.67, 150.64, 143.46, 131.85, 126.70, 126.38, 123.97, 123.15, 122.34, 121.94 (12 C aromatic), 83.79, 69.84, 69.75, 66.83 (4C, ferrocene), 34.42, 31.80, 29.21, 29.11, 29.09, 24.84, 22.64, 14.10 (8C aliphatic). MS: ($CHCl_3$: CH_3OH=3:1): *m/z* 642 $[M+1]^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-decanoyloxy-benzoate (8f)

Quantities: 0.754 g (2.6 mmol) 4-nonanoyloxy benzoic acid; 0.594 g (2.86 mmol) DCC, 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Orange crystals. Yield: 0.20 g (11.64%). IR (KBr, cm^{-1}): 3086, 3055 (ν C-H aromatic), 2924, 2850 (ν C-H aliphatic), 1743 (ν C=O), 1600, 1499 (ν C=C aromatic), 1269 (ν C-O, COO), 1204 (ν C-O, COO), 1148 (ν C-O, R-O-Ar), 850 (ν C-H aromatic p-substituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.26(d, 2H, ArH), 8.02 (d, 2H, ArH), 7.87 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.26 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 2.59 (t, 2H, CH_2COO), 1.78 (cv, 2H, CH_2), 1.29 (m, 12H, CH_2), 0.89 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 171.66, 164.12 (2C esteric), 155.14, 152.58, 150.68, 150.65, 143.46, 131.85, 126.70, 126.38, 123.97, 123.15, 122.34, 121.95 (12 C aromatic), 83.79, 69.84, 69.75, 66.84 (4C, ferrocene), 34.43, 31.86, 29.41 ÷ 29.09, 24.85, 22.67, 14.11 (9C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 656 $[M]^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-stearoyloxybenzoate (8g)

Quantities: 1.058 g (2.6 mmol) 4-stearoyloxy benzoic acid; 0.594 g (2.86 mmol) DCC, 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Red crystals. Yield: 0.20 g (9.95%). IR (KBr, cm^{-1}): 3098, 3080 (ν C-H aromatic), 2920, 2851 (ν C-H aliphatic), 1747 (ν C=O), 1597, 1497 (ν C=C aromatic), 1263 (ν C-O, COO), 1199 (ν C-O, COO), 1157 (ν C-O, R-O-Ar), 850 (ν C-H aromatic p-substituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.27 (d, 2H, ArH), 8.02 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.27 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 2.60 (t, 2H, CH_2COO), 1.77 (cv, 2H, CH_2), 1.26 (m, 20H, CH_2), 0.88 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 171.64, 164.12 (2C esteric), 155.14, 152.59, 150.68, 150.65, 143.46, 131.85, 126.71, 126.38, 123.97, 123.15, 122.34, 121.94 (12 C aromatic), 83.79, 69.84, 69.75, 66.84 (4C, ferrocene), 34.41, 32.62, 31.91, 29.70 ÷ 28.92, 24.83, 22.68, 14.12 (17 C aliphatic). MS: ($CHCl_3$: CH_3OH=3:1): *m/z* 768 $[M]^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-(Z)-(octadec-9-enoyloxy)benzoate (8h)

Quantities: 0.738 g (2.6 mmol) 4-(Z)-(octadec-9-enoyloxy)benzoic acid; 0.594 g (2.86 mmol) DCC, 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Red crystals. Yield: 0.19 g (9.47%). IR (KBr, cm^{-1}): 3099, 3078 (ν C-H aromatic), 2924, 2853 (ν C-H aliphatic), 1748 (ν C=O), 1643 (ν C=C), 1599, 1497 (ν C=C aromatic), 1263 (ν C-O, COO), 1199 (ν C-O, COO), 1157 (ν C-O, R-O-Ar), 821 (ν C-H aromatic p-substituted). ^{1}H-RMN ($CDCl_3$, 400 MHz): δ 8.26 (d, 2H, ArH), 8.02 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.26 (d, 2H, ArH), 5.36 (m, 2H, CH=CH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 2.59 (t, 2H, CH_2COO), 2.03 (t, 4H, CH_2) 1.77 (cv, 2H, CH_2), 1.26 (m, 20H, CH_2), 0.88 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 171.67, 164.12 (2C esteric), 155.13, 152.58, 150.66, 150.64, 143.47, 131.85, 130.0, 129.9, 126.70, 126.37, 123.97, 123.16, 122.34, 121.94 (12 C aromatic + 2C, CH=CH), 83.78, 69.84, 69.75, 66.83 (4C, ferrocene), 34.41, 31.91, 29.77 ÷ 28.96, 27.24, 27.16, 24.82, 22.69, 14.12 (15C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 766 $[M]^+$.

