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The liquid crystalline properties of some ferrocene-containing Schiff bases

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The synthesis and characterization of new ferrocene-containing mesomorphous compounds is described. In order to induce mesogenic behavior, the structure of the substituent was systematically modified. Derivatives with no more than two rings in the core did not exhibit liquid crystalline properties. The synthesized products were characterized using NMR, IR and mass spectroscopy, DSC and polarized optical microscopy. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: liquid crystals; ferrocenomesogens; Schiff bases; azo-aromatic compounds

INTRODUCTION

Generally, in the study of liquid crystals a major objective is the possibility of controlling liquid crystalline properties of a material via control of the molecular structure. Obtaining liquid crystals with a wide mesomorphic domain is possible using a careful combination of structural elements such as linear shape, rigidity and high value of length/width ratio. The structural factors affect the interaction nature between liquid crystalline molecules and are very important for obtaining adequate mesomorphic behavior. Even small changes of the shape and structure of the molecules could have a great influence over the type of mesophase and transition temperature domain.[1] The presence of ferrocene in mesomorphous molecules induces some interesting properties, because the sandwich structure including an iron atom allows physical (color, electronic density, magnetism and polarizability) and chemical properties to be changed.[2–19] The three-dimensional structure of ferrocene affects mesophase stability, but this effect could counteract structural factors imposed by the nature of the mesogenic unit.

In this paper, the synthesis of some Schiff bases having the ferrocenyl moiety connected to a mesogenic core is reported. For the purpose of inducing mesomorphism, the length of the rigid core was varied by increasing the number of aromatic rings from two to three units, simultaneously with the introduction of an esteric linking group. Thus, to balance the rigidity of molecules, terminal substituents were connected to the rigid core through an etheric/esteric bridge (Fig. 1).

Initially, ferrocene derivatives **Ia** and **Ib,** with two benzene rings in the mesogenic core, were obtained. The fact that they did not exhibit any liquid crystalline properties clearly indicates the negative influence of the bulky metallocene in the system. Hence, compounds **II** and **III,** with three rings in the core, were prepared.

RESULTS AND DISCUSSIONS

The general approach used in the synthesis of the ferrocene derivatives was to build separately the amino compounds containing the ferrocenyl moiety, by reducing the corresponding nitroarylferrocenes (Scheme 1), followed by reaction with alkyl/acyloxy aldehydes (Scheme 3). The arylferrocenes, 4-ferrocenylbenzoic acid, 4-ferrocenylphenol and 4-ferrocenylnitrobenzene were obtained by reaction of the diazonium salts of either 4-aminobenzoic acid, 4-aminophenol or 4-nitroaniline with ferrocene (Scheme 1). Reduction of the nitrocompounds was performed with $Na_2S \times 9H_2O$ or $SnCl_2 \times 2H_2O$. The 4-alkyl/acyloxyaldehydes were

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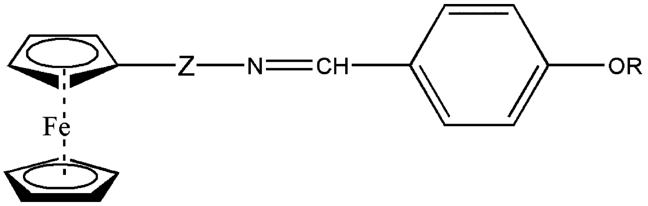


Ia: Z = -C_6H_4-, R = -$C_{18}H_{37}$

Ib: Z = -C_6H_4-, R = -OC-$C_{17}H_{35}$

IIa: Z = -C_6H_4-COO-C_6H_4-, R = -$C_{18}H_{37}$

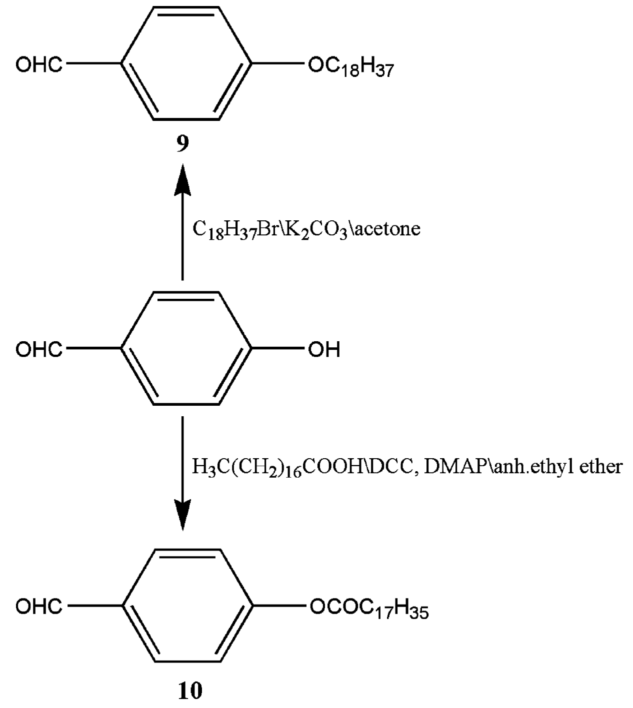
IIb: Z = -C_6H_4-COO-C_6H_4-, R = -OC-$C_{17}H_{35}$

IIIa: Z = -C_6H_4-OCO-C_6H_4-, R = -$C_{18}H_{37}$

IIIb: Z = -C_6H_4-OCO-C_6H_4-, R = -OC-$C_{17}H_{35}$

Figure 1. General structure of ferrocene containing Schiff bases.

synthesized by treating 4-hydroxybenzaldehyde with stearyl bromide or stearic acid (Scheme 2).



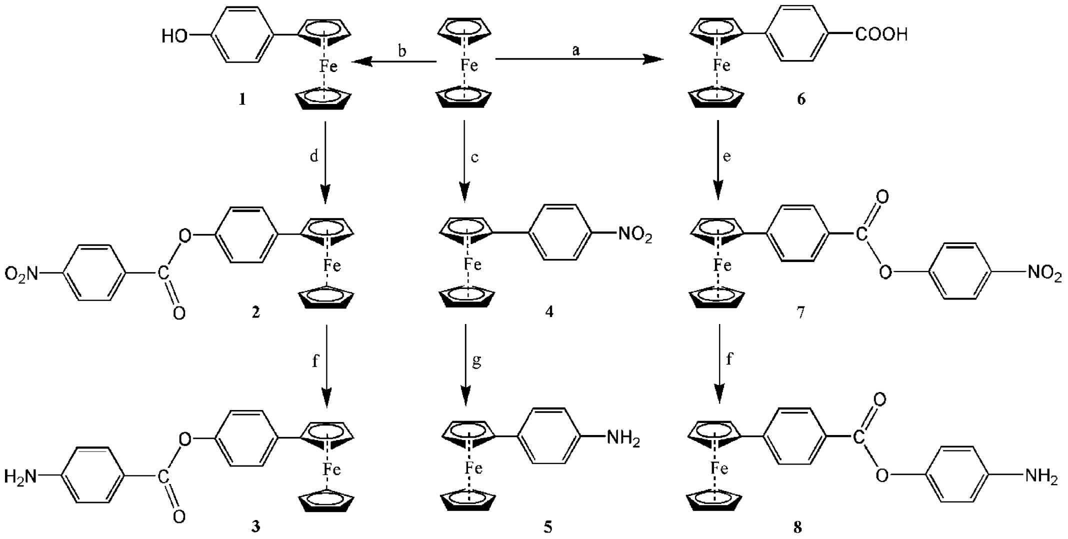
Scheme 2. Synthesis of aldehyde compounds.

