

49. 1,1'-Disubstituted Ferrocene-Containing Thermotropic Liquid Crystals of Structure $[\text{Fe}\{(\eta^5\text{-C}_5\text{H}_4)\text{COOC}_6\text{H}_4\text{XC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1}\}_2]$ ($\text{X} = \text{OOC}$ or COO). Influence of the Orientation of the Central Ester Function on the Mesogenic Properties

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The two series **I** and **II** of 1,1'-disubstituted ferrocenes which differ by the direction of the ester function included in the rigid organic part were synthesized and their liquid crystal properties examined. These latter were found to be strongly dependent on the orientation of the connecting ester group and on the alkyl chain length.

Introduction. – Much interest is currently devoted to metallomesogens [1]. First, these compounds, which combine the properties of liquid crystals and the characteristics of metals, have allowed fundamental studies at the interface of chemistry, physics, molecular electronics, and material science. New technologies could emerge from this interdisciplinary field of research. Secondly, a specific arrangement of organic frameworks around a metallic core opens the way to new geometries and new topologies, in comparison with purely organic liquid crystals, thus allowing to explore more deeply the relationship between structure and mesogenic properties.

Most of the metallomesogens studied so far are coordination complexes built up from one or two transition-metal centers coordinated to monodentate or chelating ligands. Mononuclear Ni, Cu, Rh, Pd, Pt [1], and dinuclear Rh [2], Mo [3], Ru [4], Ni [5], Cu [6], and Pd [7] complexes containing liquid crystals were reported and generated much enthusiasm. Much less attention was devoted to organotransition metallomesogens. Monosubstituted [8] and 1,1'-disubstituted [9] ferrocene-containing liquid crystals were reported, and the first family of mesogenic (butadiene)iron-tricarbonyl derivatives was recently described [10].

Ferrocene-containing liquid crystals are interesting for three major reasons: *i*) they have a high thermal stability, giving rise to reversible transitions without decomposition, *ii*) they are soluble in common organic solvents, making their characterization straightforward, and *iii*) their three-dimensional structure offers multiple possibilities for the design of substituted derivatives. These properties prompted us to undertake a systematic study to exploit the ferrocene as a valuable organometallic unit to be incorporated into mesogenic materials.

Recently, we reported the first 1,3-disubstituted ferrocene-containing metallomesogens and showed, by comparison of their mesomorphic properties with those of the

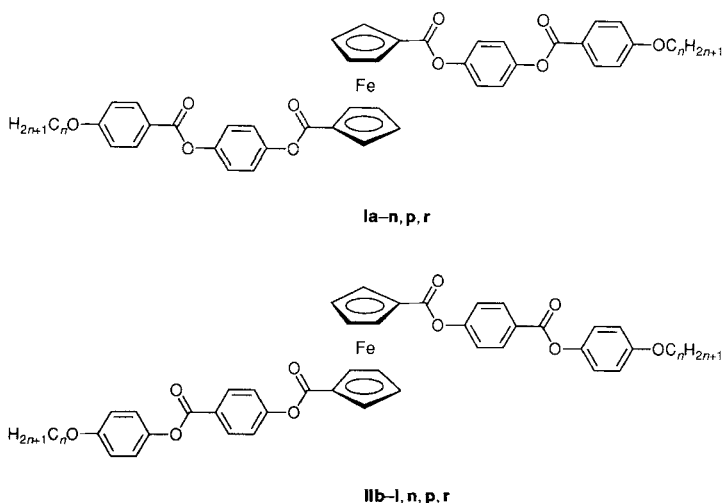
¹⁾ Part of Ph.D. Thesis of J.-L. M. and of J. S.

corresponding 1,1'-isomeric structures, the strong influence of structural isomerism on the liquid-crystal behavior [11]. Indeed, the 1,1'-disubstituted ferrocene derivatives were either monotropic or non-mesogenic, while the 1,3-disubstituted ones showed, in all cases, enantiotropic behavior with a wide anisotropic domain. These results clearly demonstrated that fine tuning of the mesogenic properties was possible, and that the substitution positions were of prime importance for obtaining stable mesophases.

To further investigate the importance of structural parameters on the liquid-crystal behavior, we decided to examine the influence of the functional groups present in the rigid organic part. It was already known, from studies performed on organic liquid crystals, that the nature and the stability of the mesophases strongly depend on the type (ester, amide, or imine) and on the direction (OOC or COO) of the connecting functional groups [12].

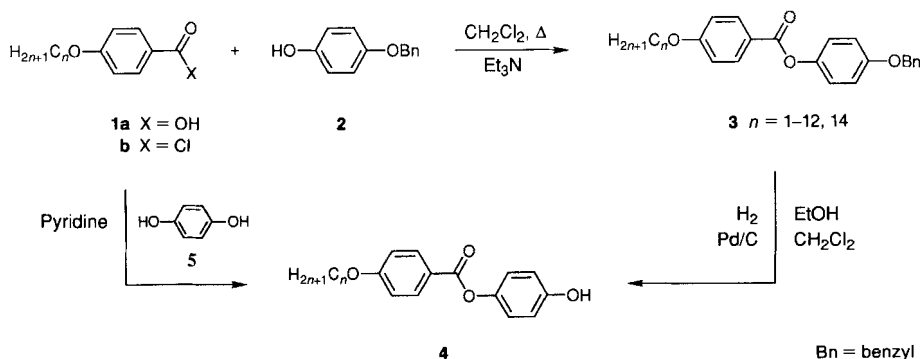
In the present paper, we describe the synthesis, characterization, and mesogenic properties of two series of 1,1'-disubstituted ferrocenes which differentiate in the orientation of the central ester functions linking aromatic rings.

