The liquid crystalline behaviour of ferrocene derivatives containing azo and imine linking groups

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The liquid crystalline behaviour of ferrocene derivatives containing azo and imine linking groups

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The synthesis and mesogenic properties of some Schiff bases containing ferrocene, azobenzene units and flexible end chains with 17 or 18 carbon atoms are reported. The compounds have been characterized by ^{1}H-NMR and ^{13}C-NMR spectroscopy, DSC and optical microscopy in polarized light.

1. Introduction

The importance of organometallic compounds in the field of liquid crystals is well known and established [1–4]. Liquid crystalline compounds containing a metallic atom in their structure combine properties of the metal with those of the mesogens, leading to processable materials with interesting magnetic, electronic, optic and anisotropic properties. The presence of a transitional metal can improve the optical properties of such compounds.

There have been many studies focused on the synthesis and mesomorphic properties of ferrocene-based metallomesogens [5–23]. The aromatic character and reactivity of ferrocene facilitate easy substitution reactions to monosubstituted [9–13], disubstituted (1,1-, 1,2-, 1,3-) [14–23] and trisubstituted (1,1′,3-) [24, 25] derivatives. Compared with polysubstituted derivatives, little work has been reported on monosubstituted ferrocene compounds [26]. This could be attributed to their unfavourable molecular shape geometry (L-shape) and also to the repulsive steric effects of the ferrocene unit. Nevertheless, molecular modelling studies on monosubstituted ferrocene-based mesogens confirmed that the appearance of mesomorphic behaviour depends on the length/width ratio of the molecules [27]. The systematic investigations of Loubser and Imrie [11] showed that monosubstituted ferrocene-based mesogens must contain at least three aromatic rings in order for the length/width ratio to be large enough and that

the nature of the linking group adjacent to the ferrocenyl unit is very important.

Our research group is interested in the design of ferrocene-based mesogens with new interesting structures, in which the ferrocenyl unit is connected as a terminal group onto a rod-like molecule and the compounds are represented by the general structure shown in figure 1 [28–31]. Some of the synthesized compounds contain an azo group in the molecule, permitting reversible *trans–cis* isomerization under UV irradiation, which may permit the use of such compounds as light modulators for microdisplays. Literature studies showed that the reversible *trans–cis* photoisomerization of azo chromophores could be used to design and exploit novel photoactive materials based on liquid crystals [32, 33].

The structure of the synthesized compounds was systematically varied by changing the linking group between the aromatic rings and the length of the terminal substituents, considering that the appearance of liquid crystalline behaviour depends on length/diameter ratio of the molecules. The presence of the azo and imine units determine the increase of the polarities of the moieties, keeping the linear pattern, whereas the terminal substituents are needed to balance rigidity with flexibility of the molecule.

2. Experimental

2.1. *Materials*

All reactions involving DCC and DMAP were performed under a dry nitrogen atmosphere. CH_2Cl_2 (P_2O_5) was distilled prior to use. Ferrocene (Aldrich),

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where **I**, $X_1 = CH; Y_1 = Y_2 = X_2 = N; R = H$
II, $X_1 = CH; Y_1 = Y_2 = X_2 = N; R = C_{18}H_{37}$
III, $X_1 = CH; Y_1 = Y_2 = X_2 = N; R = COC_{17}H_{35}$
IV, $X_1 = Y_1 = X_2 = N, Y_2 = CH; R = C_{18}H_{37}$
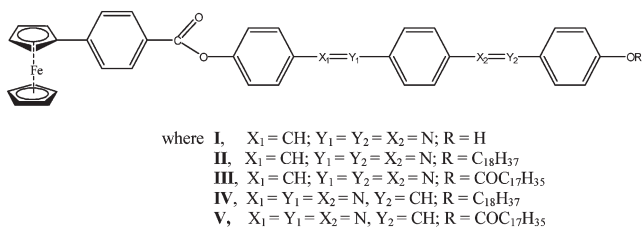**V**, $X_1 = Y_1 = X_2 = N, Y_2 = CH; R = COC_{17}H_{35}$

Figure 1. General structure of synthesized compounds.

tetrabutylammonium iodide (Aldrich), dicyclohexyl carbodiimide (Aldrich), 4-*N*,*N*-dimethylaminopyridine (Aldrich), 4-hydroxybenzaldehyde (Aldrich) were used as received. 4-Ferrocenylbenzoic acid was prepared following literature procedures [34].

Silica gel 60 (Merck) or Al_2O_3 (active, neutral, Merck) were used for column chromatography (CC). Thin-layer chromatography (TLC) was performed on silica gel or Al_2O_3 plates (Merck, silica gel F_{254}, aluminium oxide F_{254}).

2.2. Techniques

Confirmation of the structures of the intermediates and final products was obtained by ^1H and ^{13}C NMR using a Jeol ECA 600 MHz spectrometer with tetramethylsilane as internal standard. IR spectra were recorded using a Nicolet Magna 550 FTIR spectrometer (NaCl crystal window). Mass spectra were recorded on a Jeol JMS-AX 505 mass spectrometer using the FAB^+ method for ionization. Elemental analysis was performed on a Fisons EA1108 CHN, and melting points were recorded on a Boetius Karl Zeiss Jena microscope. 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 rates of $10°C\,min^{-1}$ under nitrogen atmosphere, with samples measured in closed lid aluminium pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase standards.

The molecular simulations were performed using the Hyperchem program [35]. 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 find out 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 $0.05\,kJ\,mol^{-1}Å^{-1}$. Minimization was performed using the steepest-descent and conjugate-gradient algorithm described by Fletcher and Reeves.

2.3. Syntheses of intermediates

2.3.1. 4-Ferrocenylbenzoic acid (1). A mixture of 7 g 4-aminobenzoic acid (50 mmol), 80 ml water and 12 ml HCl 32% was cooled to 0–5°C with an ice-salt bath. A solution of 20 ml solution $NaNO_2$ (3.5 g, 50 mmol), was added dropwise while stirring. After the addition was complete, the solution was stirred for 30 min. below 5°C. Ferrocene (9.3 g, 50 mmol) and tetrabutylammonium iodide (1.5 g) were dissolved in 100 ml ethyl ether and cooled to 0–5°C. The above prepared diazonium salt solution was added dropwise while stirring. After the completion of addition, the reaction mixture was stirred for additional 5 h, at room temperature. The isolated solid was dissolved in 500 ml water containing 5 g NaOH, at 90°C and was filtrated while hot. On cooling, the sodium salt of 4-ferrocenylbenzoic acid crystallized. Filtration and acidification of the salt gave 4-ferrocenylbenzoic acid (red solid). Yield: 65 % (9.9 g), m.p. 240°C (dec). IR (KBr, cm^{-1}): 3468, 3371, 1620, 1529, 1454, 1284, 1101, 815. ^1H-NMR δ_H ($CDCl_3$): 7.99 (d, 2H, ArH), 7.50 (d, 2H, ArH), 4.68 (t, 2H, C_5H_4), 4.37 (t, 2H, C_5H_4), 3.99 (s, 5H, C_5H_5).

