

Synthesis and Liquid Crystalline Behavior of Some Monosubstituted Ferrocene Containing Schiff Bases

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Two series of monosubstituted ferrocene containing Schiff bases with liquid crystalline properties were obtained by condensation of 4-formyl-4'-alkyloxy-azobenzene or 4-formyl-4'-alkanoyloxy-azobenzene with 4-amino-4'-ferrocenyl-azobenzene. The synthesized compounds presented nematic or smectic enantiotropic mesophases, with partial thermal decomposition before isotropisation.

Keywords: liquid crystals, ferrocenomesogens, Schiff bases

Due to their thermal stability, electrochemical, photo and semiconducting properties, ferrocene containing liquid crystals is one of the most studied classes in the field of liquid crystals containing organometallic moieties. These properties can be used to prepare unique and interesting materials. During the time, several classes of ferrocene containing liquid crystals were investigated and different systems of classification were used taking into account the degree of the substitution of the ferrocenic unit, the type of the connecting groups between the aromatic rings, the type of the terminal chains [1-11].

Liquid crystals containing monosubstituted ferrocene are structurally calamitic. These molecules contain a ferrocenic unit, mesogenic unit, lateral substituent and terminal flexible chain [3].

Most of the monosubstituted ferrocenomesogens exhibit predominantly nematic and smectic A mesophases but the researchers [12] found that rich mesomorphism (TGBA, Blue phase, SmC*, SmA and N*) can be obtained when iminic linkage is used to extend the electronic conjugation and when a flexible chain $(-(\text{CH}_2)_{11}-\text{O}-)$ is directly connected to ferrocenic unit.

In our previous studies different ferrocene containing Schiff bases, with one azo linking group were investigated for the view point of liquid crystalline properties [6,7].

The goal of this paper is to present, for comparative studies, the synthesis and liquid crystalline properties of some monosubstituted ferrocene containing Schiff bases including two azobenzenic units, with the expectation of obtaining compounds with increased thermal stability and high polarisability [12-14]. Two classes of Schiff bases were obtained, which differ by the nature of the linking group (etheric or esteric) between the rigid and flexible parts of the molecules.

Experimental part

Materials

The reagents and solvents were purchased from different sources (Aldrich, Merck etc) and were used without further purification. Silica gel 60 (Aldrich) or Al₂O₃ (active, neutral, Merck) were used for column chromatography (CC). Thin-layer chromatography (TLC) was performed on silica gel or Al₂O₃ plates (Merck, silica gel F₂₅₄, aluminum oxide F₂₅₄). 4-Formyl-4'-alkyloxy-

azobenzenes or 4-formyl-4'-alkanoyloxy-azobenzenes were prepared in accordance with literature data [15].

Techniques

The confirmation of the chemical structures of the intermediates and final products was obtained by ¹H-NMR and ¹³C-NMR spectra, using a Bruker Avance DRX 400 MHz spectrometer with tetramethylsilane as internal standard. IR spectra were recorded using a Nicolet Magna 550 FT-IR spectrometer (NaCl crystal window). 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-4000R camera for image capture, the transitions being confirmed by DSC analysis (Mettler Toledo DSC1). Heating and cooling cycles were run at rates of 10°C/min under nitrogen atmosphere, with samples measured in closed lid aluminum pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase standards. 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).

Synthesis

Syntheses of 4-nitro-4'-ferrocenylazobenzene (2)

A mixture of 4-amino-4'-nitroazobenzene (5 g, 20.66 mmol), 6.5 mL water and 6.5 mL hydrochloric acid 32 % was cooled to 0°C with an ice-salt bath. 1.43 g (20.72 mmol) of NaNO₂ was dissolved in 2 mL water and then 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 (1.92 g, 10.32 mmol) was dissolved in 50 mL diethyl ether and 0.1 g tetrabutylammonium iodide as PTC was added. 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 stirred for 24 h at room temperature. The deep red organic layer was collected, dried with anhydrous MgSO₄ and evaporated to give a brown solid. The product was purified by column chromatography on silica gel with a *n*-hexane: CH₂Cl₂ = 1:1 mixture as elution solvent to give green crystals (0.72g, 8.48%). m.p = 255 °C.

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¹H-NMR(CDCl₃) δ: 8.40 (d, 2H, ArH), 8.04 (d, 2H, ArH), 7.92 (d, 2H, ArH), 7.64 (d, 2H, ArH), 4.77 (t, 2H, C₂H₄), 4.45 (t, 2H, C₂H₄), 4.08 (s, 5H, C₅H₅). ¹³C-NMR (CDCl₃) δ: 156.12, 150.54, 148.39, 145.42, 126.43, 124.78, 123.78, 123.24 (8 C aromatic), 83.21, 70.15, 69.95, 66.99 (4 C, ferrocene).

FT-IR (KBr, cm⁻¹): 3102, 3084, 2924, 2849, 1591, 1520, 1341, 1138, 1103, 856, 810.