Results and Discussion. – *Syntheses.* The investigated ferrocenes **I** and **II** were synthesized by esterification of ferrocene-1,1'-dicarbonyl dichloride [13] with the hydroxy-esters



4 (Scheme 1) and **9** (Scheme 2), respectively. The reactions were performed in CH₂Cl₂ under reflux in the presence of Et₃N. Purification by column chromatography and crystallization (see *Exper. Part*) gave the targeted ferrocene derivatives in good yields.

The hydroxy-esters **4** ($n = 1-8$ [14], **9**, **10** [15], **11-14**, **16** [16], **18**) were prepared following two different pathways (Scheme 1). The 4-(alkoxy)benzoic acids **1a** ($n = 1-12$, **14**) [17] were converted into the corresponding acyl chlorides **1b** ($n = 1-12$, **14**) with SOCl₂. These were reacted with hydroquinone monobenzyl ether (**2**) in CH₂Cl₂ under reflux in the presence of Et₃N to give **3** ($n = 1-12$, **14**). Removal of the benzyl protecting group under standard conditions (H₂, Pd/C) in EtOH/CH₂Cl₂ gave **4** ($n = 1-12$, **14**).

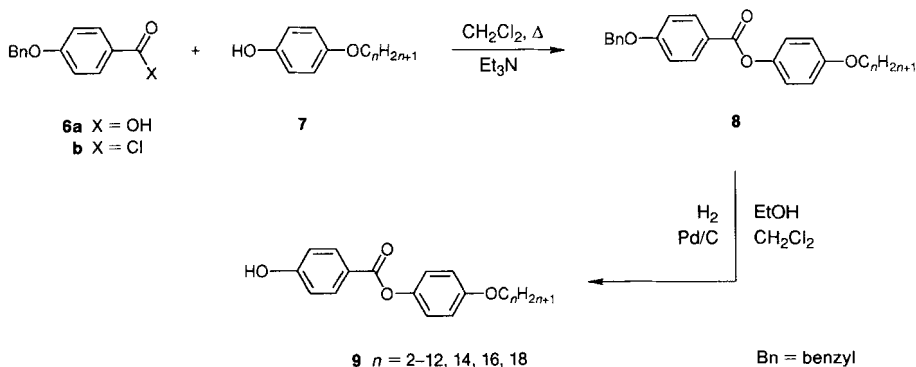
Scheme 1^{a)}

^{a)} Esters **4** with $n = 1-12, 14$ were prepared following the protection/deprotection route *via* **3**, and esters **4** with $n = 13, 16, 18$ were prepared by the direct route.

Alternatively, the hydroxy-esters **4** ($n = 13, 16, 18$) were obtained in one step, following the literature procedure [14], from 4-(alkoxy)benzoyl chloride **1b** ($n = 13, 16, 18$) and hydroquinone (**5**) in pyridine. Hydroxy-esters **4** prepared following the protection/deprotection route were easily purified by crystallization (see *Exper. Part*), but those obtained by the direct route required purification by column chromatography and crystallization. Therefore, the indirect reaction sequence proved more efficient.

To avoid column chromatography during the purification stage (see above), the hydroxy-esters **9** ($n = 2-8$ [18–20], 9–12, 14, 16, 18) were synthesized following a protection/deprotection procedure. The 4-(benzyloxy)benzoic acid (**6a**) was treated with SOCl₂ to give acyl chloride **6b** (Scheme 2). Reaction of **6b** with 4-(alkoxy)phenols **7** ($n = 2-12, 14, 16, 18$) [21] in CH₂Cl₂ under reflux in the presence of Et₃N and catalytic 4-pyrrolidinopyridine gave esters **8** ($n = 2-12, 14, 16, 18$). Removal of the benzyl protecting group (H₂, Pd/C, EtOH/CH₂Cl₂) afforded **9** ($n = 2-12, 14, 16, 18$) which were purified by crystallization from hexane.

Scheme 2



Mesogenic Properties. The disubstituted ferrocenes **I** and **II** were characterized by a combination of differential scanning calorimetry (DSC) and thermal polarized optical microscopy. The transition temperatures and enthalpy changes are reported in *Tables 1* and *2*, and the phase diagrams are illustrated in *Figs. 1* and *2*. The mesomorphic properties of **If–h** ($n = 6–8$) were recently reported [11].

None of the ferrocenes of type **I** showed liquid-crystal behavior on heating. They clearly and directly melted into an isotropic liquid. The melting point decreased, as the number of C-atoms in the alkyl chain increased up to $n = 8$. Then, the crystal-to-liquid transition temperature reached a limit value at *ca.* 165–170°. On cooling from the isotropic melt, the first members of the series, **Ia–f** ($n = 1–6$), gave rise to a monotropic nematic phase. The mesophase was identified by the appearance of nematic droplets [22] and by the formation of a typical nematic *schlieren* texture. A representative example is shown in *Fig. 3*. Comparison of the difference between the melting point and the crystallization temperature (*Fig. 1*) would seem to indicate that insufficient supercooling of the isotropic melt probably prevented **Ig–n, p, r** ($n = 7–14, 16, 18$) from forming mesophases.