4-((4-ferrocenyl-phenylazo)phenyl) 4-(E)-(octadec-9-enoyloxy)benzoate (8i)

Quantities: 0.738 g (2.6 mmol) 4-(E)-(octadec-9-enoyloxy) benzoic acid; 0.594 g (2.86 mmol) DCC, 1g (2.6 mmol) 4-ferrocenyl-4'-hydroxyazobenzene. Red crystals. Yield: 0.16 g (7.98%). IR (KBr, cm^{-1}): 3097, 3076 (ν C-H aromatic), 2920, 2851 (ν C-H aliphatic), 1748 (ν C=O), 1643 (ν C=C), 1599, 1499 (ν C=C aromatic), 1265 (ν C-O, COO), 1199 (ν C-O, COO), 1157 (ν C-O, R-O-Ar), 820 (ν C-H aromatic p-substituted). ^{1}HRMN ($CDCl_3$, 400 MHz): δ 8.26 (d, 2H, ArH), 8.02 (d, 2H, ArH), 7.88 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.26 (d, 2H, ArH), 5.39 (m, 2H, CH=CH), 4.73 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 2.59 (t, 2H, CH_2COO), 1.98 (t, 4H, CH_2) 1.77 (cv, 2H, CH_2), 1.26 (m, 20H, CH_2), 0.88 (t, 3H, CH_3). ^{13}C-RMN ($CDCl_3$, 100 MHz): δ 171.61, 164.09 (2C esteric), 155.12, 152.58, 150.66, 150.63, 143.45, 131.84, 130.55, 130.15, 126.69, 126.37, 123.96, 123.15, 122.33, 121.93 (12 C aromatic + 2C, CH=CH), 83.78, 69.83, 69.75, 66.82 (4C, ferrocene), 34.40, 32.61, 31.90, 29.66 ÷ 28.91, 24.82, 22.68, 14.12 (15C aliphatic). MS: ($CHCl_3$:CH_3OH=3:1): *m/z* 766 $[M]^+$.

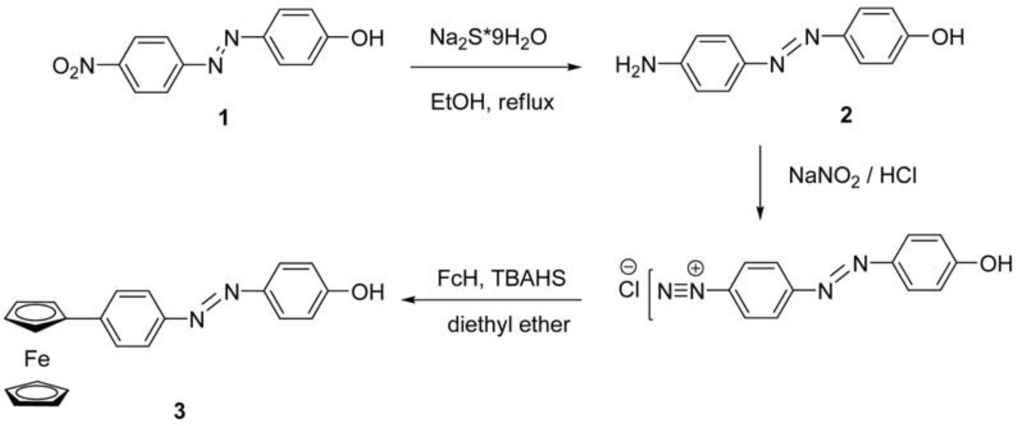
3. Results and Discussions

3. 1. Synthesis

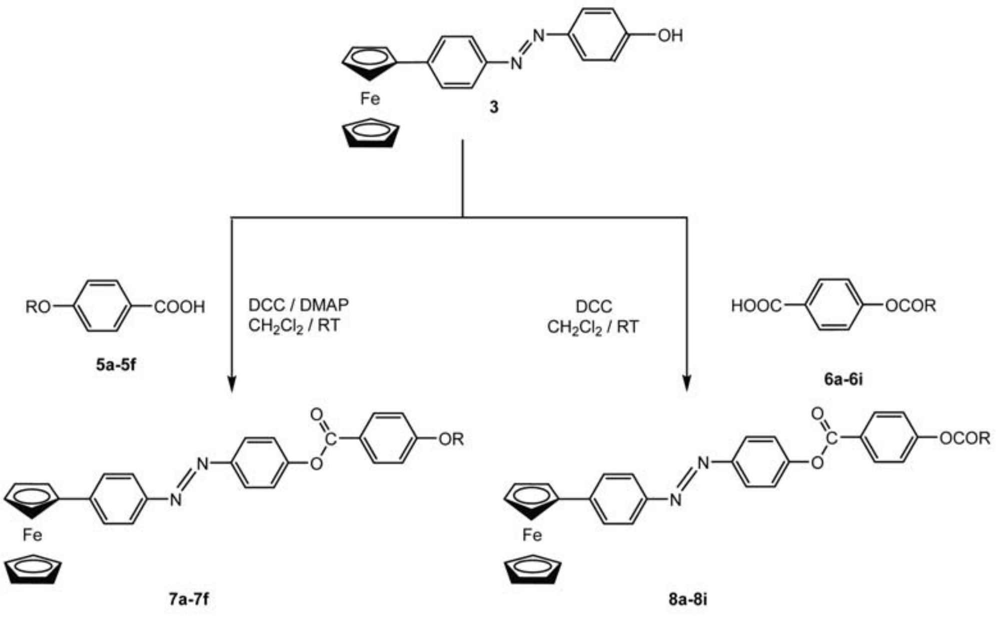
Synthesis of the ferrocenyl containing liquid crystals implied the esterification of 4-ferrocenyl-4’-hydroxyazobenzene with some alkylated or acylated 4-hydroxybenzoic acids. The 4-ferrocenyl-4’-hydroxyazobenzene (**3**) was obtained by the arrylation of ferrocene with the diazonium salt of 4-amino-4’-hydroxyazobenzene using tetrabutylammonium hydrogen sulfate (TBAHS) as phase transfer catalyst (Scheme 1).[18,19]