Syntheses of 4-amino-4'-ferrocenyl-azobenzene (3)

4-ferrocenyl-4'-nitroazobenzene (2.6g 6.32 mmol) was dissolved under reflux in 40 mL of ethanol. A hot solution containing 4.55g (18.95 mmol) of sodium sulfide nonahydrated, 18 mL of water and 18 mL of ethanol was added over a solution of 4-ferrocenyl-4'-nitroazobenzene. The progress of the reaction was monitored by TLC using silica gel and n-hexane : CH₂Cl₂ = 1:1 mixture as eluent. The product was purified by column chromatography on silica gel with n-hexane: CH₂Cl₂ = 1:1 mixture to give purple crystals (2.15g, 89.21 %). m.p = 181°C.

¹H-NMR(CDCl₃) δ: 7.87 – 7.82 *²(d, 2H, ArH), 7.63 (δ, 2H, ArH), 6.81 (d, 2H, ArH), 4.76 (t, 2H, C₂H₄), 4.42 (t, 2H, C₂H₄), 4.10 (s, 5H, C₅H₅). ¹³C-NMR(CDCl₃) δ: 151.09, 149.28, 145.83, 141.75, 126.35, 124.93, 122.53, 114.71 (8 C aromatic), 84.24, 69.76, 69.48, 66.69 (4 C, ferrocene).

FT-IR (KBr, cm⁻¹): 3464, 3354, 3090, 3049, 1620, 1595, 1294, 1134, 843, 815.

General procedure for the synthesis of monosubstituted ferrocene Schiff base (5a ÷ 5f)

The condensation reaction of 4-amino-4'-ferrocenyl-azobenzene (3) with 4-formyl-4'-alkyloxy-azobenzenes (4) in an equimolar ratio in absolute ethanol gives the Schiff bases (5a ÷ 5f). 4-amino-4'-ferrocenyl-azobenzene (3) was dissolved under reflux in absolute ethanol (50 ml) and a hot solution of (4) aldehyde in 70 mL absolute ethanol and two drops of glacial acetic acid were added. The mixture was stirred under reflux for 2 h. After cooling, the precipitate was collected by suction filtration and washed several times with hot absolute ethanol. The resulting solids were recrystallized from chloroform.

4-(4-ferrocenylphenyl)azo)-N-(4-((4-hexyloxyphenyl)azo)benzylidene)aniline (5a)

Quantities: 0.61 g (1.61 mmol) 4-amino-4'-ferrocenyl-azobenzene, 0.5 g (1.61 mmol) 4-formyl-4'-hexyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 45.49 % (0.49 g).

¹H-NMR (CDCl₃) δ: 8.58 (s, 1H, CH=N), 8.07 (d, 2H, ArH), 8.00 ÷ 7.93 *³(d, 2H, ArH)], 7.87 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.37 (d, 2H, ArH), 7.02 (d, 2H, ArH), 4.73 (t, 2H, C₂H₄), 4.39 (t, 2H, C₂H₄), 4.06 (s, 5H, C₅H₅), 4.05 (t, 2H, CH₂O), 1.83 (cv, 2H, CH₂), 1.50 (cv, 2H, CH₂), 1.37 (m, 4H, CH₂), 0.92 (t, 3H, CH₃). ¹³C-NMR (CDCl₃) δ: 162.40 (iminic carbon) 159.80, 154.88, 154.10, 151.47, 151.18, 147.30, 143.25, 137.62, 129.89, 126.49, 125.17, 124.03, 123.15, 123.10, 121.74, 115.02 (16 C aromatic), 84.15, 69.90, 69.74, 68.65 (4 C, ferrocene), 66.92, 31.64, 29.28, 25.76, 22.62, 13.97 (6 C aliphatic). FT-IR (KBr, cm⁻¹): 3090, 6051, 2941, 2862, 1595, 1265, 853.

4-(4-ferrocenylphenyl)azo)-N-(4-((4-heptyloxyphenyl)azo)benzylidene)aniline (5b)

Quantities: 0.588 g (1.54 mmol) 4-amino-4'-ferrocenyl-azobenzene, 0.5 g (1.54 mmol) 4-formyl-4'-heptyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 50 % (0.53 g)

¹H-NMR (CDCl₃) δ: 8.59 (s, 1H, CH=N), 8.08 (d, 2H, ArH), 8.00 ÷ 7.93 *³(d, 2H, ArH)], 7.87 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.03 (d, 2H, ArH), 4.73 (t, 2H, C₂H₄), 4.40 (t, 2H, C₂H₄), 4.07 (s, 5H, C₅H₅), 4.06 (t, 2H, CH₂O), 1.83 (cv, 2H, CH₂), 1.47 (cv, 2H, CH₂), 1.38 (m, 6H, CH₂), 0.91 (t, 3H, CH₃). ¹³C-NMR (CDCl₃) δ: 162.37 (iminic carbon)

159.83, 154.84, 154.07, 151.42, 151.13, 147.25, 143.24, 137.57, 129.89, 126.48, 125.16, 124.02, 123.14, 123.09, 121.75, 114.99 (16 C aromatic), 84.10, 69.88, 69.74, 68.61 (4 C, ferrocene), 66.90, 31.82, 29.74, 29.29, 26.05, 22.63, 14.03 (7 C aliphatic). FT-IR (KBr, cm⁻¹): 3088, 3048, 2928, 2855, 1599, 1584, 1566, 1248, 854.