2.3.2. 4-Formylphenyl 4-ferrocenylbenzoate (2). To a solution containing 4-hydroxibenzaldehyde (0.25 g, 2.047 mmol), 4-ferrocenylbenzoic acid (0.626 g, 2.047 mmol) and a catalytic amount of DMAP, in anhydrous CH_2Cl_2, a solution of DCC (0.464 g, 2.25 mmol) dissolved in 8 ml dry CH_2Cl_2 was added while stirring. After 12 h of stirring, the dicyclohexylurea was filtered off and the solution was concentrated. The solid residue was purified by CC on Al_2O_3 (CH_2Cl_2:hexane=2:1). Yield: 63 % (0.53 g), m.p. 194–196°C. IR (KBr, cm^{-1}): 1720 (>C=O), 1697, 1600, 1273, 1291, 885. ^1H NMR δ_H ($CDCl_3$): 10.01 (s, 1H, CHO), 8.01 (d, 2H, ArH), 7.97 (d, 2H, ArH), 7.58 (d, 2H, ArH), 7.42 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.42 (t, 2H, C_5H_4), 4.04 (s, 5H, C_5H_5). m/z: 409 $[M-1]^+$.

2.3.3. 4-Octadecyloxybenzaldehyde (3). 4-Hydroxybenzaldehyde (0.25 g, 2.05 mmol), anhydrous K_2CO_3 (0.283 g, 2.05 mmol) and stearyl bromide (0.79 g, 2.37 mmol) were refluxed for 56 h in 50 ml acetone. After cooling, the salts were filtered off and the solution was concentrated. The solid residue was purified by CC on Al_2O_3 (CH_2Cl_2:hexane=1:1). Yield: 85 % (0.65 g), m.p. 55–60°C. IR (KBr, cm^{-1}): 2918, 2848, 1689

(>C=O), 1602, 1471, 1257, 1166, 833. ^{1}H NMR δ_H (CDCl$_3$): 9.85 (s, 1H, -CHO), 7.81 (d, 2H, ArH), 6.97 (d, 2H, ArH), 4.01 (t, 2H, -OCH$_2$-), 1.79 (m, 2H, -CH$_2$-), 1.44–1.23 (m, 30H, 15 × CH$_2$), 0.86 (t, 3H, -CH$_3$). m/z: 374 [M-1]$^+$.

2.3.4. 4-Octadecanoyloxybenzaldehyde (4).

To a solution containing 4-hydroxybenzaldehyde (0.5 g, 4.09 mmol), stearic acid (1.164 g, 4.09 mmol) and a catalytic amount of DMAP, in 100 ml anhydrous CH$_2$Cl$_2$, DCC (0.93 g, 4.5 mmol) in 15 ml anhydrous CH$_2$Cl$_2$ was added while stirring. After 12 h of stirring, the dicyclohexylurea was filtered off and the solution was concentrated. The solid residue was purified by CC on neutral Al$_2$O$_3$ (CH$_2$Cl$_2$:hexane=2:1). Yield: 60% (0.96 g), m.p. 51–55°C. IR (KBr, cm^{-1}): 2918, 2848, 1751 (>C=O), 1685, 1656, 1589, 1465, 1384, 1219, 1157, 925, 840. ^{1}H NMR δ_H (CDCl$_3$): 9.96 (s, 1H, -CHO), 7.91 (d, 2H, ArH), 7.26 (d, 2H, ArH), 2.57 (t, 2H, -OC-CH$_2$-), 1.75 (m, 2H, -CH$_2$-), 1.40–1.24 (m, 28H, 14 × CH$_2$), 0.86 (t, 3H, -CH$_3$). m/z: 388 [M-1]$^+$.

2.3.5. 4-Nitro-4′-hydroxyazobenzene (5).

4-Nitroaniline (3 g, 21.7 mmol) was suspended in 7 ml water, then 6.5 ml HCl 32% was added and the mixture cooled to 0–5°C with an ice-salt bath. A solution of sodium nitrite (1.498 g, 21.7 mmol) in 8 ml water was added dropwise while stirring. After the addition was complete, the solution was stirred for 30 min below 5°C. The prepared diazonium salt solution was added dropwise while stirring, over a solution containing phenol (2.1 g, 22.4 mmol) in 28 ml CH$_3$COONa.3H$_2$O 20%. After the completion of addition, the reaction mixture was stirred for additional 2 h at room temperature. The orange solid product was filtered off, washed with water and purified by recrystallization from benzene. Yield: 84% (4.55 g), m.p. 225°C. IR (KBr, cm^{-1}): 3404, 1604, 1585, 1506, 1336, 1138, 846.

2.3.6. 4-Nitro-4′-octadecyloxyazobenzene (7).

4-Nitro-4′-hydroxyazobenzene (2 g, 82.3 mmol), anhydrous K$_2$CO$_3$ (1.139 g, 82.3 mmol) and stearyl bromide (3.17 g, 95.2 mmol) were refluxed for 56 h in 150 ml acetone. After cooling, the products were filtered off and washed with acetone. The mass was suspended into CH$_2$Cl$_2$. The inorganic salts were removed by filtration. The product was recovered by evaporation of the solvent and purified by CC on silica gel (CH$_2$Cl$_2$:hexane=2:1). Yield: 77% (3.08 g), m.p. 90–95°C. IR (KBr, cm^{-1}): 2918, 2848, 1602, 1585, 1517, 1571, 1467, 1340, 725. ^{1}H NMR δ_H (CDCl$_3$): 8.37 (d, 2H, ArH), 7.97 (m, 4H, ArH), 7.03 (d, 2H, ArH), 4.06 (t, 2H, -OCH$_2$-), 1.83 (m, 2H, -CH$_2$-), 1.48–1.26 (m,

30H, 15 × CH$_2$), 0.88 (t, 3H, -CH$_3$). ^{13}C NMR δ_C (CDCl$_3$): 162.9, 156.1, 148.2, 146.8, 125.6, 124.7, 123.1, 114.9, (8 C, aromatic), 68.5 (-OCH$_2$-), 31.98–14.17 (17 C, aliphatic).

2.3.7. General procedure for preparing amino compounds 6 and 8.

Nitro azo compounds **5** and **7** were dissolved in hot ethanol and Na$_2$S.9H$_2$O, dissolved in hot 1:1 water–ethanol mixture, was added. The mixture was refluxed while stirring for 6 h.

For 4-amino-4′-hydroxyazobenzene (**6**), quantities were 2.5 g (10.28 mmol) 4-nitro-4′-hydroxyazobenzene, 150′ml hot ethanol, and 7.41g (30.86 mmol) Na$_2$S.9H$_2$O dissolved in 60 ml hot 1:1 water–ethanol mixture. After cooling, the reaction mixture was poured into water and pH was adjusted with HCl 32%. After transferring the suspensions to a separating funnel, the organic layer was extracted with 5 × 30 ml ethyl acetate. The combined organic layers were washed with water and dried over anhydrous MgSO$_4$ and solvent was removed by evaporation. The product did not require further purification. Yield: 99% (2.17g), m.p. 185–190°C (dec). IR (KBr, cm^{-1}): 3429, 3359, 3338, 1589, 1234, 1147, 840. ^{1}H NMR δ_H (DMSO): 9.99 (s, 1H, -OH), 7.68 (d, 2H, ArH), 7.63 (d, 2H, ArH), 6.91 (d, 2H, ArH), 6.68 (d, 2H, ArH), 5.91 (s, 2H, -NH$_2$). ^{13}C NMR δ_C (DMSO): 159.71, 152.41, 146.12, 143.45, 124.99, 124.2, 116.26, 113.99.