Mesogenic properties

The thermal properties of compounds **II** and **III** were investigated by combination of differential scanning calorimetry (DSC) and polarized optical microscopy. Four of the synthesized compounds presented liquid crystalline properties with characteristic textures. The phase transitions changed both with rigid core structure and etheric/esteric bridge between rigid core and flexible chain (Table 1).

In the case of ferrocene derivatives, the study revealed that the length : diameter ratio plays an important role if considering mesophase stabilization.[6,10–12] In order to obtain more information regarding the liquid crystalline behavior of the synthesized compounds, some conformational theoretical studies were performed.[23] The main geometric characteristics of the compounds are presented in Table 2.

The first members of the series, **Ia, Ib**, showed a flexible : rigid ratio that was larger compared with the ratio



Scheme 1. Synthesis of amino-compounds: (a) $Cl^-N_2^+$–C_6H_4–COOH, Bu_4NI, ethyl ether; (b) $Cl^-N_2^+$–C_6H_4–OH, Bu_4NI, ethyl ether; (c) $Cl^-N_2^+$–C_6H_4–NO_2, Bu_4NI, ethyl ether; (d) HOOC–C_6H_4–NO_2, DCC, DMAP, CH_2Cl_2; (e) HO–C_6H_4–NO_2, DCC, DMAP, CH_2Cl_2; (f) $SnCl_2$ $2H_2O$, ethanol; (g) Na_2S $9H_2O$, ethanol.

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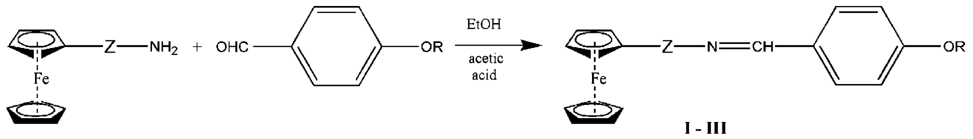
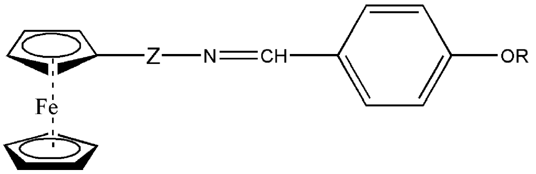
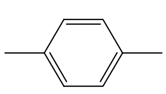
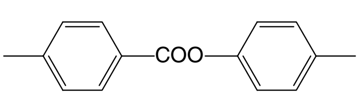
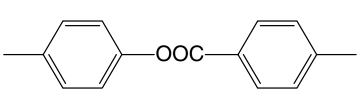


Ia: Z = $-C_6H_4-$, R = $-C_{18}H_{37}$, **Ib**: Z = $-C_6H_4-$, R = $-OC-C_{17}H_{35}$, **IIa**: Z = $-C_6H_4-COO-C_6H_4-$, R = $-C_{18}H_{37}$, **IIb**: Z = $-C_6H_4-COO-C_6H_4-$, R = $-OC-C_{17}H_{35}$, **IIIa**: Z = $-C_6H_4-OCO-C_6H_4-$, R = $-C_{18}H_{37}$, **IIIb**: Z = $-C_6H_4-OCO-C_6H_4-$, R = $-OC-C_{17}H_{35}$

Scheme 3. Synthesis of Schiff bases.

Table 1. Phase transition temperatures of ferrocene containing Schiff bases



No.	R	Z	Phase transitions (°C)
Ia	$-C_{18}H_{37}$		$K \xrightarrow{112} I$
Ib	$-OC-C_{17}H_{35}$		$K \xrightarrow{115} I$
IIa	$-C_{18}H_{37}$		$K_1 \underset{34}{\overset{80}{\rightleftharpoons}} K_2 \underset{118}{\overset{133}{\rightleftharpoons}} LC \underset{142}{\overset{144}{\rightleftharpoons}} I$
IIb	$-OC-C_{17}H_{35}$		$K_1 \underset{82}{\overset{114}{\rightleftharpoons}} K_2 \underset{104}{\overset{126}{\rightleftharpoons}} LC \underset{151}{\overset{153}{\rightleftharpoons}} I$
IIIa	$-C_{18}H_{37}$		$K_1 \underset{32}{\overset{97}{\rightleftharpoons}} K_2 \underset{76}{\overset{114}{\rightleftharpoons}} LC \underset{143}{\overset{145}{\rightleftharpoons}} I$
IIIb	$-OC-C_{17}H_{35}$		$K_1 \underset{55}{\overset{66}{\rightleftharpoons}} K_2 \underset{67}{\overset{129}{\rightleftharpoons}} LC \underset{151}{\overset{155}{\rightleftharpoons}} I$

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

Table 2. Geometric parameters of the synthesized products

	Rigid core (Å)		Flexible		
Sample code	Length (l_1)	Diameter (d)	segment (Å) Length (l_2)	Ratio $(l_1 + l_2)/d$	Ratio $l_2 : l_1$
Ia	13.9	6	21.7	5.93	1.56
Ib	14.7	6	20.4	5.85	1.38
IIa	20.3	6	21.7	7.00	1.07
IIb	21.0	6	20.4	6.9	0.97
IIIa	20.3	6	21.6	6.98	1.06
IIIb	20.9	6	20.4	6.88	0.97

of compounds **IIa, IIb** and **IIIa, IIIb**, which resulted in an increase in disorder in the system. Because of the decrease in intermolecular interaction, molecules were too flexible to give liquid crystalline properties and melted at 112 and 115 °C, respectively.

