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Ferrocènes et ruthénocènes cristaux liquides: structures symétriques et non-symétriques

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Julio Santiago

Chimiste diplômé de l'Université de Neuchâtel
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de M. Julio Santiago

UNIVERSITÉ DE NEUCHÂTEL
FACULTÉ DES SCIENCES

La Faculté des sciences de l'Université de Neuchâtel sur le rapport des membres du jury,

M. R. Deschenaux, Mme H. Stoeckli-Evans, MM. S.M. Kelly (Bâle) et D. Guillon (Strasbourg)

autorise l'impression de la présente thèse.

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Publications

R. Deschenaux, J.-L. Marendaz, J. Santiago, "1,1'-Disubstituted Ferrocene-Containing Thermotropic Liquid Crystals of Structure $[Fe\{\eta^5\text{-}C_5H_4)COOC_6H_4XC_6H_4OC_nH_{2n+1}\}_2]$ (X=OOC or COO). Influence of the Orientation of the Central Ester Function on the Mesogenic Properties", *Helv.Chim. Acta.*, **1993**, *76*, 865.

R. Deschenaux and J. Santiago, "Disubstituted Rhutenocene-containing Thermotropic Liquid Crystals: a Novel Family of Metallomesogens", *J. Mater. Chem.*, **1993**, *3*, 219.

R. Deschenaux, M. Rama, and J. Santiago, "Unsymmetrically 1,1'-Disubstituted Ferrocene-containing Thermotropic Liquid Crystals", *Tetrahedron lett.*, **1993**, *34*, 3293.

R. Deschenaux, J. Santiago, D. Guillon and B. Heinrich, "1,3-disubstituted Ferrocene-containing Thermotropic Liquid Crystals of structure $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}1,3\text{-}(COOC_6H_4OC_nH_{2n+1})_2]$", *J. Mater. Chem.*, **1994**, *4*, 679 .

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49. 1,1′-Disubstituted Ferrocene-Containing Thermotropic Liquid Crystals of Structure $[Fe\{(\eta^5\text{-}C_5H_4)COOC_6H_4XC_6H_4OC_nH_{2n+1}\}_2]$ (X = OOC or COO). Influence of the Orientation of the Central Ester Function on the Mesogenic Properties

by Robert Deschenaux*, Jean-Luc Marendaz[1], and Julio Santiago[1])

Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, CH 2000 Neuchâtel

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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

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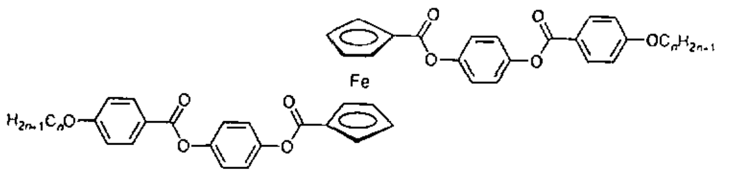
[1]) Part of Ph. D. Thesis of *J.-L. M.* and of *J. S.*

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.

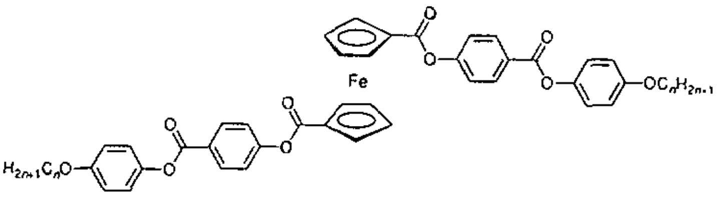
To further investigate the importance of structural parameters on the liquid-crystal behavior, we decided to examine the influence of the functional groups present in the rigid organic part. It was already known, from studies performed on organic liquid crystals, that the nature and the stability of 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