Starting from 4-ferrocenyl-4’-hydroxyazobenzene (**3**) two series of ferrocenyl containing liquid crystals have been obtained. The **7a÷7f** series was obtained by the esterification of **3** with **5a÷5f** 4-alkyloxybenzoic acids (R = -C_6H_{13}÷-$C_{10}H_{21}$ and -$C_{18}H_{37}$) in the presence of N,N’-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP). The second series was obtained by the esterification of **3** with **6a** ÷ **6i** 4-alkanoyloxybenzoic acids (R = -C_4H_9÷-C_9H_{19} and -$C_{17}H_{35}$) or 4-alkenoyloxybenzoic acids (R = *trans*-$C_{17}H_{33}$ and *cis*-$C_{17}H_{33}$), in the presence of DCC at room temperature, in CH_2Cl_2 (Scheme 2). These esterifications were performed without DMAP which may behave as a catalyst for unwanted trans-esterification reactions.

The 4-alkyloxybenzoic acid **5a÷5f** were prepared in accordance with literature data *via* etherification of 4-hydroxybenzoic acid with the corresponding *n*-bromoalkanes in the presence of potassium hydroxide.[20] 4-Nitro–4’-hydroxyazobenzene was obtained accordingly to modified literature data.[16]



Scheme 1. Synthesis of 4-ferrocenyl-4’-hydroxyazobenzene



Scheme 2. Synthesis of the final compounds: **5a–5f** and **7a–7f**, R = -C_nH_{2n+1}, n = 6–10, 18
6a–6g and **8a–8g**, R = -C_nH_{2n+1}, n = 4–9, 17; **6h**, **6i**
and **8h** and **8i**, R = 9-*cis*-$C_{17}H_{33}$ and R = 9-*trans*-$C_{17}H_{33}$

The 4-alkanoyloxybenzoic acids or 4-alkenoyloxybenzoic acids, **6a÷6i** were prepared by esterification of 4-hydroxybenzoic acid with the corresponding acids in the presence of N,N'-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP), in ethyl ether, at room temperature.[21]

All intermediates and final compounds were purified by flash chromatography using silica gel and *n*-hexane: CH_2Cl_2 = 1:1 as eluent. The structure and purity of the obtained compounds were confirmed by ^{1}H NMR, ^{13}C NMR, FT-IR and mass spectrometry.

3. 2. Liquid Crystalline Properties

The liquid crystalline properties of all final compounds were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). It was found that 12 compounds exhibited liquid crystalline properties, mainly monotropic nematic. The textures were assigned by visual comparison with those reported in the literature.[22]

According to DSC and POM investigations, compounds **8g** (n = 17), **8h** (n = 7, *cis*), **8i** (n = 17, *trans*) do not present liquid crystalline properties. Only compounds **7d** and **8d** presented enantiotropic nematic liquid crystalline properties. The phase transition temperatures and the associated enthalpy changes of all mesogenic compounds are summarized in Table 1.

Taking into consideration the importance of thermal stability for the whole interval of the mesophase existence, thermogravimetric studies have been performed for both **7a ÷ 7f** and **8a ÷ 8i** series. Thermogravimetric data evidenced a very good thermal stability for all compounds, the T_{onset} values (temperatures at which degradation processes with loss of mass begin) being with around 100 °C higher than the isotropisation values (T_{onset} values in Table 1).

Figure 1a shows the DSC curves of **7b** as an example for all compounds that exhibit monotropic nematic phases. On the first heating, the DSC evidenced two endothermic peaks, which correspond to a solid-solid transition (at 161

Table 1.Transition temperatures (T/°C) and associated transition enthalpy values (ΔH/kJmol^{-1})

	T/°C [ΔH/kJmol^{-1}]								
Sample	**heating**				**cooling**				**T_{onset}**
	K_1–K_2	**K_2–N**	**N–I**	**K_1 or K_2–I**	**I–N**	**N–K_1**	**K_1–K_2**	**K_2–K_3**	**(°C)**
7a	102 [–7.4]	–	–	196 [–31.9]	177 [1.9]	142 [31.6]	84 [0.8]	–	292
7b	161 [–16.8]	–	–	182 [–40.7]	179 [1.8]	139 [34.3]	–	–	299
7c	118– [–15.6]	–		171 [–33.7]	167 [1.4]	124 [25.9]	–	–	294
7d	155 [–4.2]	161 [–36.4]	173 [–2.1]	–	169 [1.8]	130 [38.7]	111 [1.1]	–	298
7e	109 [–10.5]	–	–	154 [–40.4]	147 [0.8]	112 [31.3]	–	–	291
7f	–	–	–	138 [–41.61]	138 [1.3]	122 [38.6]	–	–	305
8a	133 [–0.8]	–	–	184 [–52.5]	168 [0.1]	116 [49.3]	101 [2.8]	–	267
8b	102 [–2.9]	–	–	205 [–40.2]	192 [1.4]	156 [32.1]	–	–	275
8c	–	–	–	187 [–58.0]	187 [1.7]	155 [38.1]	138 [0.5]	52 [3.8]	277
8d	136 [–10.7]	181 [–37.3]	191 [–1.8]	–	190 [2.1]	141 [36.5]	121 [1.2]	–	283
8e	–	–	–	178 [–44.5]	176 [1.5]	130 [37.9]	–	–	279
8f	89 [–1.2]	–	–	174 [–40.2]	175 [1.7]	132 [35.3]	70 [1.6]	–	277
8g	–	–	–	147 [–61.8]	–	–	–	–	270
8h	–	–	–	143 [–98.1]	–	–	–	–	265
8i	–	–	–	154 [–112.9]	–	–	–	–	273