In order to increase the intermolecular interactions, the lengths of the rigid core of compounds **IIa, IIb** and **IIIa, IIIb** were modified by introducing an aromatic cycle and an esteric linking group. The introduction of an esteric group in the rigid core resulted in a slightly increased length of the rigid unit. At the same time, an increase of the polarities and physical interactions of these compounds was obtained. The result was the appearance of the mesophases.

Compounds **IIa, IIb** and **IIIa, IIIb** showed an enantiotropic behavior 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 behavior could be induced by repulsion effects between the hydrogen atom of the azomethinic group and the aromatic system, as could be seen from the geometries of the compounds (Fig. 2). Additionally, due to the internal rotation of the two cyclopentadienylic rings of ferrocene, molecules could be easily reoriented, with a low requested energy, even in solid state.[20]

In the case of compound **IIa**, on the third heating, three endothermic peaks (at 80, 133 and 144 °C, respectively) were observed, which indicates the formation of two enantiotropic liquid-crystalline phases (Fig. 3).

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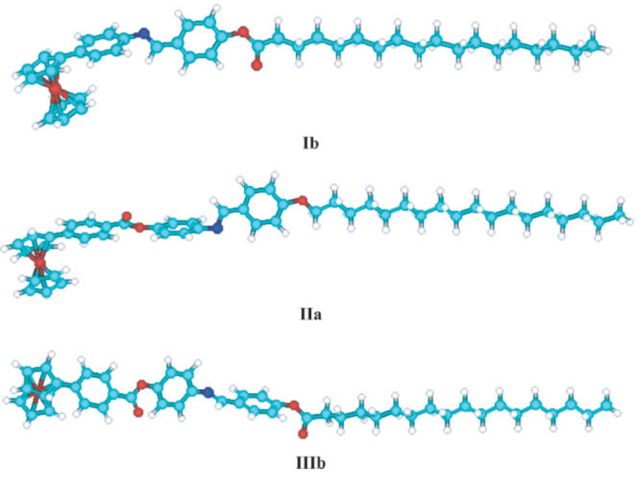

Figure 2. Geometry of some ferrocene-containing Schiff bases. This figure is available in colour online at www.interscience.wiley.com/AOC.

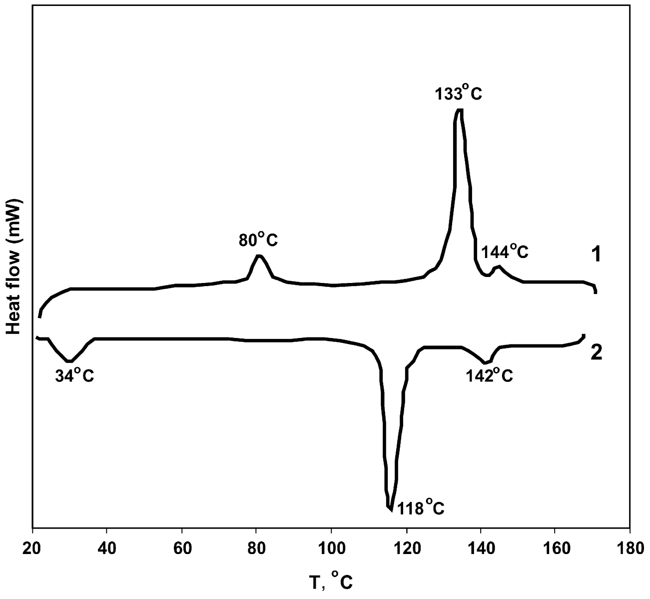

Figure 3. DSC thermogram of sample **IIa**: 1, third heating; 2, second cooling.

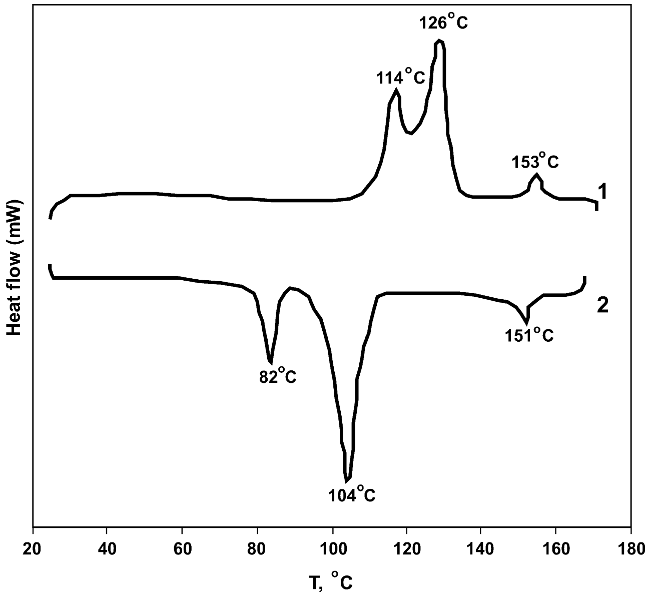

Figure 4. DSC thermogram of sample **IIb**: 1, third heating; 2, second cooling.

Polarized optical microscopy revealed the formation of an anisotropic melt between 87 (melting point) and 145 °C (clearing point), which confirmed the DSC data. When cooled from the isotropic melt, the nematic phases appeared either in the Schlieren texture or in the homeotropic one (Fig. 5).

The introduction of a second esteric group in the rigid core of compound **IIb** had a double result: a slight increase of the length of the rigid unit, if considering the esteric group a part of it, and an intensification of physical interactions. More than that, the flexible chain, presenting a methylenic group less, was shorter with about 1 Å. The liquid crystalline behavior was maintained, with a slight increase in the mesomorphic domain, both on heating and cooling (Fig. 4). The presence of a second esteric group in the rigid core led to a slight increase of the clearing temperature of about 9 °C, compared with the analogous compound **IIa**.

Compounds **IIIa** and **IIIb** differ from **II** by the orientation of the esteric function in the rigid core. A comparison of the phase behavior of compounds **IIIa** and **IIIb** with **II** showed that compounds in the two series had almost comparable clearing temperatures, confirming that the physical intermolecular interactions are very similar. Moreover, the flexible : rigid ratio was almost the same. The same result was reported by C. Imrie *et al.* in relation to isomeric monosubstituted ferrocene derivatives.[7]

The DSC of compound **IIIa** showed three endothermic peaks at 97, 114 and 145 °C. Compared with the **IIa** analogous, the liquid crystalline phase was more stable, both on heating and cooling cycles.

Typical textures were observed by means of polarized optical microscopy. On the second heating, at 137 °C, the nematic phase appeared in the homeotropic texture, bright flashes being observed when the sample was touched with a spatula. When cooled from the isotropic melt, the nematic phases appeared in the Schlieren texture (Fig. 8).