For 4-Amino-4′-octadecyloxyazobenzene (**8**), quantities were 2.33 g (4.7 mmol) 4-nitro-4′-octadecyloxyazobenzene, 150 ml hot ethanol and 3.389g (14.1mmol) Na$_2$S.9H$_2$O dissolved in 20 ml hot 1:1 water–ethanol mixture. After cooling, the product was filtered off and washed with water. Purification: CC/Al$_2$O$_3$/CH$_2$Cl$_2$. Yield: 73% (1.6 g), m.p. 96°C. IR (KBr, cm^{-1}): 3556, 3386, 2918, 2848, 1602, 1249, 842. ^{1}H NMR δ_H (CDCl$_3$): 7.83 (d, 2H, ArH), 7.77 (d, 2H, ArH), 6.98 (d, 2H, ArH), 6.74 (d, 2H, ArH), 4.02 (t, 2H, -OCH$_2$-), 3.98 (s, 2H, -NH$_2$), 1.80 (m, 2H, -CH$_2$-), 1.47–1.26 (m, 30H, 15 × CH$_2$), 0.88 (t, 3H, -CH$_3$). ^{13}C NMR δ_C (CDCl$_3$): 160.8, 148.9, 147.0, 145.6, 124.6, 124.0, 114.7, 114.6 (8 C, aromatic), 68.3 (-OCH$_2$-), 31.9÷14.17 (17 C, aliphatic).

2.3.8. General procedure for preparing intermediate Schiff bases 9 and 10.

To a stirred solution containing 4-amino-4′-hydroxyazobenzene and aldehydic compounds **3** or **4**, in methanol, a few drops of glacial acetic acid were added. The solution was refluxed with stirring for 4 h. The product was filtered while hot and the solid was washed on filter with hot methanol. The resulting solid was recrystallized from methanol.

For 4-oxi-4′-(octadecyloxybenzylideneimino)azobenzene **(9)**, quantities were 0.75 g (2.0 mmol) 4-octadecyloxybenzaldehyde in 50 ml methanol, 0.426 g (2.00 mmol) 4-amino-4′-hydroxyazobenzene and glacial acetic acid (2 drops). Yield: 62.2% (0.71 g), m.p. (liquid crystal): 139°C (Cr$_1$/Cr$_2$), 146°C (Cr$_2$/LC), 153°C (LC/I), 147°C (I/LC), 136°C (LC/Cr$_2$), 128°C (Cr$_2$/Cr$_1$). IR (KBr, cm^{-1}): 3473, 3415, 2918, 2848, 1616, 1570, 1398, 1253, 854. ^{1}H NMR δ_H (DMSO): 8.6 (s, 1H, -CH), 7.92 (d, 2H, ArH), 7.87 (d, 2H, ArH), 7.80 (d, 2H, ArH), 7.38 (d, 2H, ArH), 7.08 (d, 2H, ArH), 6.97 (d, 2H, ArH), 4.09 (t, 2H, -O-CH$_2$-), 1.77 (m, 2H, -CH$_2$-), 1.46–1.27 (m, 30H, 15 × CH$_2$), 0.88 (t, 3H, -CH$_3$). ^{13}C NMR δ_C (DMSO): 162.4 (>C=N), 161.29, 160.7, 154.2, 150.8, 148.4, 131.2, 129.6, 125.1, 123.7, 122.2, 116.5, 115.6 (12C, aromatic), 68.7 (-O-CH$_2$-), 31.8–14.2 (17 C, aliphatic). m/z: 569 [M]$^+$.

For 4-oxi-4′-(octadecanoyloxybenzylideneimine)azobenzene **(10)**, quantities were 1 g (2.57 mmol) 4-octadecanoyloxybenzaldehyde in 100 ml methanol, 0.548 g (2.57 mmol) 4-amino-4′-hydroxyazobenzene and glacial acetic acid (two drops). Yield: 49% (0.73 g), m.p. (liquid crystal): 140°C (Cr$_1$/Cr$_2$), 169°C (Cr$_2$/LC), 194°C (LC/I), 190°C (I/LC), 148°C (LC/Cr$_2$), 129°C (K$_2$/K$_1$). IR (KBr, cm^{-1}): 3469, 3415, 2918, 2848, 1749, 1635, 1618, 1575, 1400, 1209, 1153, 856. m/z: 583 [M]$^+$.

2.4. Syntheses of final products

2.4.1. General procedure for preparing Schiff bases I and II.
To a stirred solution containing the amino and aldehyde type compounds in toluene, a few drops of glacial acetic acid were added. The solution was refluxed with stirring for 4 h. The mixture was filtered off and the solid was washed on filter with toluene.

For 4-{[4-(4-hydroxyphenylazo)phenylimino]methyl}phenyl 4-ferrocenylbenzoate **(I)**, quantities were 1.252 g (3.05 mmol) 4-formylphenyl 4-ferrocenylbenzoate in 100 ml toluene and 0.65 g (3.05 mmol) 4-amino-4′-hydroxyazobenzene. The mixture was filtered while hot and the solid was washed on filter with hot toluene. Yield: 43.3% (0.8 g), m.p. 300°C (dec.). IR (KBr, cm^{-1}): 3439, 1703, 1627, 1600, 1500, 1415, 1280, 1207, 1182, 1091, 848. m/z: 605 [M]$^+$.
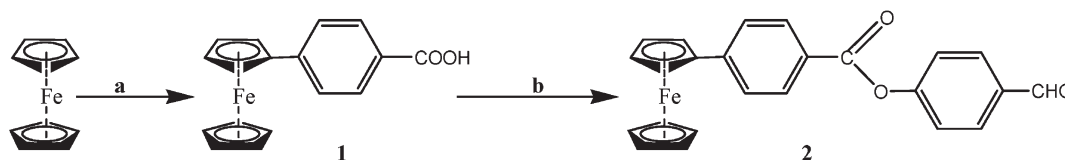
For 4-{[4-(4-octadecyloxyphenylazo)phenylimino]methyl}phenyl 4-ferrocenylbenzoate **(II)**, quantities were 0.3 g (0.73 mmol) 4-formylphenyl 4-ferrocenylbenzoate in 30 ml toluene and 0.34 g (0.73 mmol) 4-amino-4′-octadecyloxyazobenzene. The product was purified by CC/silica gel/CH$_2$Cl$_2$:petroleum ether:TEA=1:4:3%, Yield: 38% (0.238 g), m.p. (liquid crystal): 116°C (Cr$_1$/Cr$_2$), 142°C (Cr$_2$/LC), 165°C (LC/I), 156°C (I/LC), 137°C (LC/Cr$_2$), 101°C (Cr$_2$/Cr$_1$). IR (KBr, cm^{-1}): 2918, 2848, 1718, 1693, 1629, 1600, 1500,

1271, 1253, 1219, 1151, 837. ^{1}H-NMR δ_H (CDCl$_3$, 50 °C): 8.52 (s, 1H, -CH=N-), 8.13 (d, 2H, ArH), 8.02 (d, 2H, ArH), 7.95 (m, 4H, ArH), 7.61 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.34 (d, 2H, ArH), 7.02 (d, 2H, ArH), 4.75 (t, 2H, C$_5$H$_4$), 4.43 (t, 2H, C$_5$H$_4$), 4.06 (m, 7H, C$_5$H$_5$ and -O-CH$_2$-), 1.82 (m, 2H, -CH$_2$-), 1.43–1.26 (m, 32H, 16 × CH$_2$), 0.88 (t, 3H, -CH$_3$).