4-(4-ferrocenylphenyl)azo)-N-(4-((4-octyloxyphenyl)azo)benzylidene)aniline (5c)

Quantities: 0.563 g (1.47 mmol) 4-amino-4'-ferrocenyl-azobenzene, 0.5 g (1.47 mmol) 4-formyl-4'-octyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 52.17 % (0.54 g)

¹H-NMR (CDCl₃) δ: 8.58 (s, 1H, CH=N), 8.07 (d, 2H, ArH), 8.00 ÷ 7.93 *³(d, 2H, ArH)], 7.87 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.37 (d, 2H, ArH), 7.02 (d, 2H, ArH), 4.73 (t, 2H, C₂H₄), 4.39 (t, 2H, C₂H₄), 4.06 (s, 5H, C₅H₅), 4.05 (t, 2H, CH₂O), 1.83 (cv, 2H, CH₂), 1.45 (cv, 2H, CH₂), 1.31 (m, 8H, CH₂), 0.90 (t, 3H, CH₃). ¹³C-NMR (CDCl₃) δ: 162.40 (iminic carbon) 159.80, 154.89, 154.10, 151.47, 151.18, 147.30, 143.25, 137.98, 129.89, 126.49, 125.16, 124.02, 123.15, 123.09, 121.74, 115.02 (16 C aromatic), 84.15, 69.90, 69.73, 68.65 (4 C, ferrocene), 66.92, 31.87, 29.40, 29.32, 29.26, 22.68, 14.04 (8 C aliphatic). FT-IR (KBr, cm⁻¹): 3092, 3048, 2922, 2853, 1599, 1584, 1564, 1248, 856.

4-(4-ferrocenylphenyl)azo)-N-(4-((4-nonyloxyphenyl)azo)benzylidene)aniline (5d)

Quantities: 0.541 g (1.42 mmol) 4-amino-4'-ferrocenyl-azobenzene, 0.5 g (1.42 mmol) 4-formyl-4'-nonyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 78.81 % (0.80 g)

¹H-NMR (CDCl₃) δ: 8.60 (s, 1H, CH=N), 8.07 (d, 2H, ArH), 8.02 ÷ 7.95 *³(d, 2H, ArH)], 7.89 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.40 (d, 2H, ArH), 7.04 (d, 2H, ArH), 4.75 (t, 2H, C₂H₄), 4.41 (t, 2H, C₂H₄), 4.07 (s, 5H, C₅H₅), 4.06 (t, 2H, CH₂O), 1.83 (cv, 2H, CH₂), 1.55 (cv, 2H, CH₂), 1.25 (m, 10H, CH₂), 0.89 (t, 3H, CH₃). FT-IR (KBr, cm⁻¹): 3092, 3046, 2918, 2849, 1599, 1585, 1566, 1246, 854

4-(4-ferrocenylphenyl)azo)-N-(4-((4-decyloxyphenyl)azo)benzylidene)aniline (5e)

Quantities: 0.520 g (1.36 mmol) 4-amino-4'-ferrocenyl-azobenzene, 0.5 g (1.36 mmol) 4-formyl-4'-decyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 40.20 % (0.40 g)

¹H-NMR (CDCl₃) δ: 8.58 (s, 1H, CH=N), 8.06 (d, 2H, ArH), 7.98 ÷ 7.94 *³(d, 2H, ArH)], 7.87 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.37 (d, 2H, ArH), 7.02 (d, 2H, ArH), 4.73 (t, 2H, C₂H₄), 4.40 (t, 2H, C₂H₄), 4.07 (s, 5H, C₅H₅), 4.06 (t, 2H, CH₂O), 1.83 (cv, 2H, CH₂), 1.47 (cv, 2H, CH₂), 1.30 (m, 10H, CH₂), 0.90 (t, 3H, CH₃). ¹³C-NMR (CDCl₃) δ: 162.41 (iminic carbon) 159.79, 154.93, 154.15, 151.47, 151.21, 147.30, 143.26, 137.63, 129.89, 126.50, 125.17, 124.03, 123.15, 123.10, 121.74, 115.03 (16 C aromatic), 84.17, 69.90, 69.73, 68.65 (4 C, ferrocene), 66.91, 31.95, 29.73 ÷ 29.34 (5 C aliphatic), 26.10, 22.69, 14.04 (10 C aliphatic). FT-IR (KBr, cm⁻¹): 3090, 3048, 2922, 2851, 1597, 1250, 854.