The introduction of a second esteric group in the rigid core, compound **IIIb**, decreased the flexible : rigid ratio to a sub-unit value, in association with intensification of lateral interactions resulting in an important increase in the isotropization temperature (around 10 °C, compared with **IIIa** analogous). At the same time, an accentuate stabilization of the mesophase took place on cooling.

The study of this sample by optical polarized microscopy revealed characteristic textures. At 92 °C, an interesting liquid

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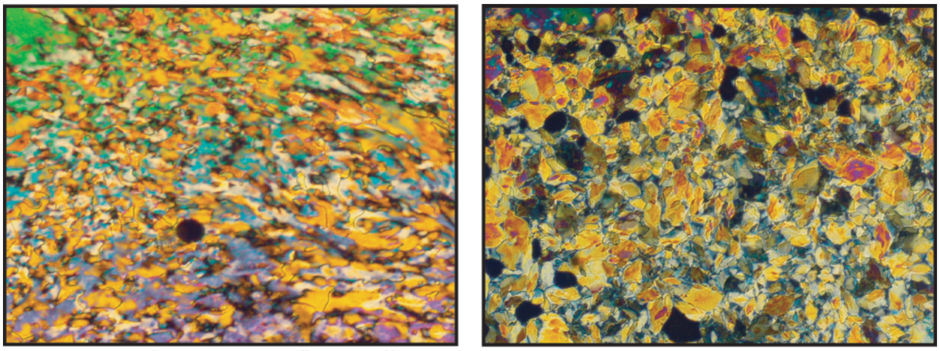

Compound **IIa**, 145 °C, first cooling Compound **IIb**, 126 °C, first cooling

Figure 5. Thermal optical micrograph of the texture displayed by **IIa** and **IIb** derivatives. This figure is available in colour online at www.interscience.wiley.com/AOC.

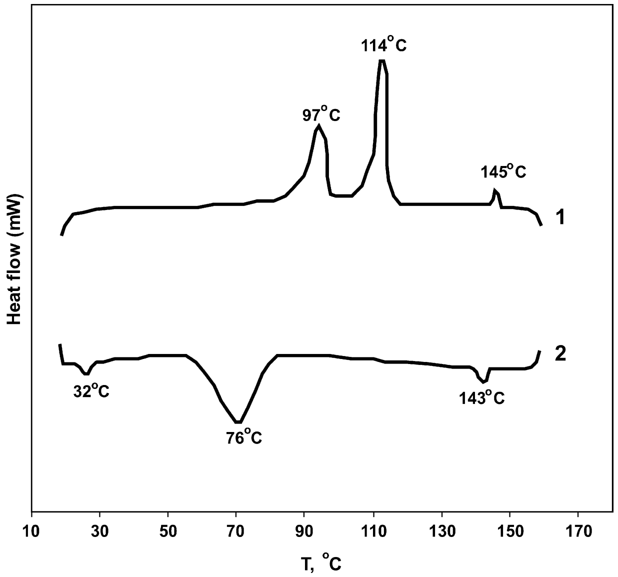

Figure 6. DSC thermogram of sample **IIIa**: 1, first heating; 2, second cooling.

crystalline texture was observed, that could be identified as a smectic C phase (Fig. 9).

On cooling from the isotropic melt, a texture with homeotropic zones developed. Simultaneously, a Schlieren texture formed from the previous homeotropic one.

EXPERIMENTAL

Materials

All reactions involving DCC and DMAP were performed under dry atmosphere of nitrogen. CH_2Cl_2 (P_2O_5) was distilled prior to use. Ferrocene (Aldrich), tetrabuthylammonium iodide (Aldrich), dicyclohexylcarbodiimide (Aldrich), 4-*N*,*N*-dimethylaminopyridine (Aldrich) and 4-hydroxybenzaldehyde (Aldrich) were used as received.

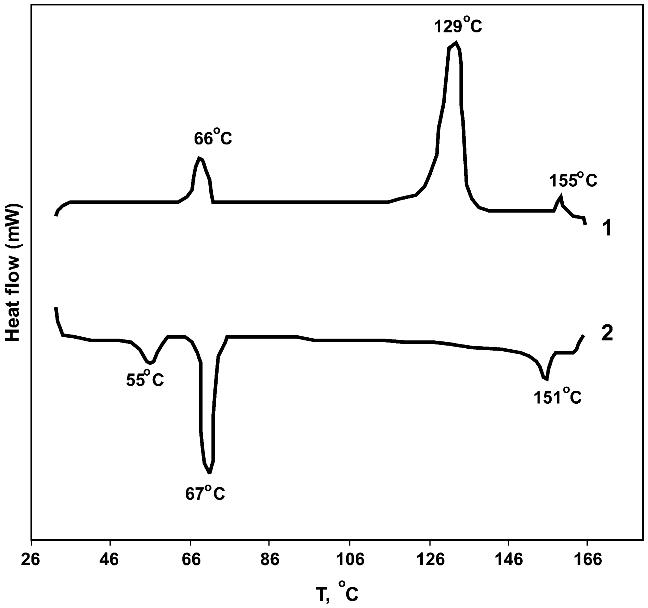

Figure 7. DSC thermogram of sample **IIIb**: 1, first heating; 2, first cooling.

4-Ferrocenylbenzoic acid and 4-ferrocenylnitrobenzene were prepared following literature procedures.[21,22]

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}, aluminum oxide F_{254}).

Techniques

Confirmation of the structures of the intermediates and final products was obtained by ^{1}H-NMR, ^{13}C-NMR, using a Jeol ECA 600 MHz spectrometer with tetramethylsilane as internal standard. IR spectra were recorded using a Nicolet Magna 550 FT-IR spectrometer (NaCl crystal window). Mass spectra were recorded on a Jeol JMS-AX 505 mass spectrometer using the FAB$^+$ method for ionization.