2.4.2. General procedure for preparing Schiff bases III and V.
To a solution containing stearic acid or 4-ferrocenylbenzoic acid and a catalytic amount of DMAP, in anhydrous CH$_2$Cl$_2$, under stirring, a solution of DCC solved in dried CH$_2$Cl$_2$ was added. After 1 h of stirring, the phenolic compound was added. After 12 h of stirring, the dicyclohexylurea was filtered off and the solution was concentrated. The solid residue was purified by CC/silica gel/CH$_2$Cl$_2$:petroleum ether:TEA=1:4:3%.

For 4-{[4-(4-octadecanoyloxyphenylazo)phenylimino]methyl}phenyl 4-ferrocenyl-benzoate **(III)**, quantities were 0.23 g (0.82 mmol) stearic acid and a catalytic amount of DMAP, 0.18 g (0.9 mmol) DCC dissolved in 10 ml anhydrous CH$_2$Cl$_2$ and 0.5 g (0.82 mmol) 4-{[4-(4-hydroxyphenylazo)phenylimino]methyl}phenyl 4-ferrocenylbenzoate. Yield: 38% (0.273 g), m.p. (liquid crystal): 130°C (Cr/LC), 168°C (LC/I), 163°C (I/LC), 125 (LC/Cr). IR (KBr, cm^{-1}): 2918, 2848, 1757, 1716, 1682, 1625, 1509, 1495, 1270, 1233, 1151, 837. ^{1}H NMR δ_H (CDCl$_3$), 8.53 (s, 1H, -CH=N-), 8.13 (d, 2H, ArH), 8.03 (m, 6H, ArH), 7.60 (d, 2H, ArH), 7.39 (d, 2H, ArH), 7.35 (d, 2H, ArH), 7.25 (d, 2H, ArH), 4.76 (t, 2H, C$_5$H$_4$), 4.43 (t, 2H, C$_5$H$_4$), 4.06 (s, 5H, C$_5$H$_5$), 2.59 (t, 2H, -OC-CH$_2$-), 1.78 (m, 2H, -CH$_2$-), 1.43–1.26 (m, 28H, 14 × CH$_2$), 0.88 (t, 3H, -CH$_3$). ^{13}C NMR δ_C (CDCl$_3$): 172.4 (>C=O), 167.4 (>C=O), 165.22 (>C=N), 160.22, 154.7, 154.2, 153.09, 151.1, 150.7, 149.4, 134.0, 130.8, 130.7, 126.5, 124.5, 124.4, 122.7, 122.6, 122.06 (16 C, aromatic) 83.3, 70.4, 70.3, 67.4 (4C, C$_5$H$_4$ and C$_5$H$_5$), 34.8–14.5 (17 C, aliphatic).

For 4-{4-[(4-octadecyloxybenzylidene)amino]phenylazo}phenyl 4-ferrocenylbenzoate **(IV)**, quantities were 0.349 g (1.14 mmol) 4-ferocenylbenzoic acid, 0.258 g (1.25 mmol) DCC, DMAP, in 70 ml anhydrous CH$_2$Cl$_2$ and 0.65 g (1.14 mmol) 4-oxy-4-(octadecyloxybenzylideneimino)azobenzene. Yield: 27% (0.26 g), m.p. (liquid crystal): 113°C (Cr$_1$/Cr$_2$), 166°C (Cr$_2$/LC), 247°C (LC/I), 240°C (I/LC), 147°C (LC/Cr$_2$), 90°C (Cr$_2$/Cr$_1$). IR (KBr, cm^{-1}): 2922, 2850, 1699, 1624, 1573, 1390, 1259, 1166, 883. ^{1}H NMR δ_H (CDCl$_3$): 8.6 (s, 1H, CH), 8.1 (d, 2H, ArH), 8.0 (d, 2H, ArH), 7.98 (d, 2H, ArH), 7.94 (d, 2H, ArH), 7.77 (d, 2H, ArH), 7.55 (d, 2H, ArH), 7.43 (d, 2H, ArH), 7.10 (d, 2H, ArH), 4.94 (t, 2H, C$_5$H$_4$), 4.5 (t, 2H, C$_5$H$_4$), 4.09 (m, 7H, C$_5$H$_5$ and

Scheme 1. Synthesis of ferrocene aldehydic compound (a, $Cl^-N_2^+C_6H_4COOH$, Bu_4NI, ethyl ether; b, $4\text{-}HOC_6H_4CHO$, DCC, DMAP, CH_2Cl_2).

-O-CH$_2$-), 1.78 (m, 2H, -CH$_2$-), 1.48–1.28 (m, 30H, $15 \times CH_2$), 0.88 (t, 3H, -CH$_3$).

For 4-{4-[(4-octadecanoyloxy-benzylidene)amino]-phenylazo}phenyl 4-ferrocenylbenzoate (**V**), quantities were 0.209 g (0.68 mmol) 4-ferocenylbenzoic acid, 0.155 g (0.75 mmol) DCC, DMAP, in 70 ml anhydrous CH_2Cl_2 and 0.4 g (0.68 mmol) 4-oxy-4-(octadecanoyloxybenzylideneimino)azobenzene. Yield: 35% (0.206g), m.p. (liquid crystal): 117°C (Cr$_1$/Cr$_2$), 139°C (Cr$_2$/Cr$_3$), 151°C (Cr$_3$/LC), 254°C (LC/I), 249°C (I/LC), 131°C (LC/Cr$_3$), 113°C (Cr$_3$/Cr$_2$), 100°C (Cr$_2$/Cr$_1$). IR (KBr, cm^{-1}): 2922, 2852, 1703, 1624, 1527, 1384, 1261, 848. ^{1}H NMR δ_H (CDCl$_3$): 8.5 (s, 1H, CH), 8.14 (d, 2H, ArH), 8.02 (m, 6H, ArH), 7.60 (d, 2H, ArH), 7.42 (d, 2H, ArH), 7.35 (d, 2H, ArH), 7.24 (d, 2H, ArH), 4.77 (t, 2H, C$_5$H$_4$), 4.45 (t, 2H, C$_5$H$_4$), 4.08 (s, 5H, C$_5$H$_5$), 2.59 (t, 2H, -OC-CH$_2$-), 1.78 (m, 2H, -CH$_2$-), 1.43–1.27 (m, 28H, $14 \times CH_2$), 0.89 (t, 3H, -CH$_3$). ^{13}C NMR δ_H (CDCl$_3$): 172.04 (>**C**=O), 165.0 (>**C**=O), 159.8 (>**C**=N), 154.4, 153.5, 153.1, 150.8, 150.4, 146.5, 133.6, 130.5, 130.3, 126.3, 125.9, 124.2, 124.18, 122.5, 122.2, 121.7 (16C, aromatic) 83.1, 70.3, 70.13, 67.18 (4C, **C**$_5$H$_4$ and **C**$_5$H$_5$), 34.5–14.26 (17C, aliphatic).