4-(4-ferrocenylphenyl)azo)-N-(4-((4-octadecyloxyphenyl)azo)benzylidene)aniline (5f)

Quantities: 0.398 g (1.04 mmol) 4-amino-4'-ferrocenyl-azobenzene, 0.5 g (1.04 mmol) 4-formyl-4'-octadecyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 17.88 % (0.15 g)

¹H-NMR (CDCl₃) δ: 8.59 (s, 1H, CH=N), 8.08 (d, 2H, ArH), 8.00 ÷ 7.93 *³(d, 2H, ArH)], 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.03 (d, 2H, ArH), 4.73 (t, 2H, C₂H₄), 4.40 (t, 2H, C₂H₄), 4.07 (s, 5H, C₅H₅), 4.05 (t, 2H, CH₂O), 1.83 (cv, 2H, CH₂), 1.47 (cv, 2H, CH₂), 1.27 (m, 28H, CH₂), 0.88 (t, 3H, CH₃). FT-IR (KBr, cm⁻¹): 3092, 3063, 2918, 2849, 1601, 1584, 1254, 854.

General procedure for the synthesis of mono-substituted ferrocenyl Schiff bases **6a** ÷ **6g**

4-amino-4'-ferrocenylazobenzene was dissolved under reflux in 60 mL of absolute ethanol. Then a hot solution of the aldehyde in 60 mL absolute ethanol and two drops of glacial acetic acid were added. The mixture was stirred under reflux for 5 h. The precipitate was collected by suction filtration and washed several times with hot absolute ethanol.

4-(4-ferrocenylphenyl)azo)-N-(4-((4-pentanoyloxyphenyl)azo)benzylidene)aniline (**6a**)

Quantities: 0.4 g (10.49 mmol) 4-amino-4'-ferrocenylazobenzene, 0.325 g (10.49 mmol) 4-formyl-4'-pentanoyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 59.49 % (0.42 g)

$^1\text{H-NMR}$ (CDCl_3) δ : 8.60 (s, 1H, CH=N), 8.10 (d, 2H, ArH), 8.03 ÷ 7.99 [3*(d, 2H, ArH)], 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.28 (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_2), 1.78 (cv, 2H, CH_3), 1.26 (cv, 2H, CH_2), 0.99 (t, 3H, CH_3).

FT-IR (KBr, cm^{-1}): 3088, 3063, 2953, 2866, 1759, 1593, 1136, 854. m/z : 674 [M+1]⁺

4-(4-ferrocenylphenyl)azo)-N-(4-((4-hexanoyloxyphenyl)azo)benzylidene)aniline (**6b**)

Quantities: 0.4 g (10.49 mmol) 4-amino-4'-ferrocenylazobenzene, 0.340 g (10.49 mmol) 4-formyl-4'-hexanoyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 48.54 % (0.35 g)

$^1\text{H-NMR}$ (CDCl_3) δ : 8.60 (s, 1H, CH=N), 8.10 (d, 2H, ArH), 8.03 ÷ 7.99 [3*(d, 2H, ArH)], 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.28 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 2.59 (t, 2H, CH_2), 1.79 (cv, 2H, CH_3), 1.26 (m, 4H, CH_2), 0.95 (t, 3H, CH_3).

FT-IR (KBr, cm^{-1}): 3092, 3053, 2949, 2864, 1753, 1593, 1141, 854. m/z : 688 [M+1]⁺

4-(4-ferrocenylphenyl)azo)-N-(4-((4-heptanoyloxyphenyl)azo)benzylidene)aniline (**6c**)

Quantities: 0.4 g (10.49 mmol) 4-amino-4'-ferrocenylazobenzene, 0.354 g (10.47 mmol) 4-formyl-4'-heptanoyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 67.93 % (0.50 g)

$^1\text{H-NMR}$ (CDCl_3) δ : 8.60 (s, 1H, CH=N), 8.10 (d, 2H, ArH), 8.03 ÷ 7.99 [3X(d, 2H, ArH)], 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.28 (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_2), 1.78 (cv, 2H, CH_3), 1.26 (m, 6H, CH_2), 0.99 (t, 3H, CH_3).

FT-IR (KBr, cm^{-1}): 3086, 3046, 2951, 2851, 1751, 1589, 1136, 851. m/z : 702 [M+1]⁺

4-(4-ferrocenylphenyl)azo)-N-(4-((4-octanoyloxyphenyl)azo)benzylidene)aniline (**6d**)

Quantities: 0.4 g (10.49 mmol) 4-amino-4'-ferrocenylazobenzene, 0.369 g (10.48 mmol) 4-formyl-4'-octanoyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 64 % (0.48 g)

$^1\text{H-NMR}$ (CDCl_3) δ : 8.60 (s, 1H, CH=N), 8.10 (d, 2H, ArH), 8.03 ÷ 7.99 [3*(d, 2H, ArH)], 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.28 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 2.59 (t, 2H, CH_2), 1.79 (cv, 2H, CH_3), 1.26 (m, 8H, CH_2), 0.91 (t, 3H, CH_3).