Ia–n, p, r

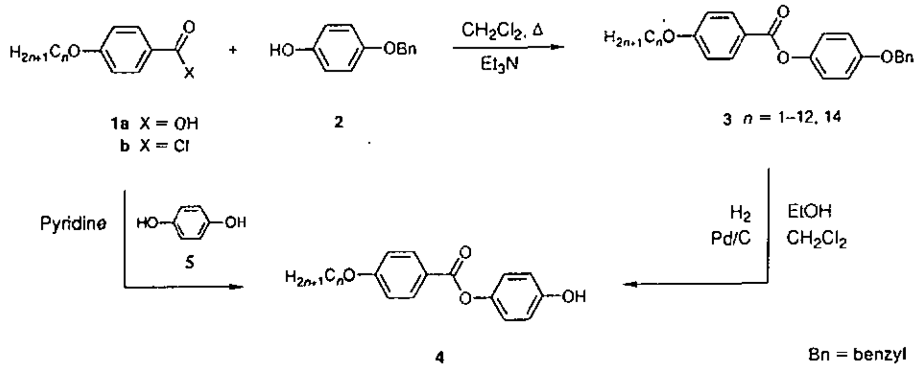


IIb–l, n, p, r

4 (*Scheme 1*) and **9** (*Scheme 2*), respectively. The reactions were performed in CH_2Cl_2 under reflux in the presence of Et_3N. 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-(alkyloxy)benzoic acids **1a** (n = 1–12, 14) [17] were converted into the corresponding acyl chlorides **1b** (n = 1–12, 14) with $SOCl_2$. These were reacted with hydroquinone monobenzyl ether (**2**) in CH_2Cl_2 under reflux in the presence of Et_3N to give **3** (n = 1–12, 14). Removal of the benzyl protecting group under standard conditions (H_2, Pd/C) in $EtOH/CH_2Cl_2$ gave **4** (n = 1–12, 14).

Scheme 1[a]

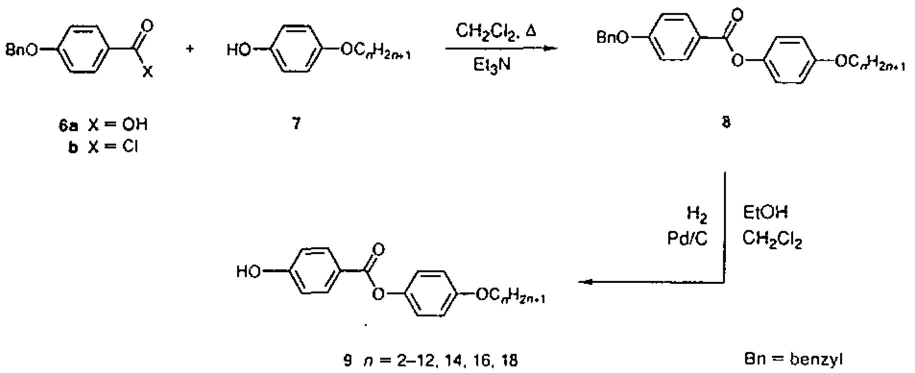


[a] Esters **4** with n = 1–12, 14 were prepared following the protection/deprotection route *via* **3**, and esters **4** with n = 13, 16, 18 were prepared by the direct route.

Alternatively, the hydroxy-esters **4** (n = 13, 16, 18) were obtained in one step, following the literature procedure [14], from 4-(alkyloxy)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 SOCl$_2$ to give acyl chloride **6b** (*Scheme 2*). Reaction of **6b** with 4-(alkyloxy)phenols **7** (n = 2–12, 14, 16, 18) [21] in CH$_2$Cl$_2$ under reflux in the presence of Et$_3$N and catalytic 4-pyrrolidinopyridine gave esters **8** (n = 2–12, 14, 16, 18). Removal of the benzyl protecting group (H$_2$, Pd/C, EtOH/CH$_2$Cl$_2$) 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	$T(\Delta H)$ 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*

	n	$T(\Delta H)$ for transitions							
		C_I/C_2[b])	C_{I-2}/I	C_{I-2}/S_A	S_A/N	S_A/I	C_{I-2}/N	N/I	Recryst.
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[c])	124
IIf	6	151[f]) (8.6)	167 (51.7)	–	148[c])[e])	–	–	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
IIn	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.