Abbreviations: K – crystalline, N – nematic, I – isotropic, T_{onset} = temperatures at which degradation processes with loss of mass begin

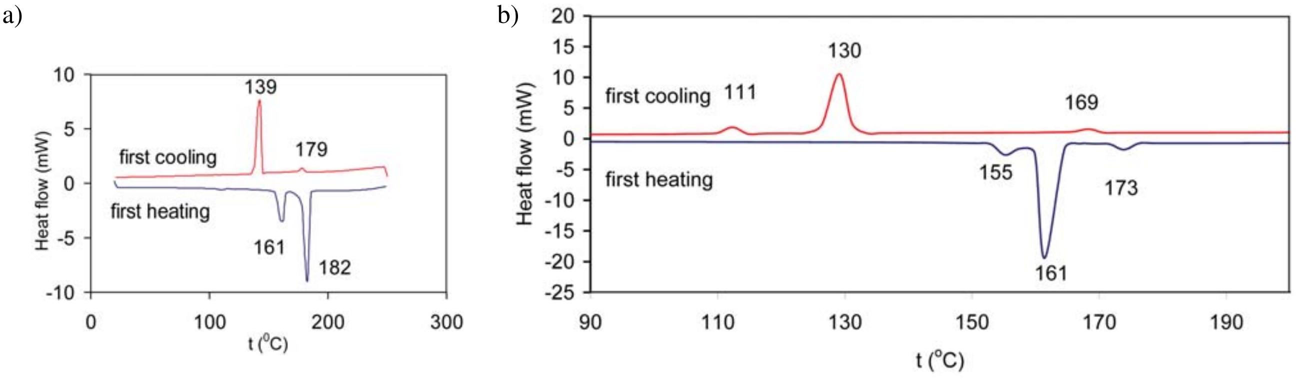


Fig. 1. DSC thermograms: a) compound **7b** and b) compound **7d**

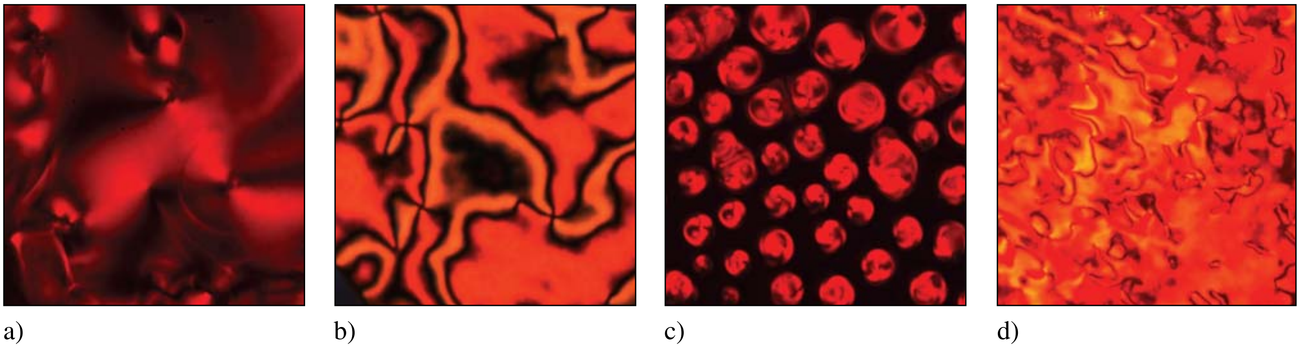

a) b) c) d)

Fig. 2. Optical textures of ferrocenomesogens of the series **7a÷7f** (on cooling): (**a**) **7a**: nematic texture at 192 °C; (**b**) **7c**: Schlieren texture at 175 °C; (**c**) **7d**: droplets texture at 172 °C; (**d**) **7f**: Schlieren texture at 138 °C.

°C) and a solid-isotropic transition at 182 °C. On the cooling cycle, the nematic mesophase was observed between the two exothermic peaks at 179 °C and 139 °C. At 139 °C the sample crystallizes from the nematic phase.

As shown in Figure 1b, on the first heating, sample **7d** exhibits three endothermic peaks: at 155 °C, corresponding to a crystalline-crystalline transition, at 161 °C corresponding to the appearence of the nematic mesophase below the clearing point detected at 173 °C. On the first cooling, three exothermic peaks were observed: 169 °C (isotropic-nematic transition), 130 °C (nematic-crystalline) and 111 °C (crystalline–crystalline transition).