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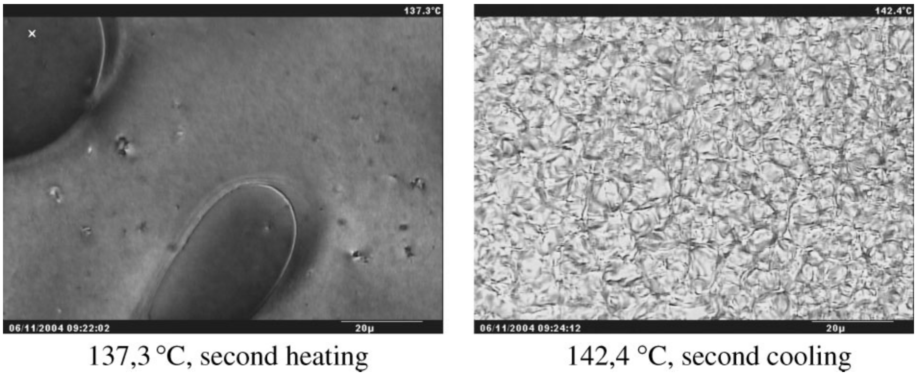
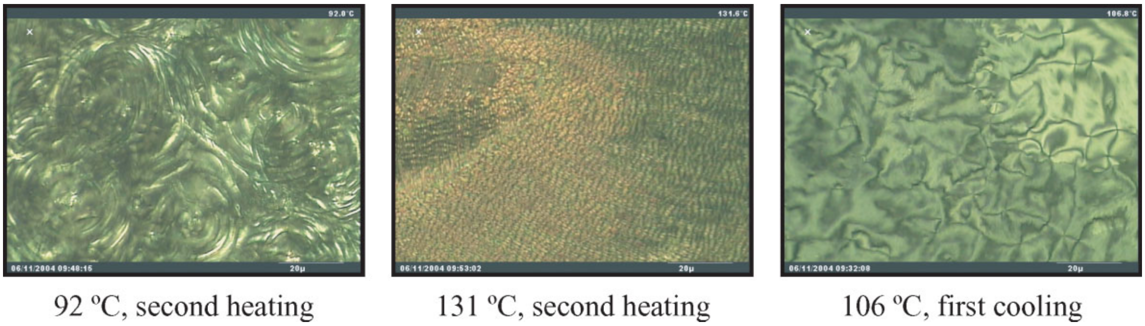


137,3 °C, second heating

142,4 °C, second cooling

Figure 8. Thermal optical micrograph of the texture displayed by **IIIa**.



92 ºC, second heating

131 ºC, second heating

106 ºC, first cooling

Figure 9. Thermal optical micrograph of the texture displayed by **IIIb** compound. This figure is available in colour online at www.interscience.wiley.com/AOC.

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 an 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 under a nitrogen atmosphere, with samples measured in closed lid aluminum pans. The mesophase type was assigned by visual comparison (under the microscope) with known phase standards.

The molecular simulations were performed using the HYPERCHEM program.[23] The initial molecular conformation of the simulated products was optimized using an MM+ field force and the value of the total potential energy of the single molecule was obtained. In order to determine the real value for minimum energy (not a local minimum), the obtained conformation was followed by a molecular dynamic cycle and re-minimized. The criterion of energy convergence was to obtain a residual root-mean-square force in the simulated system of less than 0.05 kJ/mol Å. Minimization was performed using the steepest-descent and conjugate-gradient algorithm described by Fletcher and Reeves.

Synthesis of amino compounds

General procedure for preparing arylferrocenyl derivatives

4-Aminoarylic compound, water and concentrated hydrochloric acid were mixed together and cooled to 0–5 °C with an ice–salt bath. A solution of sodium nitrite was added dropwise, under stirring. After the addition was complete, the solution was stirred for 30 min below 5 °C. Ferrocene and tetrabuthylammonium iodide were dissolved in ethyl ether and cooled to 0–5 °C. The prepared diazonium salt solution was added dropwise, under stirring. After the completion of addition, the reaction mixture was stirred for additional 5 h, at room temperature.

*4-Ferrocenylphenol (**1**)*

Quantities: 10.9 g 4-aminophenol (100 mmol), 30 ml water, 30 ml HCl 32%, 10 ml solution $NaNO_2$ (6.9 g, 100 mmol), 9.3 g ferrocene (50 mmol), 1.5 g tetrabuthylammonium iodide and 100 ml ethyl ether were used. The product was recovered by separating the organic layer and extracting the aqueous one with diethyl ether (4 × 100 ml). The combined etheric phases were washed with water and dried over anhydrous sodium sulfate. The residue remaining after removal of the solvent was subjected to chromatography (Al_2O_3, CH_2Cl_2:ethyl acetate = 15 : 1). Yield: 55% (7.8 g), m.p.: 160–163 °C. IR

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(KBr, cm^{-1}): 3514, 1606, 1523, 1263, 1174, 815, 489. ^1H-RMN δ_H(DMSO): 7.32 (d, 2H, ArH), 6.69 (d, 2H, ArH), 4.61 (t, 2H, C_5H_4), 4.23 (t, 2H, C_5H_4), 3.97 (s, 5H, C_5H_5).

*4-Ferrocenylnitrobenzene (**4**)*

Quantities: 14 g 4-nitroaniline (100 mmol), 30 ml water, 30 ml HCl 32%, 10 ml solution $NaNO_2$ (6.9 g, 100 mmol), 9.3 g ferrocene (50 mmol), 1.5 g tetrabuthylammonium iodide and 100 ml ethyl ether were used. The crude product was filtered off, washed with water and purified by CC on neutral Al_2O_3 (CH_2Cl_2:hexane = 1 : 1). Yield: 70% (13.5 g), m.p.: 169–170 °C. IR (KBr, cm^{-1}): 1595, 1506, 1388, 1342, 1282, 1107, 998, 848. ^1H-RMN δ_H ($CDCl_3$): 8.12 (d, 2H, ArH), 7.54 (d, 2H, ArH), 4.72 (t, 2H, C_5H_4), 4.45 (t, 2H, C_5H_4), 4.03 (s, 5H, C_5H_5).

*4-Ferrocenylbenzoic acid (**6**)*

Quantities: 7 g 4-aminobenzoic acid (50 mmol), 80 ml water, 12 ml HCl 32%, 20 ml solution $NaNO_2$ (3.5 g, 50 mmol), 9.3 g ferrocene (50 mmol), 1.5 g tetrabuthylammonium iodide and 100 ml ethyl ether were used. The isolated solid was dissolved in 500 ml water containing 5 g NaOH at 90 °C and was filtered 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-RMN 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).

*General procedure for preparing nitro compounds **2** and **7***

To a solution containing 4-ferrocenyl-benzoic acid and 4-nitrophenol or 4-ferrocenylphenol and 4-nitrobenzoic acid and a catalytic amount of DMAP, in anhydrous CH_2Cl_2, under stirring, a solution of DCC dissolved in dried CH_2Cl_2 was added. 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.