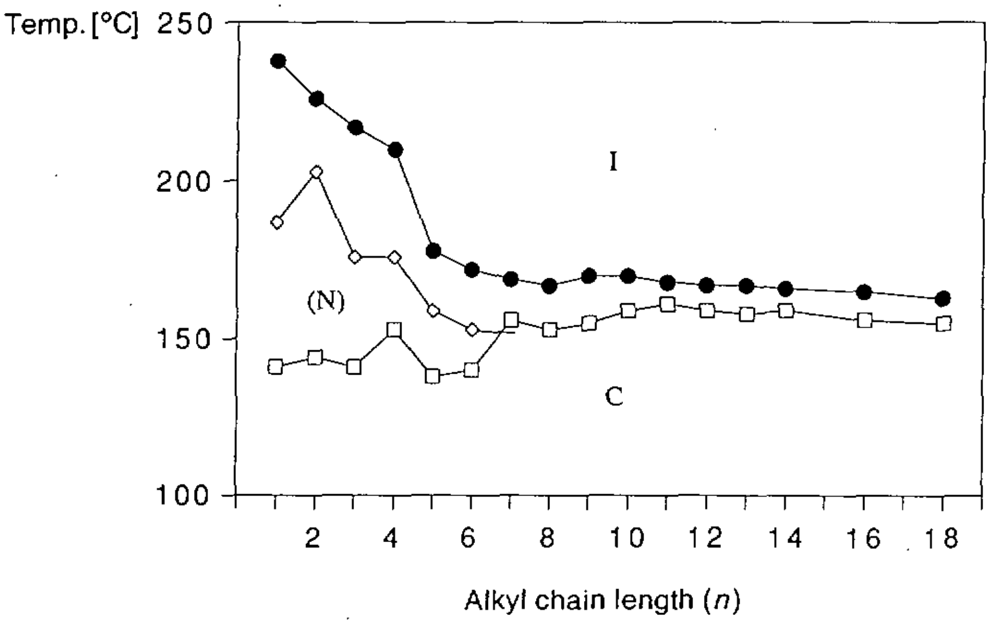


Fig. 1. *Phase diagram of ferrocenes* **I**.
●: Melting point; ◇: isotropic liquid/nematic transition; □: recrystallization.
C = crystal; I = isotropic liquid; N = nematic phase.