More complex mesomorphic properties resulted from the series **II**. The derivatives with a short alkyl chain, **Iib–d** ($n = 2–4$), gave only a monotropic nematic phase. Comparison of the crystal-to-liquid transition temperatures between **I** and **II** showed that the members of series **II** always melted at a lower temperature than their corresponding isomer **I**. During the first heating, compound **Iie** ($n = 5$) showed an enantiotropic nematic mesophase over a very narrow anisotropic domain (2°), while the nematic phase

Table 1. Phase-Transition Temperatures T [°C]^{a)} and Enthalpy Changes ΔH [kJ/mol] of Ferrocene Derivatives **I** During the First Heating-Cooling Cycle

	n	T (ΔH) for transitions			
		$C_1/C_2^b)$	C_{1-2}/I	N/I	Recryst.
Ia	1	–	238 (77.4)	187 ^{c)} (2.6)	141
Ib	2	192 ^{d)} (13.9)	226 (69.2)	203 ^{c)} (3.4)	144
Ic	3	156 ^{d)} (13.5)	217 (70.4)	176 ^{c)} (3.6)	141
Id	4	–	210 (81.2)	176 ^{c)} (3.6)	153
Ie	5	–	178 (71.2)	159 ^{c)} (3.4)	138
If	6	161 ^{d)} (25.0)	172 (40.8)	153 ^{c)} (3.0)	140
Ig	7	157 ^{d)} (9.9)	169 (46.0)	–	156
Ih	8	–	167 (63.3)	–	153
Ii	9	–	170 (68.6)	–	155
Ij	10	–	170 (68.0)	–	159
Ik	11	96 ^{d)} (60.4)	168 (65.5)	–	161
Il	12	98 ^{d)} (52.2)	167 (71.0)	–	159
Im	13	103 (66.0 ^{e)})	167 (68.8)	–	158
In	14	101 (64.7 ^{e)})	166 (72.9)	–	159
Ip	16	97 (28.1)	165 (70.3)	–	156
Ir	18	85 (44.0 ^{e)})	163 (67.7)	–	155

^{a)} C = crystal; N = nematic phase; I = isotropic liquid.

^{b)} Dependent on the crystallization conditions during the purification stage.

^{c)} Value for monotropic transition.

^{d)} Observed during the first heating cycle only.

^{e)} A smaller value was measured during the second heating cycle.

Table 2. Phase-Transition Temperatures T [°C]^{a)} and Enthalpy Changes ΔH [kJ/mol] of Ferrocene Derivatives **II** During the First Heating-Cooling Cycle

	<i>n</i>	<i>T</i> (ΔH) for transitions							Recryst.
		C_1/C_2 ^{b)}	C_{1-2}/I	C_{1-2}/S_A	S_A/N	S_A/I	C_{1-2}/N	N/I	
IIb	2	–	186 (51.5)	–	–	–	–	177 ^{c)} (3.1)	155
IIc	3	–	182 (66.3)	–	–	–	–	144 ^{c)} (^{d)})	141
IId	4	–	164 (55.5)	–	–	–	–	157 ^{c)} (3.2)	123
IIe	5	–	–	–	–	–	154(^{d)})	156 ^{e)}	124
IIf	6	151 ^{f)} (8.6)	167 (51.7)	–	148 ^{c)})	–	–	161 ^{c)} (4.0)	135
IIg	7	–	165 (68.3)	–	–	154 ^{c)} (5.9)	–	–	136
IIh	8	–	164 (73.8)	–	–	157 ^{c)} (8.3)	–	–	139
IIi	9	153 (4.6)	–	160(^{d)})	–	163(^{d)})	–	–	133
IIj	10	–	–	156 (70.4)	–	165 (9.9)	–	–	132
IIk	11	–	–	155 (73.1)	–	167 (10.6)	–	–	134
IIl	12	153(^{d)})	–	155(^{d)})	–	169 (11.5)	–	–	135
IIm	14	149(^{d)})	–	153(^{d)})	–	169 (11.0)	–	–	132
IIp	16	145(^{d)})	–	152(^{d)})	–	166 (12.9)	–	–	131

^{a)} C = crystal; N = nematic phase; S_A = smetic-A-phase; I = isotropic liquid.

^{b)} Dependant on the crystallization conditions during the purification stage.

^{c)} Value for monotropic transition.

^{d)} Not measurable due to peak overlap.

^{e)} Observed by means of polarized-light microscopy only.

^{f)} Observed during the first heating cycle only.

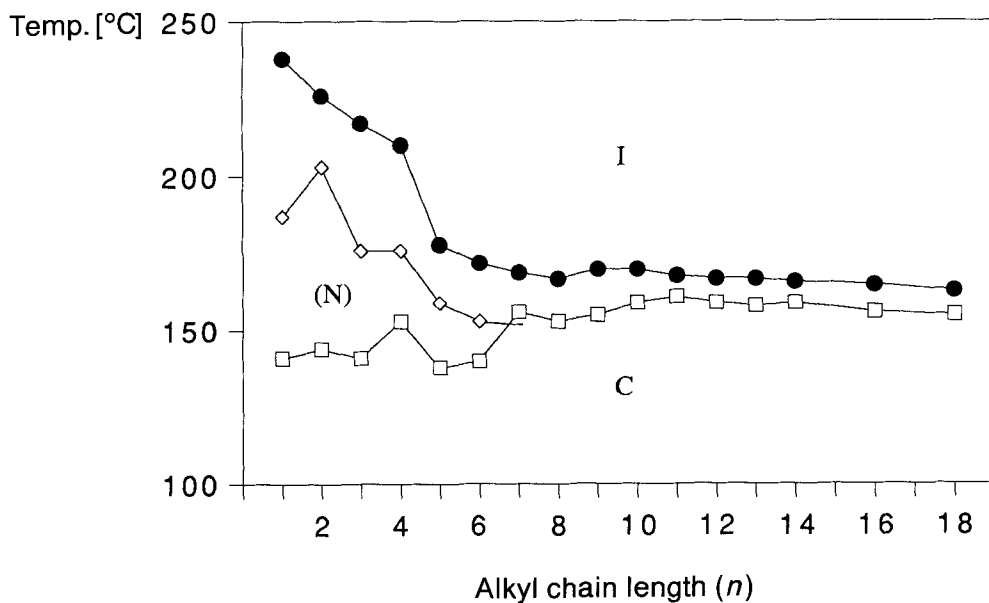


Fig. 1. Phase diagram of ferrocenes **I**.