FT-IR (KBr, cm^{-1}): 3092, 3051, 2947, 2849, 1755, 1587, 1136, 853. m/z : 716 [M+1]⁺

4-(4-ferrocenylphenyl)azo)-N-(4-((4-nonanoyloxyphenyl)azo)benzylidene)aniline (**6e**)

Quantities: 0.4 g (10.49 mmol) 4-amino-4'-ferrocenylazobenzene, 0.384 g (10.49 mmol) 4-formyl-4'-nonanoyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 52.28 % (0.40 g)

$^1\text{H-NMR}$ (CDCl_3) δ : 8.60 (s, 1H, CH=N), 8.10 (d, 2H, ArH), 8.03 ÷ 7.99 [3*(d, 2H, ArH)], 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.28 (d, 2H, ArH), 4.73 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 2.58 (t, 2H, CH_2), 1.79 (cv, 2H, CH_3), 1.31 (m, 10H, CH_2), 0.90 (t, 3H, CH_3).

FT-IR (KBr, cm^{-1}): 3096, 3061, 2945, 2849, 1755, 1587, 1140, 854. m/z : 730 [M+1]⁺

4-(4-ferrocenylphenyl)azo)-N-(4-((4-decanoyloxyphenyl)azo)benzylidene)aniline (**6f**)

Quantities: 0.4 g (10.49 mmol) 4-amino-4'-ferrocenylazobenzene, 0.398 g (10.47 mmol) 4-formyl-4'-decanoyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 47.43 % (0.37 g)

$^1\text{H-NMR}$ (CDCl_3) δ : 8.59 (s, 1H, CH=N), 8.09 (d, 2H, ArH), 8.01 ÷ 7.98 [3*(d, 2H, ArH)], 7.87 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.37 (d, 2H, ArH), 7.27 (d, 2H, ArH), 4.73 (t, 2H, C_5H_4), 4.39 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 2.58 (t, 2H, CH_2), 1.78 (cv, 2H, CH_3), 1.30 (m, 12H, CH_2), 0.89 (t, 3H, CH_3).

FT-IR (KBr, cm^{-1}): 3086, 3059, 2949, 2853, 1753, 1593, 1138, 856. m/z : 744 [M+1]⁺

4-(4-ferrocenylphenyl)azo)-N-(4-((4-stearoyloxyphenyl)azo)benzylidene)aniline (**6g**)

Quantities: 0.4 g (10.49 mmol) 4-amino-4'-ferrocenylazobenzene, 0.516 g (10.48 mmol) 4-formyl-4'-stearoyloxy-azobenzene, two drops of glacial acetic acid. Red solid, Yield 35.67 % (0.32 g)

$^1\text{H-NMR}$ (CDCl_3) δ : 8.60 (s, 1H, CH=N), 8.10 (d, 2H, ArH), 8.08 ÷ 7.99 [3*(d, 2H, ArH)], 7.88 (d, 2H, ArH), 7.62 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.28 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.07 (s, 5H, C_5H_5), 2.59 (t, 2H, CH_2), 1.78 (cv, 2H, CH_3), 1.26 (m, 28H, CH_2), 0.88 (t, 3H, CH_3).

FT-IR (KBr, cm^{-1}): 3096, 3080, 2920, 2849, 1755, 1593, 1128, 856. m/z : 856 [M+1]⁺

Results and discussions

Synthesis

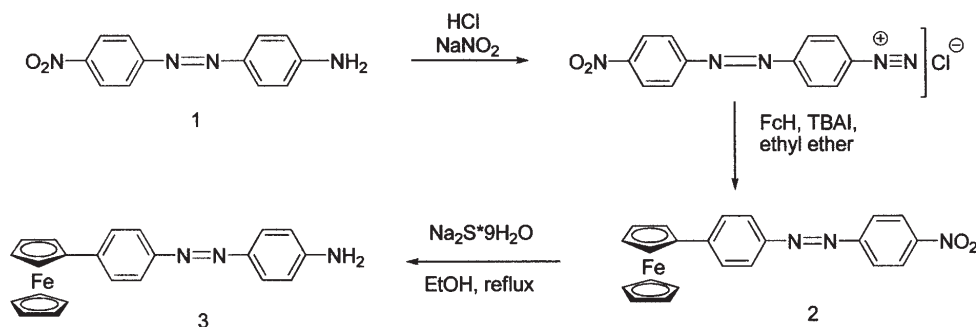
Ferrocene containing Schiff bases were prepared by the condensation reaction between 4-amino-4'-ferrocenylazobenzene (**3**) and a series of 4-formyl-4'-alkyloxyazobenzenes or 4-formyl-4'-alkanoyloxyazobenzenes (**4**) [16]. The synthesis of 4-amino-4'-ferrocenylazobenzene (**3**) is presented in scheme 1. In the first step, ferrocene was arylated with the diazonium salt of 4-amino-4'-nitroazobenzene (**1**) using TBAI (tetrabutylammonium iodide) as phase transfer catalyst (PTC), by adapting literature procedure [17]. The obtained 4-ferrocenyl-4'-nitroazobenzene (**2**) was reduced with sodium sulfide nonahydrate in boiling ethyl alcohol to form 4-amino-4'-ferrocenylazobenzene (**3**).