Figure 2 presents some typical nematic textures for the ferrocenomesogens of the series **7a ÷ 7f**.

The DSC curves of sample **8d** are presented in Figure 3a. On heating, three endothermic peaks were detected: at 136 °C, which corresponds to a solid-solid transition, at 181 °C, corresponding to solid-liquid crystalline transition, and isotropisation that occurs at 191 °C. On the first cooling, nematic mesophase was observed between 190 °C (isotropic-nematic transition) and 141 °C (nematic-solid transition). Another crystalline-crystalline transition took place at 121 °C. The polarizing microscope observations confirmed the nematic enantiotropic behavior, too.

When the crystalline sample of **8e** was heated, an endothermic peak was observed at 178 °C (Figure 3b.). This peak corresponds to a solid–isotropic transition. On

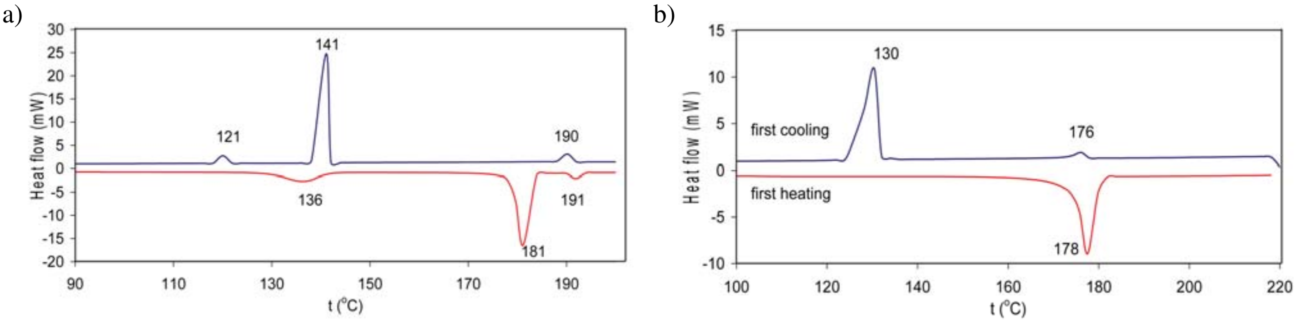
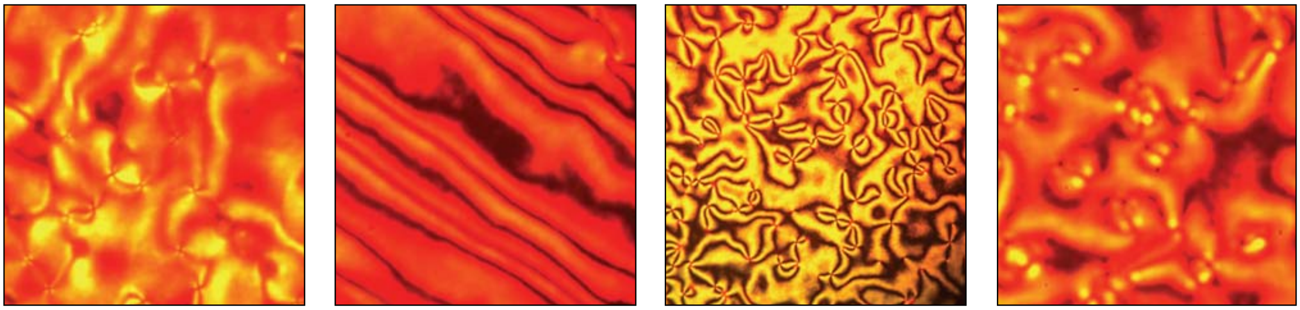


Fig. 3. DSC thermograms: a) compound **8d** and b) compound **8e**



a) b) c) d)

Fig. 4. Optical textures of nematic phases: (**a**): **8b** on cooling at 187 °C; (**b**): **8d** on heating at 189 °C; (**c**): **8e** on cooling at 166 °C; (**d**): **8f** on cooling at 167 °C

cooling two exothermic peaks are present: one peak corresponds to an isotropic–nematic transition at 176 °C and the second to a nematic– crystalline transition at 130 °C. The polarizing microscopic observations indicated that **8e** forms small droplets on cooling from the isotropic liquid. Then these small droplets come together to form a Schlieren texture (Figure 4c). The samples **8a**, **8b**, **8c**, **8d** and **8f** show similar behavior with **8e**. Figure 4 present some examples of the textures for compounds of the series **8**.

These molecules are able to from more than one crystalline structure. Such polymorphism was observed on DSC investigations and is determined by different arrangements of the ferrocene in the solid state.[23]

The thermogravimetric analyses showed that **7a÷7f** ferrocene derivatives containing an etheric terminal linking group are more stable if compared with the than the ferrocene derivatives with esteric group (the T_{onset} values are with about 30 °C higher). This is a consequence of the presence of the less stable esteric group).

On cooling, both series presented comparable isotropisation temperatures (between 138 and 179 °C for the **7a÷7f** series and 168 and 190 °C for the **8a÷8f** series. For the same number of atom carbons in the terminal chain, the nematic range values of ferrocene derivatives with esteric group increase slightly if compared with derivatives with etheric group. Probably, the higher nematic stability of compounds with esteric linking group is determined by more intensive lateral interactions between molecules. Generally, the esteric group increases the polarity of the molecules and intermolecular interactions.