●: Melting point; ◇: isotropic liquid/nematic transition; □: recrystallization.
C = crystal; I = isotropic liquid; N = nematic phase.

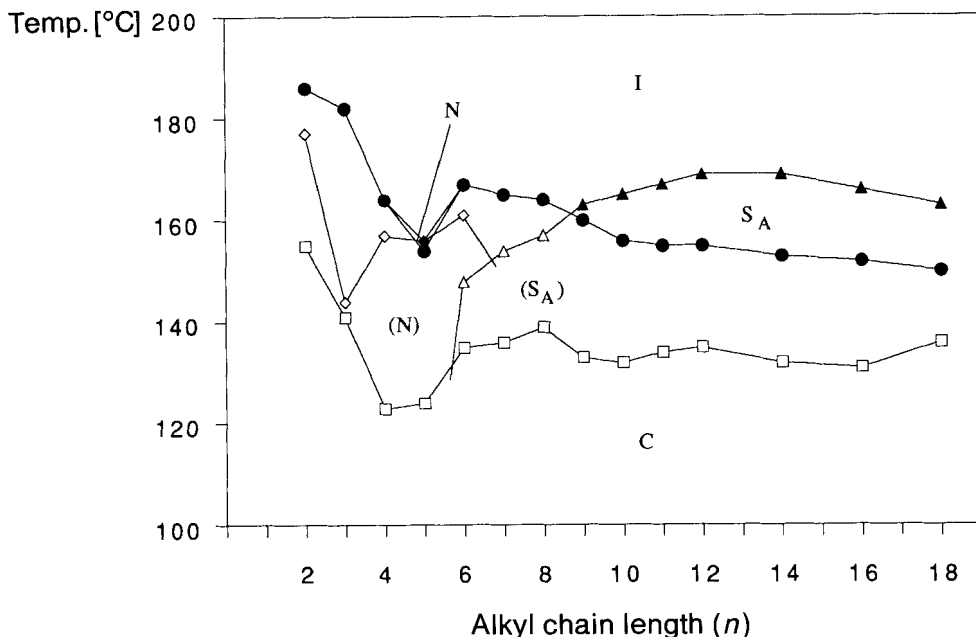


Fig. 2. Phase diagram of ferrocenes **II**. ●: Melting point; ◆: nematic/isotropic liquid transition; ▲: smectic-A/isotropic liquid transition; ◇: isotropic liquid/nematic transition; △: isotropic liquid or nematic/smectic-A transition; □: recrystallization. C = crystal; I = isotropic liquid; N = nematic phase; S_A = smectic-A phase.

only appeared at the phase transition to the liquid itself during the second heating. This behavior was due to the fact that the cooling process generated a crystal phase which was very different to the one used in the initial heating. The derivative **II**f ($n = 6$) yielded two monotropic mesophases, a nematic phase and a smectic-A one. Further increase of the alkyl chain length caused the disappearance of the nematic character and led to smectic-A liquid crystals which were first monotropic, **II**g, **h** ($n = 7, 8$), and then, from **III**i ($n = 9$) on, enantiotropic. The smectic-A range broadened from 3° (**III**i ($n = 9$)) to 16° (**II**n ($n = 14$)). During the cooling run, compounds **III** ($n = 12$), **II**n ($n = 14$), and **II**p ($n = 16$) showed, after the smectic-A solid transition, an additional crystal-to-crystal modification, which could be clearly detected by DSC and optical polarized microscopy.

An interesting phase-transitions sequence was observed for **II**r ($n = 18$; Scheme 3). On heating, a crystal-crystal transition appeared at 102°. At 143°, the material melted to a smectic-A phase, but, at 147°, recrystallized again into a new crystalline form. This latter melted at 150° to a smectic-A phase whose clearing temperature was found to be 163° ($\Delta H = 12.2$ kJ/mol). On cooling from the isotropic liquid, the smectic-A phase formed at 162°. Crystallization of the material was observed at 136°, followed by another crystal-to-crystal transformation at 132°. This melting-recrystallization process on heating (crystal 2 → smectic A → crystal 3) results in a reorganization of the molecules in the mesophase giving rise to a more stable crystalline form. Such behavior was already observed for different types of liquid crystals [23].