4-Formyl-4'-alkyloxyazobenzenes and 4-formyl-4'-alkanoyloxyazobenzenes (**4**) were prepared according to literature data [15].

The final compounds were prepared by reacting the ferrocene containing amino group (**3**) with the corresponding aldehydes (**4**) (scheme 2).

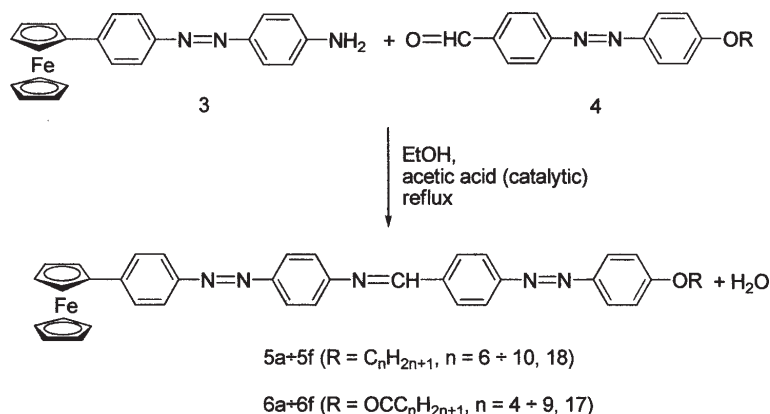
Liquid crystalline properties

The liquid crystalline properties of the synthesized Schiff bases **5a** ÷ **5f** and **6a** ÷ **6g** were investigated by polarized optical microscopy (POM) and DSC. For these ferrocene containing Schiff bases the beginning of the degradation processes partially overlap with the mesophases domains. Generally, the degradation processes appeared over 200°C and, with the exception of sample **5f**, it was not possible to evidence the isotropisation phenomenon. For this reason, and for observing the cooling cycles, the samples were firstly investigated by POM and the DSC runs were performed only until the beginning of the degradation



Scheme 1. Synthesis of 4-amino-4'-ferrocenylazobenzene

Abbreviations: FcH- ferrocene; TBAI- tetrabutylammonium iodide



Scheme 2. Synthesis of ferrocene containing Schiff bases

Sample	n	T (°C)										T _{DSC} (°C)
		ΔH (Jg ⁻¹)										
		heating					cooling					
Cr-Cr	Cr-N	Cr-Sm	Sm-N	N-I	I-N	N-Sm	Sm-Cr	N-Cr	Cr-Cr			
5a	6	-	233 -57.97	-	-	-	-	-	-	206 51.27	-	290
5b	7	-	210 -23.87	-	-	-	-	-	-	181 23.18	-	290
5c	8	161 -2.39	220 -70.32	-	-	-	-	-	-	188 38.61	-	300
5d	9	-	210 -62.14	-	-	-	-	-	-	187 31.86	-	290
5e	10	-	196 -50.24	-	-	-	-	-	-	178 51.27	-	290
5f	18	122 -7.47	-	194 -15.01	211 -0.31	263 -0.37	255 0.44	206 0.33	178 13.80	-	113 6.55	300

Cr – crystalline, N – nematic, Sm – undefined smectic phase, I – isotropic phase, T_{DSC} – temperatures until the DSC runs were performed.

Table 1
TRANSITION TEMPERATURE (T/°C)
AND ASSOCIATED TRANSITION
ENTHALPY VALUES (ΔH / Jg⁻¹) FOR
COMPOUNDS 5a ÷ 5f

processes. Tables 1 and 2 indicate the temperatures until the DSC runs were performed, too. In some cases, both microscopy and DSC evidenced polymorphism phenomena in the crystalline state. Table 1 and 2 presents phase transition temperatures and phase transition enthalpy values obtained by DSC curves (at a scanning rate of 10 K/min).