The bulky ferrocene has negative influence on the molecular ordering in mesophase. The compounds exhibit predominantly monotropic nematic liquid crystalline properties. In this type of structure, containing an azobenzene unit directly connected to ferrocenic core and with three aromatic rings, the presence of a long side chain does not stabilize the mesophase. Compound **7f**, containing 18 carbon atoms in the terminal chain presents the smallest nematic range while compounds **8g–8i** did not show any liquid crystalline behavior.

3. 3. Structure–properties Correlations. Molecular Modeling Studies

Molecular modeling studies were performed to establish structure–liquid crystalline properties correlations. The molecular modeling studies were run on Materials Studio software.[17] The building of the bulky structure of ferrocene with Amourphous Cell module used consistent-valence force field (CVFF) or consistent-valence force field augmented (CVFF_aug). In the ferrocene moiety structure, the software implied the use of a two dummy atoms placed in the middle of the cyclopentadienylic rings. Due to the presence of these fictive atoms, it was not possible to generate an amorphous cell. During the molecular modeling studies, several parameters as lengths, diameters, dipole moments and molecular asymmetry coefficients were determined. The geometries of minimum energy were obtained by *ab-initio* (DFT) calculations using the DMol3 module of the Materials Studio software.[24,25] The calculations have been performed taking into consideration all the involved electrons, using DND basic set, similar to the Gaussian 6–31G*, Perdew-Wang (PWC) functional and the following convergence criteria: energy = 1.0 e^{-5} Ha, maximum force = 0.002 Ha /Å, maximum displacement: 0.005 Å, SCF = 1.0 e^{-6}.

Because the synthesized molecules have a rod-like form, compounds **7a–7f** were enclosed in ellipsoidal contours. Diameters and lengths were determined for the minimized structures. Figure **5** presents, as an example, the ellipsoidal model for compound **7f**.

Table 2 presents the main results obtained from molecular modeling studies of **7a–7f** compounds.

Literature data predicted that for the appearance of the liquid crystalline properties, the values of the l/d asymmetry coefficient must be larger than 5.[4] Data pre-

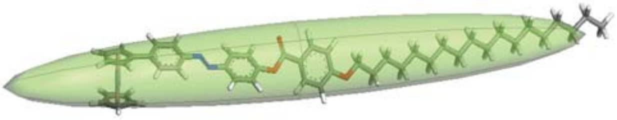


Fig. 5. Ellipsoidal model for compound **7f**

Tabel 2. Molecular modeling data for compounds **7a–7f**

Sample	n	μ (Debye)	l (Å)	d (Å)	l/d	l_r (Å)	l_f (Å)	l_r/l_f	ΔT (°C)
7a	**6**	2.84	33.7	5.25	6.4	21.1	8.3	2.5	35
7b	7	2.91	34.8	5.30	6.5	21.1	9.5	2.2	40
7c	8	2.89	36.1	5.27	6.8	21.1	10.8	1.9	43
7d	9	2.95	37.4	5.33	7.0	21.1	12.1	1.7	39
7e	10	2.91	38.9	5.31	7.3	21.1	13.3	1.5	35
7f	18	2.99	50.4	5.44	9.2	21.1	23.5	0.8	16

where: n – number of the carbon atoms in the terminal flexible chain; μ – dipole moment (D); l – total length of the molecule, from the hydrogen of the ferrocene to the end of the terminal flexible chain; d – ellipse diameter; l/d – asymmetry coefficient; l_r – length of the rigid section of the molecule; l_f – length of the flexible hydrocarbonate chain; ΔT – range of stability of the mesophases obtained from DSC investigations

sented in Table 2 evidenced l/d ratios between 6.4 and 9.2 which theoretically confirm the existence of the liquid crystalline properties for the synthesized compounds. The steric repulsion induced by bulky ferrocenyl moiety is considerable diminished by the terminal flexible hydrocarbonate chains. The range of the mesophases stability slightly increases from compound **7a** to **7c** with the increase of the asymmetry coefficient. Once the ratio l_r/l_f decreases under 2, the contribution of the flexible part become more important and the stability of the system diminishes (soft/hard control). As a consequence, the range of the mesophases stability decreases from **7c** to **7f**. In the case that $l_r \approx l_f$ the structure **7f** presents the lowest mesophase domain.

In the case of 1,1'-disubstituted ferrocenomesogens, extended "S", "U" or "Z" conformations are present. In such compounds, the rotational barriers of the cyclopentadienylic rings have an important influence for different molecular packing.[26] The same study established that in the case of the monosubstituted ferrocenes the stabilization of the mesophases seems to be rather a consequence of the molecular association between the mesogens.

Correlation between liquid crystalline properties and crystal structure can be deduced by bulk structure analysis. Taking into consideration that it was not possible to build up an amorphous cell, the calculations were performed by molecular mechanics, in vacuum, using the Forcite module. For compound **7a** four theoretical arrangements were performed: parallel stacking of ferrocene fragments head to head (a) or head to tail (b); antiparallel stacking (rectangle form) (c) and with perpendicular molecular axis (d) (Figure 6).