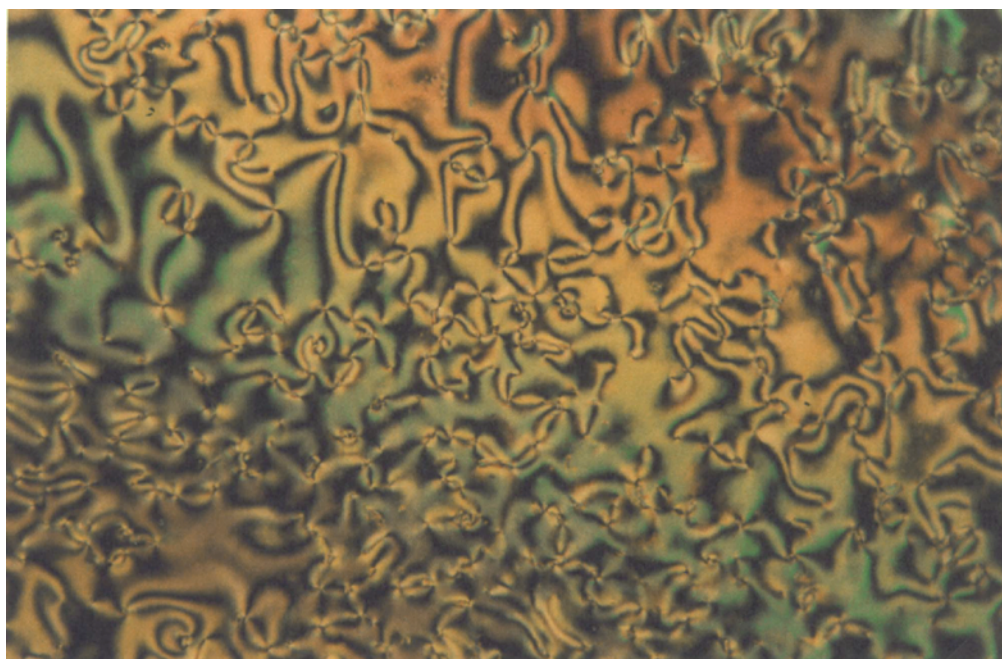


Fig. 3. Representative thermal polarized optical micrograph of the nematic schlieren texture displayed by **Ie** ($n = 5$) upon cooling from the isotropic liquid to 159° ($100\times$)

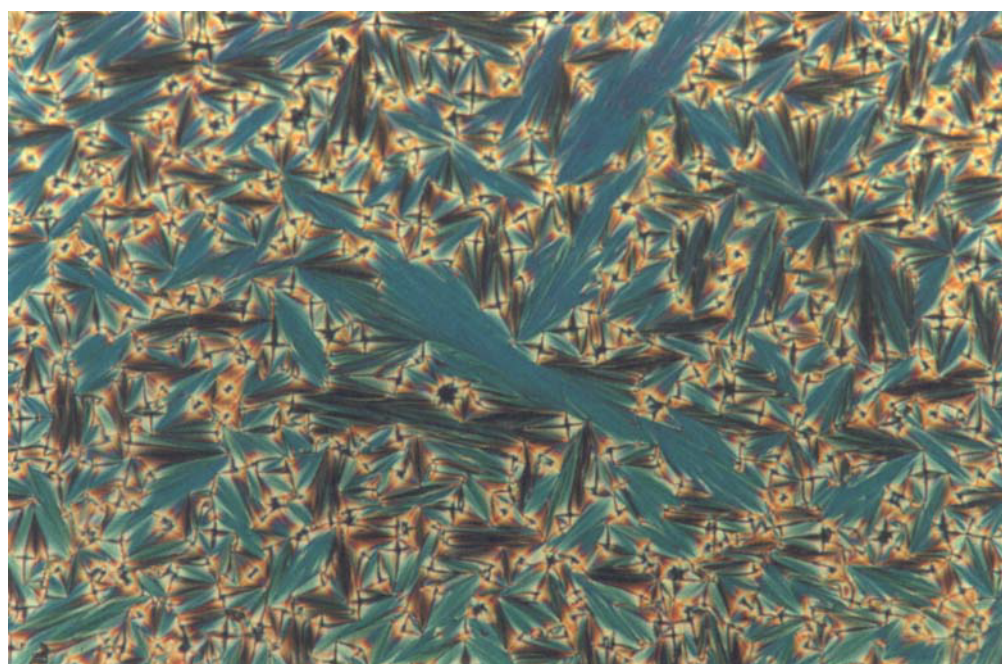
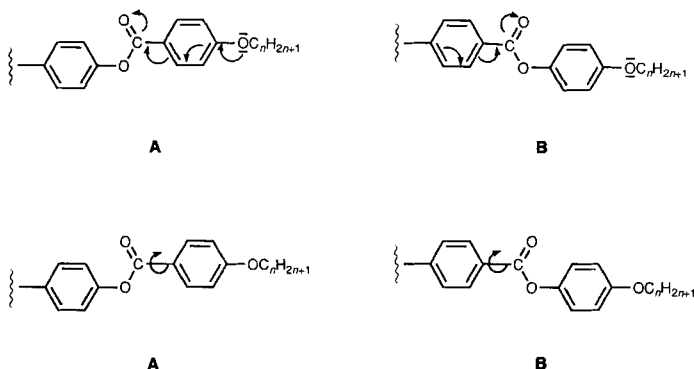


Fig. 4. Representative thermal polarized optical micrograph of the focal-conic texture displayed by **III** ($n = 12$) in the smectic-A phase upon cooling from the isotropic liquid to 164° ($200\times$)

Crystal 1 $\xrightarrow{102^{\circ}\text{C}}$ Crystal 2 $\xrightarrow{143^{\circ}\text{C}}$ Smectic A $\xrightarrow{147^{\circ}\text{C}}$ Crystal 3 $\xrightarrow{150^{\circ}\text{C}}$ Smectic A $\xrightleftharpoons[162^{\circ}\text{C}]{163^{\circ}\text{C}}$ Isotropic liquid
 $\downarrow 136^{\circ}\text{C}$
 First crystallization form
 $\downarrow 132^{\circ}\text{C}$
 Second crystallization form

The results reported above clearly demonstrate the strong influence of the central linking ester function on the mesomorphic properties. An explanation of this influence can be attempted on the basis of structural and electronic considerations. By analogy to a 1,1'-disubstituted ferrocene-containing liquid crystal, whose structure was recently determined by X-ray diffraction [24], we can assume that ferrocenes **I** and **II** adopt the *trans*-conformation (S shape; see *Formulae*). In such a conformation, derivatives **I** and **II** exhibit a C_2 axis of symmetry which is perpendicular to the plane carrying the substituents. Therefore, local, rather than overall effects must be taken into consideration for understanding the difference between **I** and **II** at the structural level.