3. Results and discussion

The Schiff bases were obtained by condensation reactions between aldehydic compounds and the corresponding amino moieties. The reactions were performed in toluene or methanol with glacial acetic acid as catalyst.

3.1. Synthesis of intermediates

The ferrocene aldehydic compound was synthesized by arylation of ferrocene followed by the esterification with 4-hydroxybenzaldehyde (scheme 1).

The 4-alkyl/acyloxyaldehydes were synthesized by treating 4-hydroxybenzaldehyde with stearyl bromide or stearic acid (scheme 2).

The amine moieties were obtained starting from 4-nitroaniline, which was diazotized and coupled to phenol (scheme 3). The nitro compounds were reduced to amine ones using Na$_2$S as reducing agent.

The condensation reaction of the intermediate compounds was realized in methanol (scheme 4).

3.2. Synthesis of final products

The final products **I** and **II** were synthesized by the condensation reaction between ferrocene aldehyde type compound and corresponding amines (scheme 5). The products **III**, **IV** and **V** were synthesized by direct esterification of compounds **I**, **9** and **10**, respectively, with stearic acid and 4-ferrocenylbenzoic acid (schemes 5–6).

3.3. Mesogenic properties

The thermal properties of compounds **II–V** were investigated by combination of differential scanning calorimetry (DSC) and polarized optical microscopy. Compounds with a flexible chain have liquid crystalline properties with characteristic textures. The phase transitions changed with the linking group (azo or imine) position and with the type of bridge (ether or ester) between the rigid core and flexible chain (table 1).
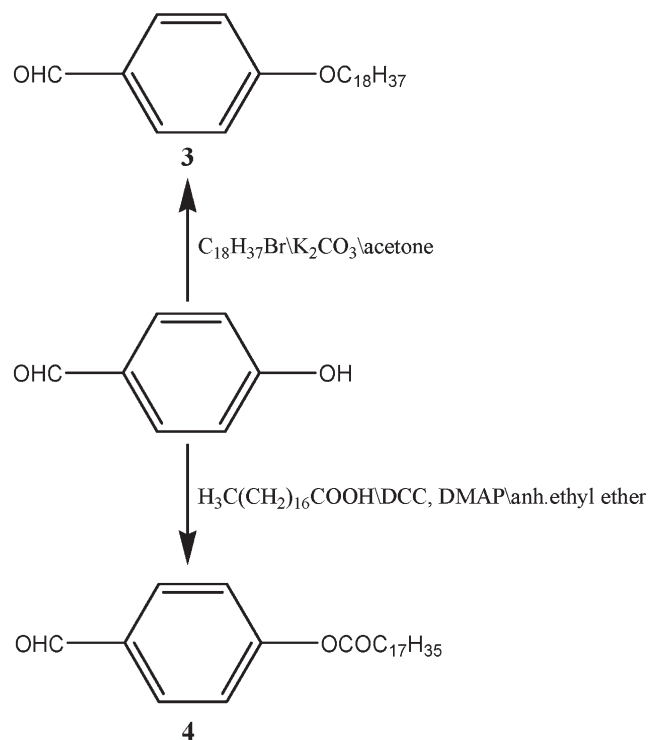
Scheme 2. Synthesis of aldehyde compounds.
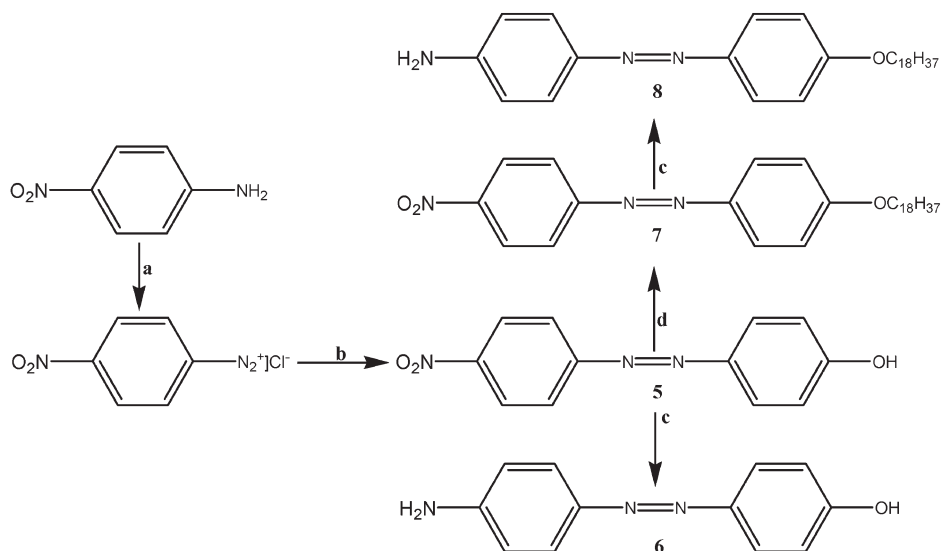
Scheme 3. Synthesis of the aminic compounds (a, HCl, NaNO$_2$; b, C$_6$H$_5$OH, CH$_3$COONa, H$_2$O; c, Na$_2$S 9H$_2$O, ethanol; d, C$_{18}$H$_{37}$Br, K$_2$CO$_3$, acetone).
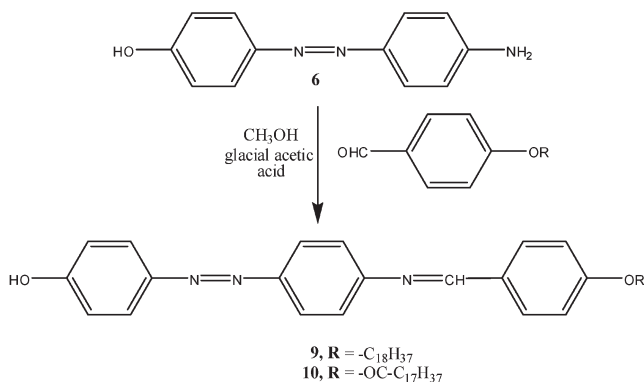

Scheme 4. Synthesis of the intermediary Schiff bases.

Compound **I**, which is without a flexible chain in its structure, did not show liquid crystalline properties due to its higher rigidity and melts at 300°C. The insertion of an azo unit into the structure and the phenol moiety increases the polarity of the molecules and, as consequence, the melting point without mesomorphic behaviour. The presence of an OH group at the end of the molecule probably results in intermolecular hydrogen bond formation, which explains the increased melting point of the compound. Attachment to the rigid core of an alkyl/acyl chain (compounds **II**–**V**) resulted in the appearance of mesophases.