The values of the obtained energies after minimization of these systems containing eight **7a** molecules are presented in Table 3.

According to the values from Table 3**,** the most favorable arrangement is the parallel head to head one. But such an arrangement allows a lot of "free" volume between two head to head molecules, so, for a better packing, the free volume was "filled up" by the insertion of tails of other molecules (Figure 6e). Such an idea came from the

Table 3. Values of the obtained energies after the minimization of systems containing eight **7a** molecules

No.	Arrangement type	Energy (kcal/mol)
1	parallel, head to head	787
2	parallel, head to tail	852
3	antiparallel	869
4	perpendicular	911

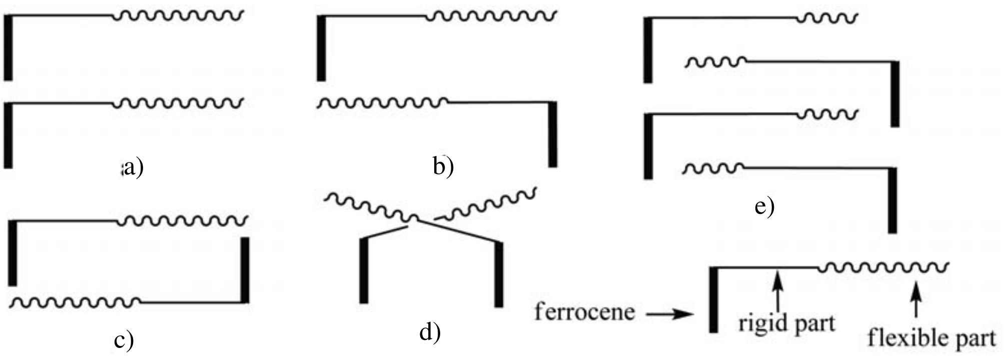


Fig. 6. Possible models for packing of the ferrocenic mesogens: parallel: a) head to head b) head to tail; c) antiparallel d) perpendicular e) intercalated

arrangement of the next system of minimum energy, **b** (parallel, head to tail, Table 3) and is similar with literature data.[27] The energy of the new minimized system (Fig 6, e) was found to be around 744 kcal/mol, inferior to both **a** or **b** arrangements.

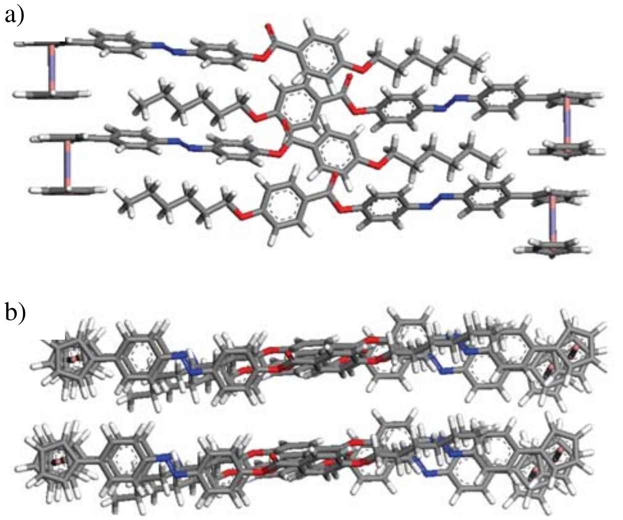


Fig. 7. Detail from stacking of eight **7a** molecules: a) side view b) top view

The arrangement of the optimized system containing eight **7a** molecules is presented in Figure 7.

Comparable values were obtained for two others compounds of the series (760 kcal/mol for **7d** and 774 kcal/mol for **7f**). The length of the terminal flexible chains does not strongly influence the values of the energies and similar packing of the molecules was obtained. These data are consistent with the liquid crystalline properties which are similar from the point of view of the type of textures, or isotropic-liquid crystalline and liquid-crystalline-crystalline transitions.

Similar molecular modeling studies were carried out for the **8a–8i** series. The geometric parameters were measured as indicated in Figure 10. The obtained data are presented in Table 4.

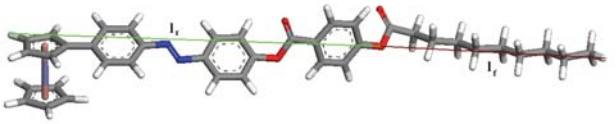
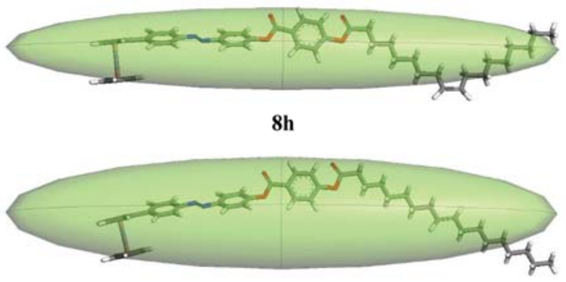


Fig. 8. Minimum energy geometry for compound **8f**

The optimized geometries for compounds **8g** and **8i** evidenced an appreciable increase of the necessary diameters of the ellipsoidal contours (Table 4, Figure 9).