Compounds 5a ÷ 5e with shorter terminal hydrocarbon chain exhibit only enantiotropic nematic mesophases. On cooling, the mesophases were observed with polarizing

microscope only for non-degraded areas. Compound 5f, with 18 carbon atoms in the terminal alkoxy chain exhibit two different types of mesophases: enantiotropic nematic and enantiotropic undefined smectic. Generally, the bulky ferrocene has negative influence on the molecular ordering in mesophase and compounds exhibit predominantly nematic mesophases. For this compound, with etheric linkage between the rigid unit and the flexible chain, the presence of a long side chain allows smectic ordering. Figure 1 presents the DSC curves of sample 5f.

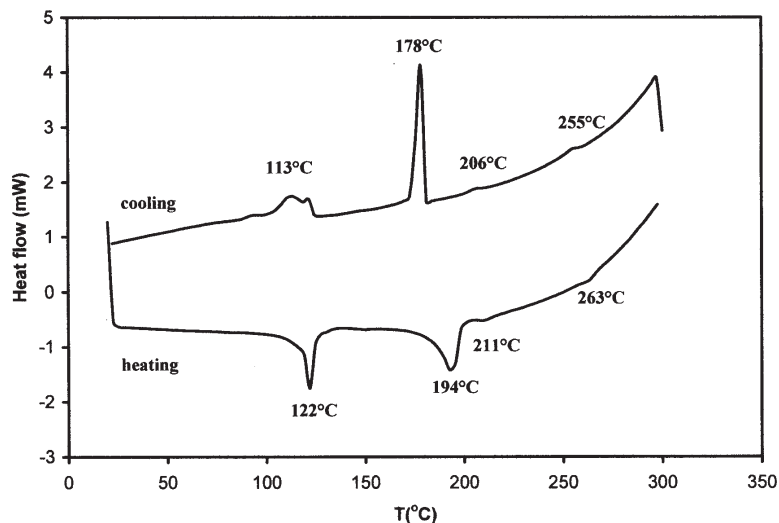
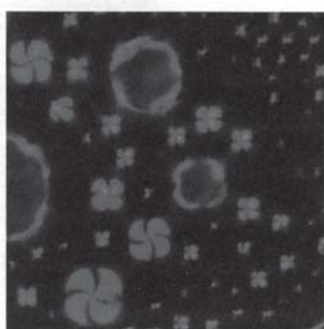


Figure 1. The DSC curves of sample **5f**



Sample **5d**: nematic texture at 220°C, on heating



Sample **5d**: nematic droplets at 279°C, on cooling



Sample **5f**: undefined smectic mesophase at 204°C, on cooling



Sample **5f**: nematic from isotropic liquid at 250°C, on cooling

Fig. 2. Nematic and smectic mesophases for compounds **5d** and **5f**

POM observations confirmed the results obtained from DSC analysis. As can be seen in figure 1, when the sample **5f** was heated from 20 to 300°C four peaks were detected on DSC curve. The first peak, at 122°C, corresponds to a solid–solid transition. On heating to the isotropic liquid a smectic like texture was observed between 194 and 211°C. On further heating homeotropic texture of nematic was observed above 211°C. The texture flashed when the sample was pressed. The transition from nematic to isotropic was observed at 263°C. On cooling from the isotropic liquid, small “droplets” appeared at 255°C. Then, these droplets consolidate to form Schlieren like texture, typical for nematic phase. On further cooling, a smectic like mesophase appeared at 206°C which crystallizes at 178°C. The peaks at 113°C correspond to successive solid – solid transitions. Figure 2 shows liquid crystalline textures of samples **5d** and **5f**.

In the case of compounds **6a ÷ 6g**, with esteric terminal chain, the liquid crystalline properties could be evidenced only for compounds containing at least 6 carbon atoms in terminal chain. In the case of compounds **6a** and **6b**, DSC

investigations evidenced only a very narrow transition solid – liquid crystalline, just before isotropisation. With increasing of the terminal chain length, the existence of the liquid crystalline domains could be observed both by POM and DSC investigations. As mentioned for compounds **5a ÷ 5f**, degradation phenomena appeared before isotropisation. In such conditions, the DSC scans were performed until the temperatures at which POM observations indicated the appearance of the degradation areas. This series of compounds exhibit enantiotropic nematic phases, with the exception of compound **6g** which presented enantiotropic nematic and monotropic, undefined smectic phases.

The peaks that appear at 205, 210 and 215°C (** in table 2) and 218°C and 244°C (* in table 2) in the DSC curves, with low values of enthalpy, occur without the change of mesophases types and, probably, are caused by phenomena of re-ordering and re-disordering in the liquid-crystalline texture. Probably, the presence of the alkanoyl terminal chain, more polar if compared with the alkoxy one is the primary cause of these changes. There is an