A combination of both electron delocalization (electrostatic interactions) and rotational motion (rigidity of the organic rod) presented above is probably at the origin of the



different mesomorphic behavior observed between **I** and **II**. These observations are in agreement with literature data [12] obtained for wholly organic liquid crystals. It is important to point out that the electronic and structural features of **A** do not prevent the formation of stable liquid crystals. Indeed, the 1,3-isomeric analogues ($n = 6-8$) of **I** gave rise to large enantiotropic nematic mesophases [11]. Most likely, the highly anisometric structure of the 1,3-ferrocene derivatives was responsible for such a behavior.

In conclusion, we have shown with the present results and with those recently published [11] that electrostatic interactions and geometrical and structural features can be used to engineer the stability and nature of the mesophase for disubstituted ferrocene-containing liquid crystals.

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Experimental Part

General. 4-(Alkyloxy)benzoic acids **1a** [17], 4-(alkyloxy)phenols **7** [18], and ferrocene-1,1'-dicarbonyl dichloride [13] were prepared following literature procedures. Hydroquinone monobenzyl ether (**2**; Fluka AG), hydroquinone (**5**; Fluka AG), and 4-(benzyloxy)benzoic acid (**6a**; Fluka AG) were used without further purification. Mesogenic properties of **3** and **8** will be reported separately. Column chromatography (CC): silica gel 60 (0.063–0.200 mm, Merck). TLC: silica-gel plates (Merck). M.p.: Büchi-510 instrument; uncorrected. Transition temp. and enthalpies: differential scanning calorimeter (Mettler DSC 30) connected to a Mettler-TA-3000 system; rate 10°/min; under N₂. Optical studies: Zeiss-Axiocrop polarizing microscope equipped with a Linkam-THMS-600 variable-temperature stage; under N₂. ¹H-NMR Spectra: Bruker-AMX-400 spectrometer at 400 MHz; in CDCl₃ rel. to the internal reference TMS. Elemental analyses: Ciba-Geigy SA, Marly, Switzerland.

M.p. and elemental analyses of all new compounds are reported below. Further anal. and spectroscopic data of **3** [25], **4** [25], **1** [25], **8** [26], **9** [26], and **II** [26] are available upon request from the authors.

4-(Benzyloxy)phenyl 4-Methoxybenzoate (3a, n = 1). A mixture of 4-methoxybenzoic acid (**1a**, $n = 1$; 3.45 g, 22.5 mmol) and SOCl₂ (16 g) was heated at reflux for 2 h. The excess of SOCl₂ was removed under vacuum. The acyl chloride **1b** was esterified with hydroquinone monobenzyl ether (**2**; 4.95 g, 24.7 mmol) in dry CH₂Cl₂ (50 ml) under reflux for 2 h in the presence of Et₃N (2.28 g, 22.5 mmol). The soln. was cooled to r.t., washed with sat. NaHCO₃ soln. and sat. NaCl soln., dried (MgSO₄), and evaporated. Purification of the resulting residue by CC (hexane/AcOEt 2:1) and by crystallization from CH₂Cl₂/EtOH gave **3a** ($n = 1$; 6.26 g, 83%). White solid. *R*_f (hexane/AcOEt 2:1) 0.42. M.p. 141°. ¹H-NMR: 3.90 (s, MeO); 5.07 (s, PhCH₂); 6.98 (d, 2 arom. H); 7.01 (d, 2 arom. H); 7.11 (d, 2 arom. H); 7.33–7.45 (m, 5 arom. PhCH₂); 8.15 (d, 2 arom. H). Anal. calc. for C₂₁H₁₈O₄ (334.38): C 75.43, H 5.43; found: C 75.05, H 5.47.

Compounds **3b–l**, **n** ($n = 2-12, 14$) were prepared according to the above procedure in 75–85% yield from the corresponding acid **1a** ($n = 2-12, 14$). Selected anal. data: Table 3.

4-Hydroxyphenyl 4-Methoxybenzoate (4a, n = 1). A mixture of **3a** ($n = 1$; 2.0 g, 6.0 mmol), 10% Pd/C (0.20 g), and CH₂Cl₂/EtOH 1:5 (150 ml) was shaken overnight under H₂ (20 bars). The solids were removed by filtration, and the soln. was evaporated. The resulting residue was crystallized from EtOH/pentane: **4a** ($n = 1$; 1.43 g, 98%). White solid. M.p. 156° ([14]: 156°). ¹H-NMR: 3.90 (s, MeO); 5.39 (br., OH); 6.79 (d, 2 arom. H); 6.98 (d, 2 arom. H); 7.02 (d, 2 arom. H); 8.15 (d, 2 arom. H).

Compounds **4b–l**, **n** ($n = 2-12, 14$) were prepared according to the above procedure in 90–95% yield from the corresponding protected ester **3** ($n = 2-12, 14$). Selected anal. data: Table 4.