In order to obtain more information regarding the liquid crystalline behaviour of the synthesized compounds, some conformational theoretical studies were performed by using Hyperchem software [35]. The main geometric characteristics and the geometry of the compounds are presented in table 2 and figure 2.

As can be seen from table 2, the low value of the length/diameter ratio in the case of compound **I** justifies the absence of liquid crystalline behaviour. Compounds **II**–**V** have a rigid core length larger than the length of flexible segment, so the ratio between the two values is less than one; analysing the DSC curves (figures 3, 4, 9
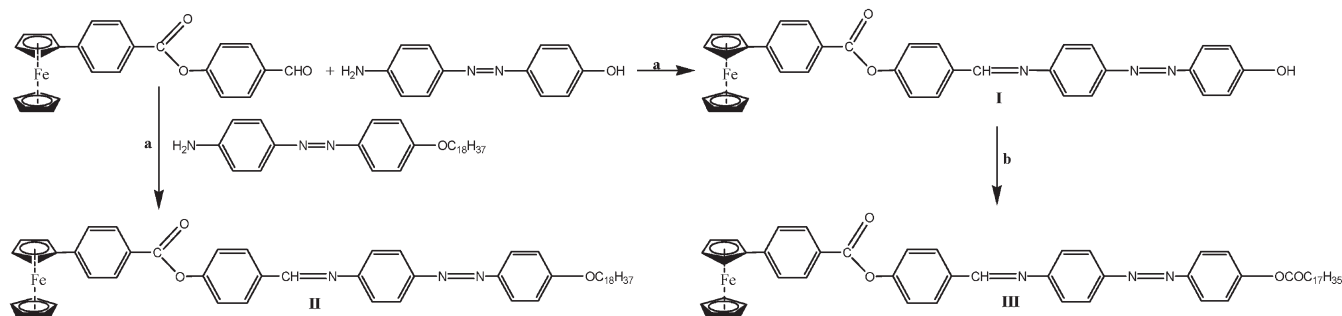
Scheme 5. Synthesis of compounds **I** and **III** (a, toluene, glacial acetic acid; b, stearic acid, DCC, DMAP, CH$_2$Cl$_2$).
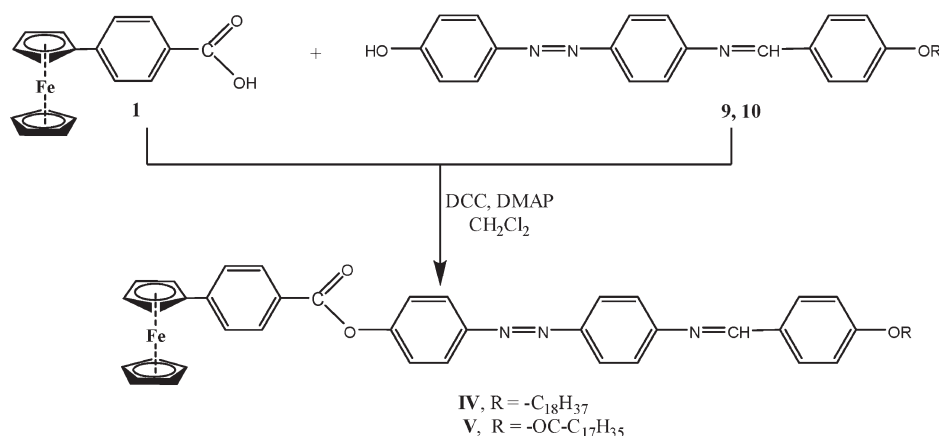
Scheme 6. Synthesis of compounds **IV** and **V**.

and 10), it seems that such a ratio is favourable for mesophase stabilization.

Compounds **II** and **III** showed enantiotropic behaviour associated with a broad liquid crystalline range. For these ferrocene derivatives, DSC curves revealed polymorphism, resulting from the different arrangements of molecules in the solid state. This behaviour could be induced by repulsion effects between the hydrogen atom of the azomethinic group and the aromatic system, as it could be seen from the geometries of compounds (figure 2).

By comparing the thermal behaviour of compounds **II** and **III** (figures 3–4) with those of some analogues synthesized in our laboratory [30], it was determined that the introduction of an azobenzene unit induces an increase of mesophase range by 12°C and 11°C, respectively. In the case of compound **II**, the mesophase appears between 142–165°C, on heating. On the DSC curve, on the third heating, three endothermic peaks (at 116°C, 142°C and respectively, 165°C) have been observed (figure 3).

When cooled from the isotropic melt, the mesophase of compound **II** appeared as a mosaic texture (figure 5).

By changing the nature of the linking group between rigid core and flexible chain, from ether into ester (compound **III**), has as result a mesophase stabilization on a 38°C interval (figure 4). A similar result has been
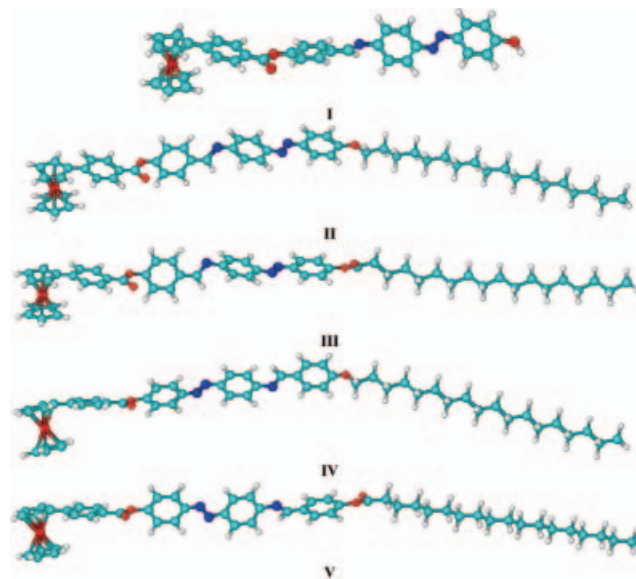
Table 1. Phase transition temperatures of the Schiff bases.

No.	Phase transitions/°C
I	$\mathrm{Cr} \xrightarrow{300} \mathrm{I}$
II	$\mathrm{Cr_1} \underset{101}{\overset{116}{\rightleftarrows}} \mathrm{Cr_2} \underset{137}{\overset{142}{\rightleftarrows}} \mathrm{N} \underset{156}{\overset{165}{\rightleftarrows}} \mathrm{I}$
III	$\mathrm{Cr_1} \underset{84}{\overset{97}{\rightleftarrows}} \mathrm{Cr_2} \underset{125}{\overset{130}{\rightleftarrows}} \mathrm{N} \underset{162}{\overset{168}{\rightleftarrows}} \mathrm{I}$
IV	$\mathrm{Cr_1} \underset{90}{\overset{113}{\rightleftarrows}} \mathrm{Cr_2} \underset{147}{\overset{166}{\rightleftarrows}} \mathrm{N} \underset{240}{\overset{247}{\rightleftarrows}} \mathrm{I}$
V	$\mathrm{Cr_1} \underset{100}{\overset{117}{\rightleftarrows}} \mathrm{Cr_2} \underset{113}{\overset{139}{\rightleftarrows}} \mathrm{Cr_3} \underset{131}{\overset{151}{\rightleftarrows}} \mathrm{N} \underset{249}{\overset{154}{\rightleftarrows}} \mathrm{I}$

Cr=crystalline phase, N=nematic phase, I=isotropic phase.