8h

8i

Fig. 9. Ellipsoidal models for compounds **8h** (*cis*) and **8i** (*trans*)

The obtained data may offer an explanation for the absence of the liquid crystalline properties for compounds **8g–8i**. In the case of the compounds **7a–7f**, the values of the ellipse diameter are very similar (between 5.25 and 5.44 Å). So, the increasing of the length of the terminal chain increases the asymmetry coefficient and all the compounds have values larger than 5. In the case of compounds **8a–8i**, the presence of the more rigid esteric group as connecting group imposes a different geometry and the diameter of the ellipse growths constantly from compound **8a** to compound **8g** (from 5.8 to 10.7 Å). As a consequence, the asymmetry coefficient of compounds **8g** and **8i** is inferior to 5 (4.6 and 4.7) and no liquid crystalline proper-

Table 4. Molecular modeling data for compounds **8a–8i**

Sample	n	μ (Debye)	l (Å)	d (Å)	l/d	l_r (Å)	l_f (Å)	l_r/l_f	ΔT (°C)
8a	4	2.8	32.1	5.8	5.5	21.1	6.1	3.4	52
8b	5	3.1	33.5	6.0	5.5	21.1	7.2	2.9	36
8c	6	3.3	34.7	6.3	5.5	21.1	8.6	2.4	33
8d	7	3.3	35.6	6.6	5.3	21.1	9.7	2.1	49
8e	8	3.4	36.5	7.1	5.1	21.1	11.0	1.9	46
8f	9	3.5	38.5	7.5	5.1	21.1	12.5	1.6	43
8g	17	3.6	49.1	10.6	4.6	21.1	22.5	0.9	–
8h	17	3.4	47.2	7.6	6.2	21.1	18.9	1.1	–
8i	17	3.6	50.5	10.7	4.7	21.1	22.5	0.9	–

where: n – number of the carbon atoms in the terminal flexible chain; μ – dipole moment (D); l – total length of the molecule, from the hydrogen of the ferrocene to the end of the terminal flexible chain; d – ellipse diameter; l/d – asymmetry coefficient; l_r – length of the rigid section of the molecule; l_f – length of the flexible hydrocarbonate chain; Δ T – range of stability of the mesophases obtained from DSC investigations ties could be evidenced. In the case of compound **7f**, which also contains 18 carbon atoms in the terminal chain and presented liquid crystalline properties, the asymmetry coefficient has the value 5.44. In the case of compound **8h**, the asymmetry coefficient is 6.2 but this value is determined by the *cis* configuration of the double bond. An important contribution to the liquid crystalline properties seems to be brought if the value of the lr/lf ratio is subunit or close to one. This fact is confirmed in compound **7f** which has the lowest range of the mesophase stability.

The DSC investigation evidenced slightly higher isotropisation temperatures and ranges of stabilities of the mesophases for compounds **8a–8f** if compared with the **7a–7f** analogues. This may be explained by the higher values of the dipole moments of compounds **8a–8f**, as a consequence of the presence of the more polar esteric linking group.

4. Conclusions

Two series of ferrocene containing liquid crystals have been synthesized through the esterification of 4-ferrocenyl-4'-hydroxyazobenzene with some alkylated or acylated 4-hydroxybenzoic acids in the presence of N,N'-dicyclohexylcarbodiimide and 4-dimethylaminopyridine. The structure of the compounds was confirmed by the usual spectral techniques.

The liquid crystalline properties were investigated by means of polarized optical microscopy in association with differential scanning calorimetry. Twelve from the fifteen synthesized ferrocene containing compounds exhibited liquid crystalline properties, mainly monotropic nematic. The presented liquid crystalline properties slightly depend on the nature of the linking group between rigid and flexible parts of the molecules and the length of the flexible side chain. The performed thermogravimetric studies evidenced a good thermal stability in the existence range of the mesophases.

Several parameters as lengths, diameters, dipole moments and molecular asymmetry coefficients were determined by performing molecular modeling studies. These data permit us to explain the lack of liquid crystalline properties of compounds **8g–8i**.

The geometries of minimum energy were obtained by *ab-initio* (DFT) calculations An arrangement of minimum energy for a system containing eight molecules of type **7a**, in which the molecules are arranged parallel "head to head" while the tails of other molecules "fill" the free volume, has been proposed.

5. Acknowledgement

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Povzetek

V delu je opisana sinteza in lastnosti novih spojin, dobljenih z estrifikacijo 4-ferocenil-4'-hidroksiazobenzena z nekaterimi 4-*n*-alkanoiloksi- ali 4-*n*-alkenoiloksibenzojevimi kislinami v prisotnosti N,N'-dicikloheksilkarbodiimida in 4-dimetilaminopiridina. Z uporabo diferenčne dinamične kalorimetrije in optične polarizacijske mikroskopije smo ugotovili, da dvanajst od skupaj petnajstih novih spojih kaže lastnosti tekočih kristalov, večinoma gre za monotropne nematične faze. Vse preiskovane spojine so v mezofaznem območju temično stabilne. S pomočjo molekularnega modeliranja smo proučevali povezavo med strukturo in lastnostmi doblejnih tekočih kristalov. Ugotovili smo, da najnižjo energijo izkazuje sistem z osmimi molekulami tipa 4-((4-ferocenil-phenilazo)phenil) 4-alkiloksibenzoat.