4-Hydroxyphenyl 4-(Tridecyloxy)benzoate (4m, n = 13). A soln. of **1a** ($n = 13$; 1.8 g, 5.6 mmol) and SOCl₂ (15 g) was stirred under reflux. After 2 h, the excess of SOCl₂ was removed under vacuum. A mixture of the acyl chloride, hydroquinone (**5**; 3.10 g, 28.2 mmol), and dry pyridine (35 ml) was stirred at r.t. for 24 h. The mixture was poured onto 2N HCl (200 ml) and a solid precipitated. This latter was recovered by filtration, stirred with sat.

Table 3. Selected Analytical Data of Compounds **3** and **8**

	<i>n</i>	Calculated		3			8		
		%C	%H	M.p. [°C]	%C	%H	M.p. [°C]	%C	%H
a	1	75.43	5.43	141	75.05	5.47			
b	2	75.84	5.79	143	75.57	5.48	137	75.90	5.79
c	3	76.22	6.12	126	76.25	6.05	148	76.31	6.17
d	4	76.57	6.43	109	76.54	6.38	135	76.39	6.58
e	5	76.90	6.71	129	76.79	6.63	131	76.86	6.70
f	6	77.20	6.98	121	77.22	7.05	118	77.07	7.13
g	7	77.48	7.22	110	77.46	7.14	122	77.34	7.33
h	8	77.75	7.46	95	77.69	7.49	126	77.77	7.52
i	9	78.00	7.67	96	77.96	7.76	125	77.95	7.65
j	10	78.23	7.88	97	78.18	7.93	122	78.22	8.00
k	11	78.45	8.07	100	78.34	7.98	122	78.28	8.07
l	12	78.65	8.25	101	78.62	8.31	120	78.35	8.37
n	14	79.03	8.58	102	78.62	8.66	119	78.99	8.83
p	16	79.37	8.88				119	79.32	9.00
r	18	79.68	9.15				118	79.71	9.29

Table 4. Selected Analytical Data of Hydroxy-esters **4** and **9**

	<i>n</i>	Calculated		4			9		
		%C	%H	M.p. [°C]	%C	%H	M.p. [°C]	%C	%H
i	9	74.13	7.92	109	74.11	7.87	150	73.93	7.98
k	11	74.97	8.39	111	75.03	8.43	141	74.93	8.34
l	12	75.34	8.60	113	75.05	8.61	139	75.31	8.83
m	13	75.69	8.80	113	75.70	8.90			
n	14	76.02	8.98	115	76.18	9.06	138	75.90	8.89
p	16	76.61	9.31				131	76.67	9.50
r	18	77.14	9.61	117	77.23	9.89	134	77.02	9.35

K₂CO₃ soln., and filtered. Purification by CC (hexane/AcOEt 3:1) and crystallization from CH₂Cl₂/EtOH afforded **4m** (*n* = 13; 1.35 g, 58%). White solid. *R*_f (hexane/AcOEt 2:1) 0.44. M.p. 113°. ¹H-NMR: 0.88 (*t*, Me); 1.27 (*m*, (CH₂)₉(CH₂)₃O); 1.47 (*m*, CH₂(CH₂)₂O); 1.82 (*m*, CH₂CH₂O); 4.04 (*t*, CH₂O); 5.32 (*br.*, OH); 6.79 (*d*, 2 arom. H); 6.96 (*d*, 2 arom. H); 7.02 (*d*, 2 arom. H); 8.12 (*d*, 2 arom. H). Anal. calc. for C₂₆H₃₆O₄ (412.57): C 75.69, H 8.80; found: C 75.70, H 8.90.

Compounds **4p**, **r** (*n* = 16, 18) were prepared according to the above procedure in 60–65% yield from the corresponding acid **1a** (*n* = 16, 18). Selected anal. data: Table 4.

Bis[4-(4-methoxybenzyloxy)phenyl] Ferrocene-1,1'-dicarboxylate (**1a**, *n* = 1). A soln. of ferrocene-1,1'-dicarbonyl dichloride (50 mg, 0.16 mmol), **4a** (*n* = 1; 94 mg, 0.38 mmol), dry Et₃N (14 mg, 0.32 mmol), and dry CH₂Cl₂ (5 ml) was heated at reflux for 2 h. The soln. was cooled to r.t., washed with sat. NaHCO₃ soln., dried (MgSO₄), and evaporated. The resulting residue was purified by CC (CH₂Cl₂/AcOEt 50:1) and crystallization from CH₂Cl₂/EtOH: **1a** (86 mg, 75%). Orange solid. *R*_f (CH₂Cl₂/AcOEt 24:1) 0.59. ¹H-NMR: 3.90 (*s*, 2 MeO); 4.62 (*t*, 4 H, Cp); 5.08 (*t*, 4 H, Cp); 6.97 (*d*, 4 arom. H); 7.21 (*d*, 4 arom. H); 7.25 (*d*, 4 arom. H); 8.14 (*d*, 4 arom. H).

Ferrocene derivatives **1b–n**, **p**, **r** (*n* = 2–14, 16, 18) were prepared according to the above procedure in 75–85% yield from the corresponding hydroxy-ester **4** (*n* = 2–14, 16, 18). Selected anal. data: Table 5.