Table 2. Geometric parameters of the synthesized products.

	Rigid core/Å				
Sample	length (l_1)	diameter (d)	Flexible segment length (l_2)/Å	Ratio (l_1+l_2)/d	Ratio l_2/l_1
I	26.2	6	–	4.36	–
II	26.8	6	21.6	8.07	0.81
III	27.1	6	20.4	7.92	0.75
IV	26.1	6	21.6	7.95	0.83
V	27.3	6	20.4	7.95	0.74

Figure 2. Geometry of ferrocene-containing Schiff bases.

Figure 3. DSC thermogram of sample **II**: 1, third heating; 2, second cooling.
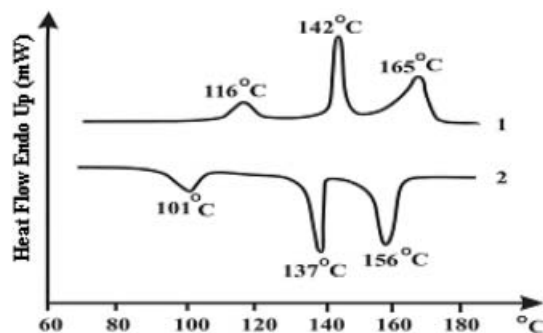

Figure 4. DSC thermogram of sample **III**: 1, third heating; 2, second cooling.

observed for the previous synthesized compounds having ester type linkage at the end of the rigid core [27, 28]. Similar behaviour appeared on cooling. Otherwise, the mesophase stabilization may be supplementary explained if considering the flexible/rigid ratio obtained from molecular modelling calculations (table 2). Figure 6 presents thermal optical micrograph of the texture displayed by compound **III.**

Typical textures were observed by using polarized optical microscopy. The nematic phase appeared on the

first heating at 170°C, and on the first cooling from the isotropic melt (figure 6).

Liquid crystalline behaviour was observed in the case of **IV** and **V** analogues and also for intermediates **9** and **10**. In contrast with the intermediates, compounds **IV** and **V** showed mesogenic properties on a very large temperature domain (~100°C), with clearing above 200°C.

The first intermediate compound, **9**, melts at 144°C and show liquid crystalline behaviour up to 153°C
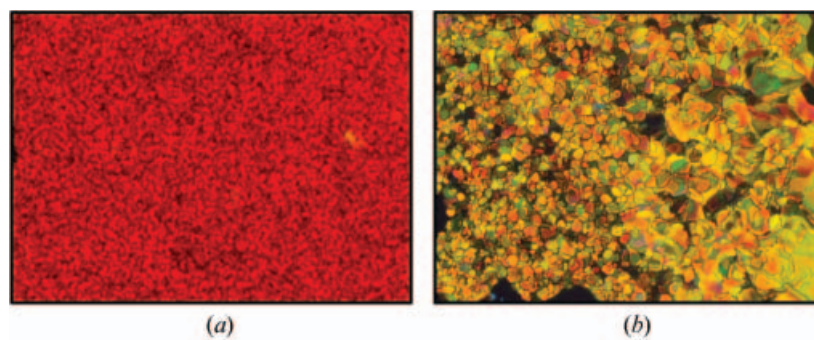

Figure 5. Thermal optical micrographs of the texture displayed by compound **II**: (a) 159.3°C, first heating; (b) 164.2°C, first cooling.
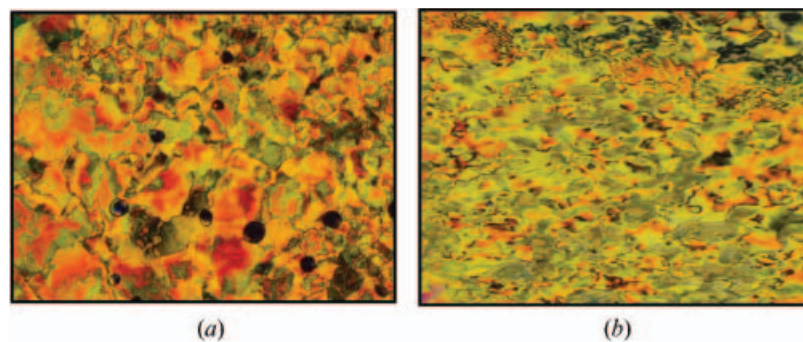

Figure 6. Thermal optical micrographs of the texture displayed by compound **III**: (a) 170.3°C, first heating; (b) 168.4°C, first cooling.

Table 3. Phase transition temperatures of the intermediate Schiff bases.

No.	Phase transitions/°C
9	$Cr_1 \underset{128}{\overset{139}{\rightleftarrows}} Cr_2 \underset{136}{\overset{146}{\rightleftarrows}} N \underset{147}{\overset{153}{\rightleftarrows}} I$
10	$Cr_1 \underset{129}{\overset{140}{\rightleftarrows}} Cr_2 \underset{148}{\overset{169}{\rightleftarrows}} N \underset{190}{\overset{194}{\rightleftarrows}} I$

Cr=crystalline phase, N=nematic phase, I=isotropic phase.

(table 3). The behaviour is an enantiotropic one, the mesophase appearing on cooling at 148°C (figure 7).

The introduction of a 4-ferrocenylbenzoic acid unit in the core of sample **9** induces significant changes on phase transitions of compound **IV** (figure 8). The increase of the length of the rigid core induces an increase of the melting point by about 20°C compared with the melting point of compound **9**. The analysis of thermal behaviour of compound **IV** comparatively with that of the **II** analogue shows that the inversion of the azo unit position with the azomethinic unit results in an increase by about 24°C of the melting point. In contrast with the **II** analogue, which presents a mesophase domain of about 23°C, compound **IV** has a larger domain (81°C). These behaviours could be explained on the basis of differences in electronic delocalization, as a consequence of the insertion of the azo unit (figure 2).

Compound **IV** exhibits a liquid crystalline phase up to 247°C. Unfortunately, on the outskirts of the sample dark fragments appeared, which indicates the beginning of degradation processes, reflected also by smaller intensities of signals on DSC curve on cooling cycle (figure **8**).