*4-Ferrocenylphenyl-4-nitrobenzoate (**2**)*

Quantities: 1.2 g (7.18 mmol) 4-ferrocenylphenol, 2 g (7.18 mmol) 4-nitrobenzoic acid, a catalytic amount of DMAP in 100 ml anhydrous CH_2Cl_2 and 1.63 g (7.91 mmol) DCC in 10 ml anhydrous CH_2Cl_2 were used. Purification: CC on neutral Al_2O_3 (CH_2Cl_2:petroleum ether = 1 : 1). Yield: 75% (2.3 g), m.p.: 175–180 °C. IR (KBr, cm^{-1}): 1734 (>C=O), 1647, 1647, 1521, 1452, 1346, 1267, 1201, 1076, 815. ^1H-RMN δ_H ($CDCl_3$): 8.37 (m, 4H, ArH), 7.51 (d, 2H, ArH), 7.16 (d, 2H, ArH), 4.72 (t, 2H, C_5H_4), 4.41 (t, 2H, C_5H_4), 4.13 (s, 5H, C_5H_5). ^{13}C-RMN δ_C ($CDCl_3$): 163.5 (>C=O), 150.9, 148.7, 137.9, 135.1, 131.4, 127.3, 123.8, 121.3 (8C aromatic), 85.48, 70.38, 69.7, 67.1, (4C, C_5H_5 and C_5H_4).

*4-Nitrophenyl-4-ferrocenylbenzoate (**7**)*

Quantities: 1.5 g (4.9 mmol) 4-nitrophenol, 1.5 g (4.9 mmol) 4-ferrocenylbenzoic acid, a catalytic amount of DMAP in 100 ml anhydrous CH_2Cl_2 and 1.01 g (5.39 mmol) DCC in 10 ml anhydrous CH_2Cl_2 were used. Purification: CC on neutral Al_2O_3 (CH_2Cl_2:hexane = 2 : 1). Yield: 84.6% (1.77 g), m.p.: 200–204 °C. IR (KBr, cm^{-1}): 1720 (>C=O), 1600, 1523, 1492, 1415, 1348, 1269, 1217, 1062, 839. ^1H-RMN δ_H ($CDCl_3$): 8.34 (d, 2H, ArH), 8.11 (d, 2H, ArH), 7.61 (d, 2H, ArH), 7.44 (d, 2H, ArH), 4.76 (t, 2H, C_5H_4), 4.45 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5). ^{13}C-RMN δ_C ($CDCl_3$): 164.6 (>C=O), 156.3, 147.5, 145.7, 130.9, 126.28, 125.6, 123.1 (8C aromatic), 83.07, 70.62, 70.36, 67.47, (4C, C_5H_5 and C_5H_4).

*General procedure for preparing amino compounds **3** and **8***

Nitroferrocenyl compounds **2** and **7** and 5 equivalents of $SnCl_2 \times 2H_2O$ were refluxed in ethanol for 6 h. After cooling, the mixture was poured over ice water and the pH value was adjusted to 7–8 using a 5% NaOH solution. The mixture was extracted with ethyl acetate, washed several times with water and dried over anhydrous $MgSO_4$. After solvent removal, the solid was purified by column chromatography (Al_2O_3, dichloromethane).

*4-Ferrocenylphenyl- 4-aminobenzoate (**3**)*

Quantities: 1.4 g (3.27 mmol) 4-ferrocenylphenyl-4-nitrobenzoate, 3.69 g (16.4 mmol) $SnCl_2 \times 2H_2O$ and 100 ml ethanol were used. Yield: 97% (1.27 g), m.p.: 203 °C. IR (KBr, cm^{-1}): 3477, 3379, 1724, 1616, 1600, 1519, 1452, 1313, 1265, 1203, 1066, 819. ^1H-RMN δ_H ($CDCl_3$): 8.03 (d, 2H, ArH), 7.47 (d, 2H, ArH), 7.12 (d, 2H, ArH), 6.71 (d, 2H, ArH), 4.65 (t, 2H, C_5H_4), 4.33 (t, 2H, C_5H_4), 4.17 (s, 2H, NH_2), 4.08 (s, 5H, C_5H_5).^{13}C-RMN δ_C ($CDCl_3$): 165.4 (>C=O), 151.5, 149.5, 136.7, 132.5, 127,2, 121.8, 118.9, 114.1 (8C aromatic), 86.0, 70.3, 69.5, 67.0 (4C, C_5H_4, C_5H_5).

*4-Aminophenyl-4-ferrocenylbenzoate (**8**)*

Quantities: 2.26 g (5.29 mmol) 4-nitrophenyl-4-ferrocenylbenzoate, 5.97 g (26 mmol) $SnCl_2 \times 2H_2O$ and 150 ml ethanol were used. Yield: 92% (1.94 g), m.p.: 122 °C. IR (KBr, cm^{-1}): 3417, 3336, 1710 (>C=O), 1624, 1602, 1504, 1273, 1184, 1089, 815. ^1H-RMN δ_H ($CDCl_3$): 8.10 (d, 2H, ArH), 7.57 (d, 2H, ArH), 7.01 (d, 2H, ArH), 6.72 (d, 2H, ArH), 4.74 (t, 2H, C_5H_4), 4.41 (t, 2H, C_5H_4), 4.05 (s, 5H, C_5H_5), 3.66 (s, 2H, NH_2).^{13}C-RMN δ_C ($CDCl_3$): 166.2 (>C=O), 146.2, 144.6, 143.6, 130.7, 126.1, 122.8, 116.1 (8C aromatic), 83.6, 70.39, 70.35, 67.43 (4C, C_5H_4, C_5H_5).

*4-Ferrocenylaniline (**5**)*

Quantities: 4 g (13 mmol) 4-nitrophenylferrocene were dissolved in 60 ml hot ethanol and 9.38 g (39 mmol) $Na_2S \times 9H_2O$, dissolved in 40 ml hot 1 : 1 water–ethanol mixture, was added. The mixture was refluxed, under stirring, for 6 h. After cooling, the crude product was filtered off and washed with water. Purification: CC on neutral Al_2O_3 (CH_2Cl_2:hexane = 2 : 1). Yield: 64% (2.3 g), m.p.: 157–159 °C. IR (KBr, cm^{-1}): 3468, 3371, 1620, 1529, 1454, 1408 1284, 1101, 815. ^1H-RMN δ_H ($CDCl_3$): 7.28 (d, 2H, ArH), 6.63 (d, 2H, ArH), 4.53 (t, 2H, C_5H_4), 4.23 (t, 2H, C_5H_4), 4.02 (s, 5H, C_5H_5).

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Synthesis of aldehydic compounds

*4-Octadecyloxybenzaldehyde (**9**)*

Aliquots of 0.25 g (2.05 mmol) 4-hydroxybenzaldehyde, 0.283 g (2.05 mmol) anhydrous K_2CO_3 and 0.79 g (2.37 mmol) stearyl bromide 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-RMN 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 $[M-1]^+$.