4-Ethoxyphenyl 4-(Benzyloxy)benzoate (**8b**, *n* = 2). A mixture of 4-(benzyloxy)benzoic acid (**6a**), SOCl₂ (13 ml), DMF (1 drop), and dry CH₂Cl₂ (10 ml) was heated under reflux for 1.5 h. The mixture was cooled to r.t. and evaporated. The acyl chloride **6b** was dissolved in dry CH₂Cl₂ (5 ml) and added, dropwise, to a soln. of 4-ethoxyphenol (**7**, *n* = 2; 3.02 g, 21.9 mmol), dry Et₃N (2.22 g, 21.9 mmol), and a cat. amount of 4-pyrrolidinopy-

Table 5. *Elemental Analyses of Ferrocenes I and II*

	<i>n</i>	Calculated		<u>I</u>		<u>II</u>		<i>n</i>	Calculated		<u>I</u>		<u>II</u>		
		%C	%H	%C	%H	%C	%H		%C	%H	%C	%H	%C	%H	
a	1	66.13	4.16	65.85	4.24			i	9	70.73	6.57	70.63	6.70	70.65	6.54
b	2	66.85	4.54	66.68	4.58	66.77	4.58	j	10	71.16	6.80	71.14	6.74	71.18	6.92
c	3	67.53	4.89	67.39	4.82	67.38	4.92	k	11	71.56	7.01	71.54	6.93	71.56	6.98
d	4	68.15	5.22	68.07	5.08	68.09	5.32	l	12	71.94	7.21	72.02	7.38	71.89	7.38
e	5	68.74	5.53	68.67	5.42	68.74	5.62	m	13	72.30	7.39	72.35	7.44		
f	6	69.28	5.81	69.19	5.89	69.28	5.89	n	14	72.65	7.57	72.56	7.59	72.58	7.72
g	7	69.80	6.08	69.84	6.01	69.71	6.14	p	16	73.28	7.91	73.03	8.05	73.19	8.01
h	8	70.28	6.33	70.38	6.30	70.19	6.48	r	18	73.86	8.21	73.82	8.36	73.97	8.29

ridine in dry CH_2Cl_2 (5 ml). The mixture was heated under reflux for 3 h, cooled to r.t., and evaporated. Crystallization of the resulting residue from EtOH gave **8b** ($n = 2$; 7.25 g, 95%). White solid. M.p. 137°. $^1\text{H-NMR}$: 1.42 (*t*, Me); 4.04 (*q*, CH_2O); 5.16 (*s*, PhCH_2); 6.91 (*d*, 2 arom. H); 7.05 (*d*, 2 arom. H); 7.10 (*d*, 2 arom. H); 7.35–7.46 (*m*, PhCH_2); 8.14 (*d*, 2 arom. H). Anal. calc. for $\text{C}_{22}\text{H}_{20}\text{O}_4$ (348.40): C 75.84, H 5.79; found: C 75.90, H 5.79.

Compounds **8c–l**, **n**, **p**, **r** ($n = 3–12$, 14, 16, 18) were prepared according to the above procedure in 80–90% yield from the corresponding 4-(alkoxy)phenol **7** ($n = 3–12$, 14, 16, 18). Selected anal. data: Table 3.

4-Ethoxyphenyl 4-Hydroxybenzoate (**9b**, $n = 2$). A mixture of **8b** ($n = 2$; 7.25 g, 20.8 mmol), 10% Pd/C (0.72 g) and THF/ CH_2Cl_2 (100 ml) was shaken overnight under H_2 (4.5 bar). The solids were removed by filtration and the soln. evaporated. The resulting residue was crystallized from hexane: **9b** ($n = 2$; 3.44 g, 64%). White solid. M.p. 207° ([18]: 204–207°). $^1\text{H-NMR}$: 1.42 (*t*, Me); 4.04 (*q*, CH_2O); 5.43 (*br.*, OH); 6.90 (*d*, 2 arom. H); 6.92 (*d*, 2 arom. H); 7.10 (*d*, 2 arom. H); 8.11 (*d*, 2 arom. H).

Compounds **9c–l**, **n**, **p**, **r** ($n = 3–12$, 14, 16, 18) were prepared according to the above procedure in 70–90% yield from the corresponding protected ester **8** ($n = 3–12$, 14, 16, 18). Selected anal. data: Table 4.

Bis[4-(4-ethoxyphenoxycarbonyl)phenyl] Ferrocene-1,1'-dicarboxylate (**IIb**, $n = 2$). A soln. ferrocene-1,1'-dicarbonyl dichloride (70 mg, 0.282 mmol), **9b** ($n = 2$; 146 mg, 0.564 mmol), dry Et_3N (57 mg, 0.564 mmol), and a cat. amount of 4-pyrrolidinopyridine in dry CH_2Cl_2 (10 ml) was heated under reflux for 3 h. The soln. was cooled to r.t. and evaporated. The resulting residue was purified by CC ($\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 10:1) and crystallization from EtOH/ CH_2Cl_2 : **IIb** (183 mg, 86%). Orange solid. R_f ($\text{CH}_2\text{Cl}_2/\text{AcOEt}$ 10:1) 0.78. $^1\text{H-NMR}$: 1.43 (*t*, 2 Me); 4.04 (*q*, 2 CH_2O); 4.66 (*t*, 4Hcp); 5.10 (*t*, 4H, Cp); 6.91 (*d*, 4 arom. H); 7.10 (*d*, 4 arom. H); 7.33 (*d*, 4 arom. H); 8.20 (*d*, 4 arom. H).

Ferrocene derivatives **IIc–l**, **n**, **p**, **r** ($n = 3–12$, 14, 16, 18) were prepared according to the above procedure in 70–90% yield from the corresponding hydroxy-ester **9** ($n = 3–12$, 14, 16, 18). Selected anal. data: Table 5.

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