Sample	n	T (°C) ΔH (Jg ⁻¹)									T _{dec} (°C)
		heating					cooling				
		Cr - Cr	Cr-Cr	Cr - N	*	**	N-Sm	Sm-Cr	N - Cr	Cr - Cr	
6a	4	-	140 -40,27	-	-	-	-	-	-	130 35,97	220
6b	5	-	127 -22,25	-	-	-	-	-	-	116 37,27	220
6c	6	-	148 -25,77	236 -57,92	-	-	-	-	206 47,09	-	250
6d	7	134 -14,8	210 -4,32	222 -49,39	-	205 0,75	-	-	194 46,24	95 14,04	250
6e	8	129 -20,61	-	212 -59,89	-	210 0,88	-	-	172 35,51	-	250
6f	9	39 -3,09	-	206 -66,87	218 -0,73	215 0,97	-	-	178 39,06	-	250
6g	17	141 -6,48	-	197 -33,6	244 -0,59	-	241 0,65	179 30,40	-	126 1,24	250

Table 2
TRANSITION TEMPERATURE (T/°C)
AND ASSOCIATED TRANSITION
ENTHALPY VALUES (ΔH/Jg⁻¹) FOR
COMPOUNDS **6a ÷ 6g**

Cr – crystalline, N – nematic, Sm – smectic, T_{DSC} – temperatures until the DSC runs were performed, * re-disordering phenomena, ** re-ordering phenomena observed by POM (these phenomena occur without changing the type of mesophase).



Sample **6g**: nematic mesophase at 206°C, on heating



Sample **6g**: nematic mesophase at 250°C (after re-disordering phenomena) on heating



Sample **6g**: undefined smectic mesophase at 213°C (on cooling)



Sample **6g**: 80°C (before crystallization)

Fig. 3. Nematic and smectic phases for compound **6g**

increase of temperature with the increasing of carbon chain, which is understandable since re-disordering phenomena require higher energies with increasing length

of the alkyl chain. Figure 3 show the optical textures of compound **6g**, photographed in polarized light.

Conclusions

Two series of ferrocene containing Schiff bases with two azobenzenic units connected through an iminic bond were synthesized and characterized by spectroscopic methods. The series differ by the nature of linkage (etheric or esteric) between the mesogenic unit and terminal chain. Investigations of the liquid crystalline properties showed that these compounds exhibit nematic and smectic enantiotropic mesophases until degradation. Partial thermal degradation occurs in the mesophase. The increase of the length of the terminal chain decrease solid-liquid crystalline transition temperatures and increase the liquid crystalline domain.

Acknowledgement: This work was supported by CNCSIS –UEFISCSU (Romania), project number PNII – IDEI 356/2008

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Manuscript received: 15.03.2011

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TRATAT DE PETROCHIMIE Vol. 1. Produse petrochimice de bază GHEORGHE IVANUȘ Editura AGIR, București, 2011


Sub egida Academiei de Științe Tehnice din România (ASTR) și a Asociației Generale a Inginerilor din România (AGIR), la Editura AGIR a văzut lumina tiparului această remarcabilă lucrare, tocmai în anul Internațional al Chimiei (IYC-2011). Autorul, profesor doctor inginer Gheorghe Ivănuș, membru titular al ASTR, ne oferă rodul activității de o viață în petrochimie, în industrie, cercetare, proiectare-dezvoltare dar și în învățământul tehnic superior.

Volumul masiv, de peste o mie de pagini, este bine organizat în nouă capitole: materii prime, hidrocarburi (cel mai amplu), compuși halogenați, acizi și derivați, epoxizi, compuși hidroxilici, compuși carbonilici, metanolul și hidrogenul.

Supus unei presiuni considerabile (mai ales de media superficial informată tehnic și economic), termenul "petrochimie" pare că se devalorizează în opoziție cu orientarea spre surse neconvenționale și regenerabile. În realitate, chiar în prognozele pesimiste, apogeul producției petrochimice se situează, la nivel mondial, peste câteva decenii după care ar putea urma o perioadă de descreștere. În țara noastră, industria petrochimică își are începutul cu vreo șaptezeci de ani în urmă, dar trebuie să observăm cu multă părere de rău, după anul 1990, a marcat un regres considerabil determinat de o abordare deficitară din punct de vedere tehnic, economic și politic. Strategia dezvoltării durabile a țării noastre trebuie să aibă în vedere nu numai asigurarea resurselor energetice ci, mai ales, modul în care se folosesc aceste resurse (atât din țară cât și din import) pentru o eficiență maximă în sprijinul dezvoltării economice.

Tratatul se adresează unui larg cerc de specialiști care lucrează în cercetare, dezvoltare-proiectare, în învățământul universitar dar se adresează celor care lucrează în exploatarea instalațiilor petrochimice și rafinăriilor petroliere. Totodată, tratatul oferă o amplă bază de informare studenților din învățământul superior de specialitate. Am fi bucuroși ca el să ajungă sub privirile celor care, la nivel guvernamental, gândesc la perspectiva industrială a țării.

Cartea este menită să devină o lucrare de referință în domeniul petrochimiei și așteptăm cu interes extinderea ei cu volumele următoare: Produse macromoleculare și Bunuri de consum.


G. IVAN, dr.ing.