*4-Octadecanoyloxybenzaldehyde (**10**)*

Quantities: 0.5 g (4.09 mmol) 4-hydroxybenzaldehyde, 1.164 g (4.09 mmol) stearic acid, a catalytic amount of DMAP in 100 ml anhydrous CH_2Cl_2 and 0.93 g (4.5 mmol) DCC in 15 ml anhydrous CH_2Cl_2 were used. 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_2O_3 (CH_2Cl_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-RMN 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 $[M-1]^+$.

Synthesis of ferrocene containing Schiff bases

General procedure

To a stirred solution containing the amino and aldehydic compounds in ethanol, a few drops of glacial acetic acid were added. The solution was refluxed with stirring for 6 h. The mixture was filtered while hot and the solid was washed on filter with hot ethanol. The resulting solid was recrystallized from ethanol or purified by CC.

*4-Octadecyloxybenzylidene-4-ferrocenylphenylamine (**I a**)*

Quantities: 0.3 g (1.08 mmol) 4-ferrocenylaniline in 30 ml ethanol, 0.405 g (1.08 mmol) 4-octadecyloxybenzaldehyde and glacial acetic acid (one or two drops) were used. The product was recrystallized from ethanol. Yield: 74.4% (0.51 g), m.p.: 109–112 °C. Anal. found: C, 77.69; H, 8.77; N, 2.18. Calcd for $C_{41}H_{55}FeNO$: C, 77.71; H, 8.75; N, 2.21. IR (KBr, cm^{-1}): 2918, 2848, 1606, 1570, 1516, 1469, 1309, 1247, 1168, 1029, 842. ^{1}H-RMN δ_H ($CDCl_3$): 8.38 (s, 1H, CH), 7.78 (d, 2H, ArH), 7.43 (d, 2H, ArH), 7.09 (d, 2H, ArH), 6.91 (d, 2H, ArH), 4.58 (t, 2H, C_5H_4), 4.25 (t, 2H, C_5H_4), 3.98 (s, 5H, C_5H_5), 3.95 (t, 2H, $-OCH_2-$), 1.74 (m, 2H, $-CH_2-$), 1.40–1.19 (m, 30H, 15 × CH_2), 0.81 (t, 3H, $-CH_3$). m/z: 631 $[M-2]^+$.

*4-(4-Ferrocenylphenyliminomethyl)benzoic acid heptadecyl ester (**Ib**)*

Quantities: 0.25 g (0.90 mmol) 4-ferrocenylaniline in 30 ml ethanol, 0.35 g (0.90 mmol) 4-octadecanoyloxybenzaldehyde and glacial acetic acid (catalytic) were used. The product was recrystallized from ethanol. Yield: 46% (0.269 g), m.p.: 115 °C. Anal. found: C, 76.06; H, 8.24; N, 2.12. Calcd for. $C_{41}H_{53}FeNO_2$: C, 76.03; H, 8.25; N 2.16. IR (KBr, cm^{-1}): 2914, 2848, 1751, 1685, 1656, 1598, 1465, 1384, 1219, 1157, 925, 840. ^{1}H-RMN δ_H ($CDCl_3$): 8.49 (s, 1H, CH), 7.92 (d, 2H, ArH), 7.49 (d, 2H, ArH), 7.18 (m, 4H, ArH), 4.64 (t, 2H, C_5H_4), 4.31 (t, 2H, C_5H_4), 4.03 (s, 5H, C_5H_5), 2.56 (t, 2H, $-OC-CH_2-$), 1.75 (m, 2H, $-CH_2-$), 1.57–1.24 (m, 28H, 14 × CH_2), 0.86 (t, 3H, $-CH_3$). m/z: 645 $[M-2]^+$.

*4-Ferrocenylbenzoic acid 4-[(4-octadecyloxybenzylidene)amino]phenyl ester (**IIa**)*

Quantities: 0.3 g (0.755 mmol) 4-aminophenyl-4-ferrocenylbenzoate in 30 ml ethanol, 0.282g (0.755 mmol) 4-octadecyloxy-benzaldehyde and glacial acetic acid (one or two drops) were used. Purification: CC/silicagel/CH_2Cl_2: petroleum ether : TEA = 1 : 4:3%. Yield: 43.9% (0.25 g), m.p. (liquid crystal): 79 °C (K_1/K_2), 133 °C (K_2/CL), 144 °C (CL/I), 143 (I/CL), 118 °C (CL/K_2), 34 °C (K_2/K_1). Anal found: C, 76.51; H, 7.90; N, 1.91. Calcd for $C_{48}H_{59}FeNO_3$: C, 76.48; H, 7.89; N, 1.86. IR (KBr, cm^{-1}): 2918, 2848, 1726 (>C=O), 1604, 1570, 1508, 1255, 1180, 813. ^{1}H-RMN δ_H ($CDCl_3$): 8.41 (s, 1H, CH), 8.13 (d, 2H, ArH), 7.85 (d, 2H, ArH), 7.59 (d, 2H, ArH), 7.25 (m, 4H, ArH), 6.99 (d, 2H, ArH), 4.75 (t, 2H, C_5H_4), 4.42 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 4.02 (t, 2H, $-O-CH_2-$), 1.79 (m, 2H, $-CH_2-$), 1.51–1.26 (m, 30H, 15 × CH_2), 0.88 (t, 3H, $-CH_3$). ^{13}C-RMN δ_C ($CDCl_3$): 163.2 (>C=O), 159.9 (–CH=N–), 157.8, 147.9, 146.7, 144.0, 128.4, 128.2, 126.8, 124.7, 123.7, 120.26, 119.7, 112.6, (12 C aromatic), 81.3, 67.9, 67.8, 66.2, 64.9 (5 C, C_5H_5, C_5H_4 and $-O-\mathbf{C}H_2-$), 29.8, −12.0 (17 C, aliphatic). m/z: 752 $[M-1]^+$.