The increase of the length of the mesogenic unit by insertion of an ester type linking group between the rigid core and the flexible chain (compound **10**) results in both an increase of the melting point by about 23°C compared with its analogue, compound **9**, and in an increase of the mesogenic domain (by about 18°C),
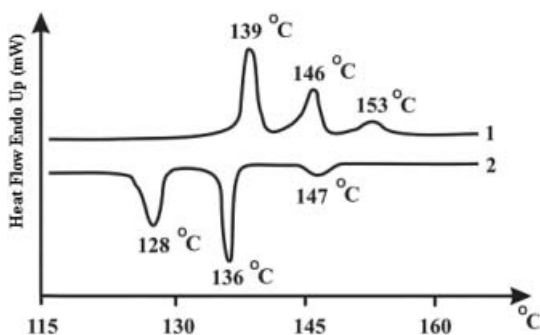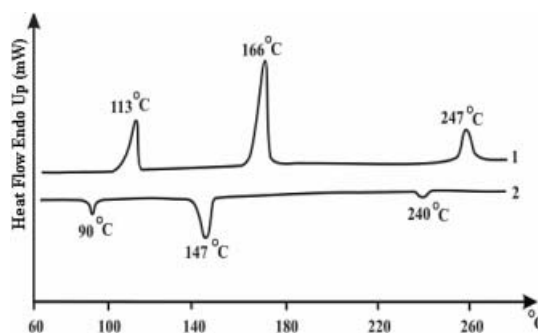

Figure 8. DSC thermogram of sample **IV**: 1, first heating; 2, first cooling.

(figure 9). At the same time, the presence of the ester unit at the end of the rigid core changes the connection angle with the aliphatic chain, which may favour a better packing of the molecules and determine the increase of packing and of clearing temperature. The behaviour is an enantiotropic one, with typically nematic textures. Some representative micrographs are shown in figure 10.

The insertion of a 4-ferrocenylbenzoic unit into the mesogenic core of compound **10** gives rise to compound **V**, which exhibited multiple transitions over a large temperature domain (137°C) (figure 11).

The compound displayed a nematic mesophase, confirmed by polarized optical microscopy. Representative examples of images of the mesophases are shown in figure 12.

On cooling, at 250°C the mesophase appears as nematic droplets. At 190°C, starting from the border limit of the sample, an ordering process begins including the entire sample; on optical micrograph a texture of nematic type has been observed (132.8°C).

On heating and on cooling cycles, DSC curves of compound **V** revealed multiple polycrystalline transitions, which could be due to some conformational reorganization of molecules by passing through into

Figure 7. DSC thermogram of sample **9**: 1, first heating; 2, first cooling.
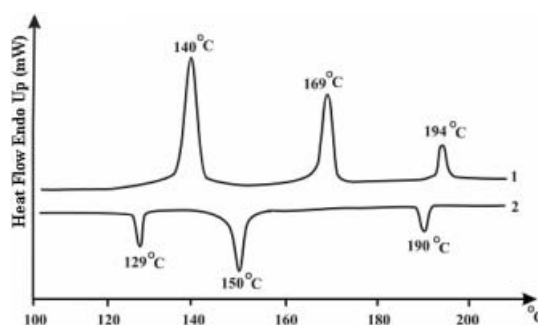

Figure 9. DSC thermogram of sample **10**: 1, first heating; 2, first cooling.
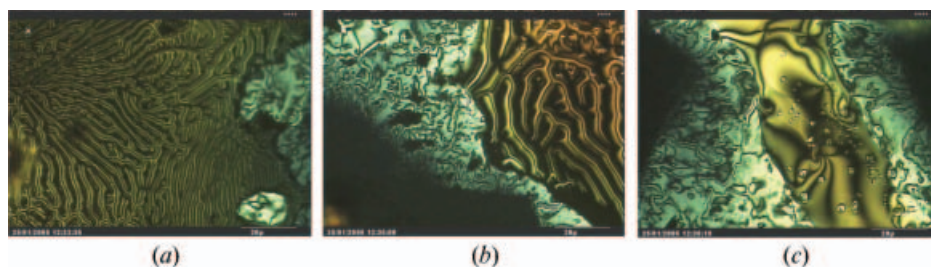
Figure 10. Thermal optical micrographs of the texture displayed by compound **10**: (a) 186.9°C, first heating; (b) 181.6°C, second cooling; (c) 173.9°C, second cooling.

more stable crystalline configuration. In the same time, the presence of two ester groups at both ends of the mesogenic core induces strengthening of lateral interactions, reflected by and, an important increase of the isotropization temperature.
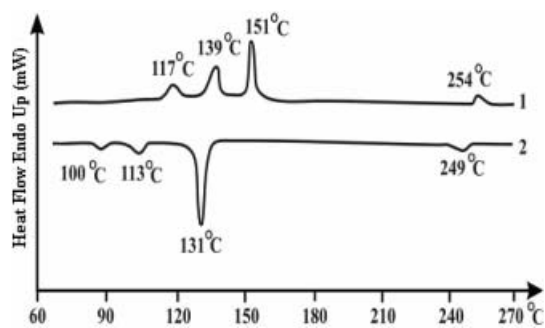
In contrast with **II** and **III** analogues, the increase of melting and clearing temperatures of **IV** and **V** compounds indicate that their polarities are larger.

4. Conclusions

The monosubstituted ferrocene-based mesogens reported here represent a new class of liquid crystals containing azo and imine linking groups. The study focused on structure–mesomorphous properties relationship of the synthesized compounds and proved that monosubstituted ferrocenyl unit can stabilize a liquid crystalline phase. Such compounds could have possible applications in optoelectronic devices.

Figure 11. DSC thermogram of sample **V**: 1, first heating; 2, first cooling.
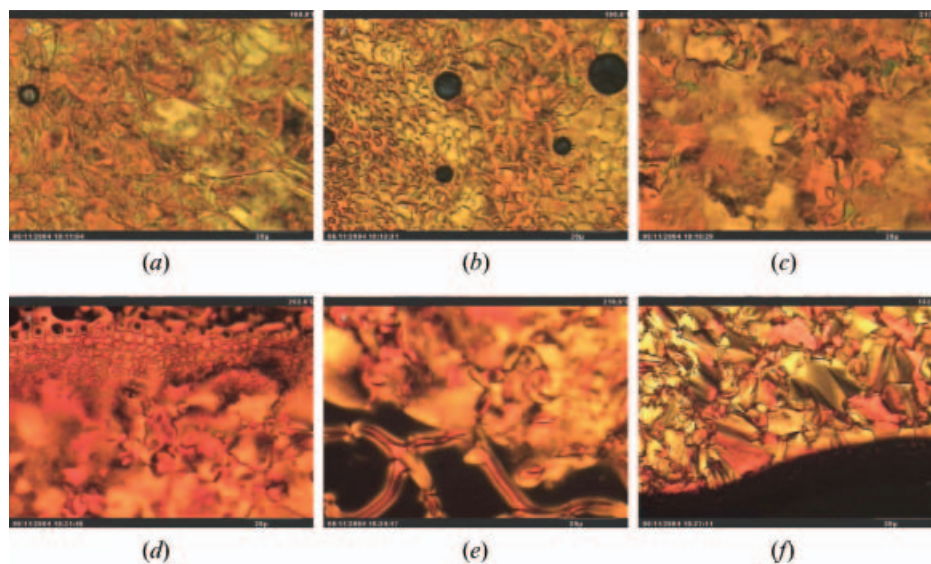
Acknowledgements

Figure 12. Thermal optical micrographs of the texture displayed by compound **V**: (a) 160.8°C, heating; (b) 190°C, heating; (c) 217.7°C, heating; (d) 252.5°C, heating; (e) 218.9°C, cooling; (f) 132.8°C, cooling.

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