*4-Ferrocenylbenzoic acid 4-[(4-octadecanoyloxybenzylidene)amino]phenyl ester (**IIb**)*

Quantities: 0.35 g (0.881 mmoli) 4-aminophenyl-4-ferrocenylbenzoate in 30 ml ethanol, 0.342 g (0.881 mmol) 4-octadecanoyloxybenzaldehyde and glacial acetic acid (one or two drops) were used. Purification: CC/silicagel/CH_2Cl_2: petroleum ether : TEA = 1 : 4:3%. Yield: 53.2% (0.36 g), m.p. (liquid crystal): 114 °C (K_1/K_2), 126 °C (K_2/CL), 153 °C (CL/I), 151 (I/CL), 104 °C (CL/K_2), 82 °C (K_2/K_1). Anal found: C, 75.09; H, 7.51; N, 1.84. Calcd for $C_{48}H_{57}FeNO_4$: C, 75.08; H, 7.48; N, 1.82. IR (KBr, cm^{-1}): 2920, 2848, 1761, 1724, 1602, 1504, 1265, 1178, 815. ^{1}H-RMN δ_H ($CDCl_3$): 8.47 (s, 1H, CH), 8.13 (d, 2H, ArH), 7.95 (d, 2H, ArH), 7.59 (d, 2H, ArH), 7.26 (m, 4H, ArH), 7.22 (d, 2H, ArH), 4.75 (t, 2H, C_5H_4), 4.43 (t, 2H, C_5H_4), 4.06 (s, 5H, C_5H_5), 2.58 (t, 2H, $-OC-CH_2-$), 1.77 (m, 2H, $-CH_2-$), 1.43 ÷ 1.26 (m, 28H, 14 × CH_2), 0.88 (t, 2H, $-CH_3$). ^{13}C-RMN δ_C ($CDCl_3$): 172.3 (>C=O), 165.7 (>C=O), 159.6 (–CH=N–), 153.6, 149.9, 149.6, 146.5, 134.1, 130.1, 130.4, 126.9, 126.1, 122.8, 122.5, 122.2 (12C aromatic), 83.4, 70.4, 70.3, 67.4 (4C, C_5H_4 and C_5H_5), 34.8–14.5 (17C aliphatic). m/z: 766 $[M-1]^+$.

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*4-[(4-Octadecyloxybenzylidene)amino]benzoic acid 4-ferrocenylphenyl ester (**IIIa**)*

Quantities: 0.2 g (0.503 mmol) 4-ferrocenylphenyl-4-aminobenzoate in 20 ml ethanol, 0.188 g (0.503 mmol) 4-octadecyloxy-benzaldehyde and glacial acetic acid (one or drops) were used. Purification: CC/silicagel/CH_2Cl_2:petroleum ether: TEA = 1 : 4:3%. Yield: 63% (0.425 g), m.p. (liquid crystal): 97 °C (K_1/K_2), 114 °C (K_2/CL), 145 °C (CL/I), 143 °C (I/CL), 76 °C (CL/K_2), 32 °C (K_2/K_1). Anal found: C, 76.50; H, 7.86; N, 1.84. Calcd for $C_{48}H_{59}FeNO_3$: C, 76.48; H, 7.89; N, 1.86. IR (KBr, cm^{-1}): 2918, 2848, 1753, 1593, 1571, 1251, 1165, 812. ^{1}H-RMN δ_H ($CDCl_3$): 8.43 (s, 1H, CH), 8.25 (d, 2H, ArH), 7.87 (d, 2H, ArH), 7.49 (d, 2H, ArH), 7.26 (m, 4H, ArH), 7.13 (d, 2H, ArH), 4.72 (t, 2H, C_5H_4), 4.39 (t, 2H, C_5H_4), 4.14 (s, 5H, C_5H_5), 4.03 (t, 2H, $-O-CH_2-$), 1.79 (m, 2H, $-CH_2-$), 1.44 ÷ 1.26 (m, 30H, 15 × CH_2), 0.88 (t, 2H, $-CH_3$). ^{13}C-RMN δ_C ($CDCl_3$): 163.05 (>C=O), 160.05 (–CH=N–), 156.8, 153.7, 148.28, 137.1, 133.4, 131.6, 128.4, 125.2, 124.8, 121.5, 118.6, 120.6 (12C aromatic), 69.8, 67.9, 67.3, 66.7, 65.0 (C_5H_4, C_5H_5 and $-OCH_2$), 29.5-11.7 (17C, aliphatic). m/z: 752 $[M-1]^+$.

*4-[(4-Octadecanoyloxybenzylidene)amino]benzoic acid 4-ferrocenylphenyl ester (**IIIb**)*

Quantities: 0.35 g (0.88 mmol) 4-ferrocenylphenyl-4-aminobenzoate in 25 ml ethanol, 0.342 g (0.88 mmol) 4-octadecanoyloxy-benzaldehyde and glacial acetic acid (one or two drops) were used. Purification: CC/silicagel/CH_2Cl_2: petroleum ether : TEA = 1 : 4:3%. Yield: 63% (0.425 g), m.p. (liquid crystal): 66 °C (K_1/K_2), 129 °C (K_2/CL), 155 °C (CL/I), 151 °C (I/CL), 67 °C (CL/K_2), 55 °C (K_2/K_1). Anal found: C, 75.05; H, 7.47; N, 1.80; calcd for $C_{48}H_{57}FeNO_4$: C, 75.08; H, 7.48; N, 1.82. IR (KBr, cm^{-1}): 2918, 2848, 1751, 1723, 1627, 1595, 1278, 1211, 1161, 825. ^{1}H-RMN δ_H ($CDCl_3$): 8.45 (s, 1H, –CH–), 8.25 (d, 2H, ArH), 7.97 (d, 2H, ArH), 7.49 (d, 2H, ArH), 7.28 (m, 2H, ArH), 7.25 (d, 2H, ArH), 7.16 (d, 2H, ArH), 4.72 (t, 2H, C_5H_4), 4.40 (t, 2H, C_5H_4), 4.14 (s, 5H, C_5H_5), 2.59 (t, 2H, $-O-CO-CH_2-$), 1.77 (m, 2H, $-CH_2-$), 1.43–1.26 (m, 28H, 14 × CH_2), 0.88 (t, 3H, $-CH_3$). ^{13}C-RMN δ_C ($CDCl_3$): 172.03 (>**C**=O), 165.05 (>C=O), 160.07 (–CH=N–), 156.8, 153.7, 149.28, 137.1, 133.4, 131.6, 130.4, 127.2, 126.8, 122.3, 121.6, 120.9 (12C aromatic), 70.32, 69.61, 68.03, 67.05 (4C, C_5H_4, C_5H_5), 34.5–14.2 (17C aliphatic). m/z: 766 $[M-1]^+$.

CONCLUSIONS

A series of ferrocene liquid crystals was synthesized and characterized. The size of the rigid core of the substituent on ferrocene was found to play an important role in determining the thermal properties of these compounds.

Ferrocene derivatives **Ia** and**Ib,** with no more than two aromatic rings in the rigid core, do not exhibit liquid crystalline properties. Ferrocene derivatives **IIa, IIb** and **IIIa, IIIb** presented broad enantiotropic liquid crystalline phases.

The change in the orientation of the ester function between two aromatic cycles induces the stabilization of the mesophase, especially on cooling, compounds **IIIa** and **IIIb** presenting the smallest value of the flexible : rigid ratio. At the same time, the clearing temperatures are almost the same as those of the analogous **II**. These behaviors are explained by the change in the dipole moment in the rigid core.

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