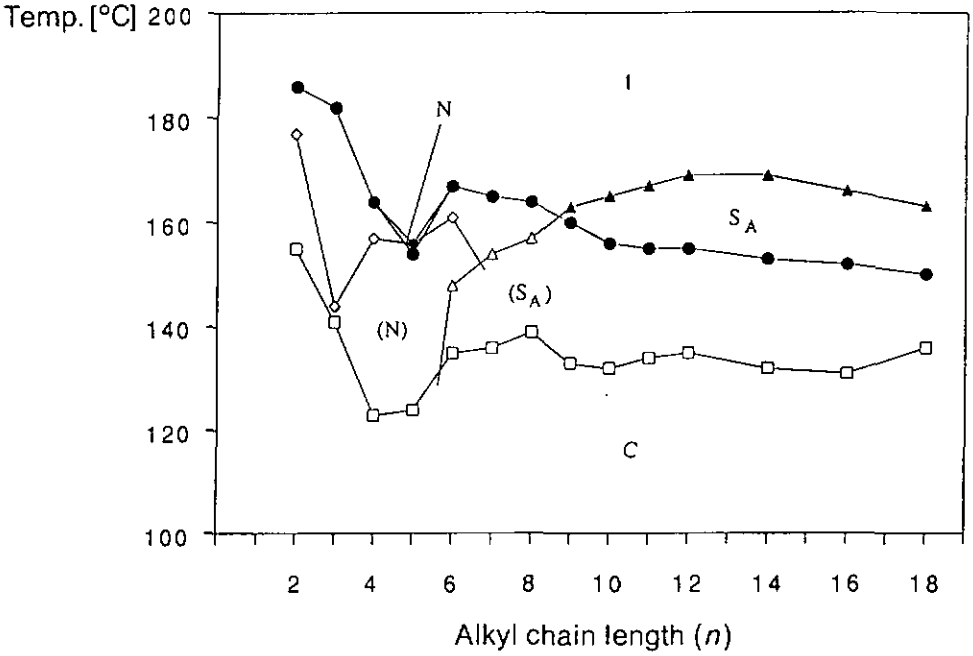


Fig. 2. *Phase diagram of ferrocenes* **II**. ●: Melting point; ◆: nematic/isotropic liquid transition; ▲: smectic-A/isotropic liquid transition; ◇: isotropic liquid/nematic transition; △: isotropic liquid or nematic/smectic-A transition; □: recrystallization. C = crystal; I = isotropic liquid; N = nematic 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 **IIf** ($n = 6$) 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, **IIg, h** ($n = 7, 8$), and then, from **IIi** ($n = 9$) on, enantiotropic. The smectic-A range broadened from 3° (**IIi** ($n = 9$)) to 16° (**IIn** ($n = 14$)). During the cooling run, compounds **IIl** ($n = 12$), **IIn** ($n = 14$), and **IIp** ($n = 16$) 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 **IIr** ($n = 18$; *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].

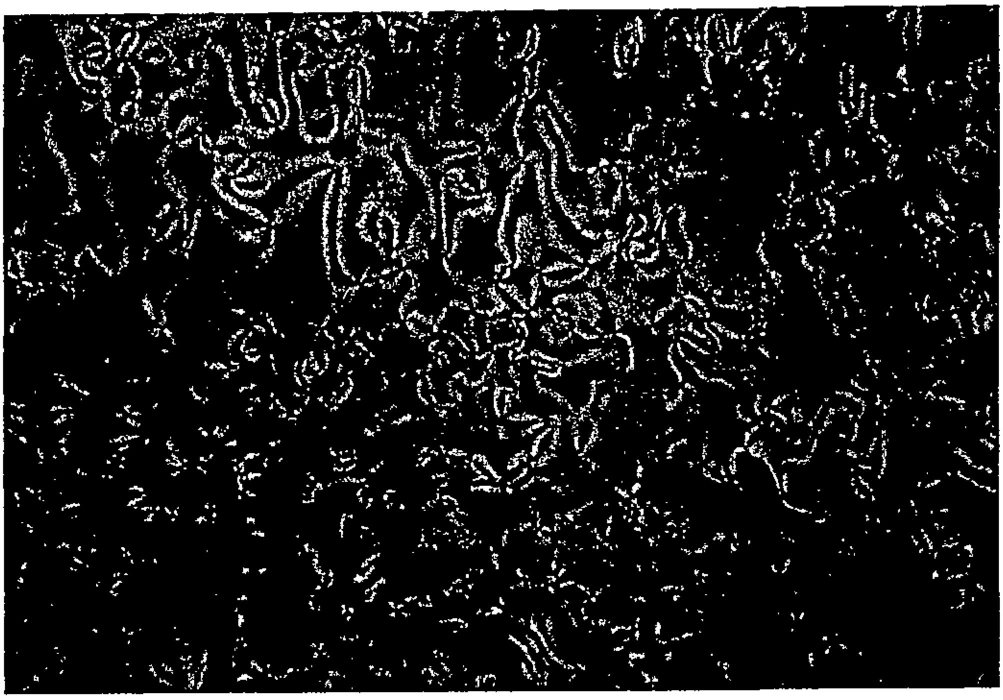


Fig. 3. *Representative thermal polarized optical micrograph of the nematic* schlieren *texture displayed by* **Ie** (*n* = 5) *upon cooling from the isotropic liquid to 159°* (100 ×)

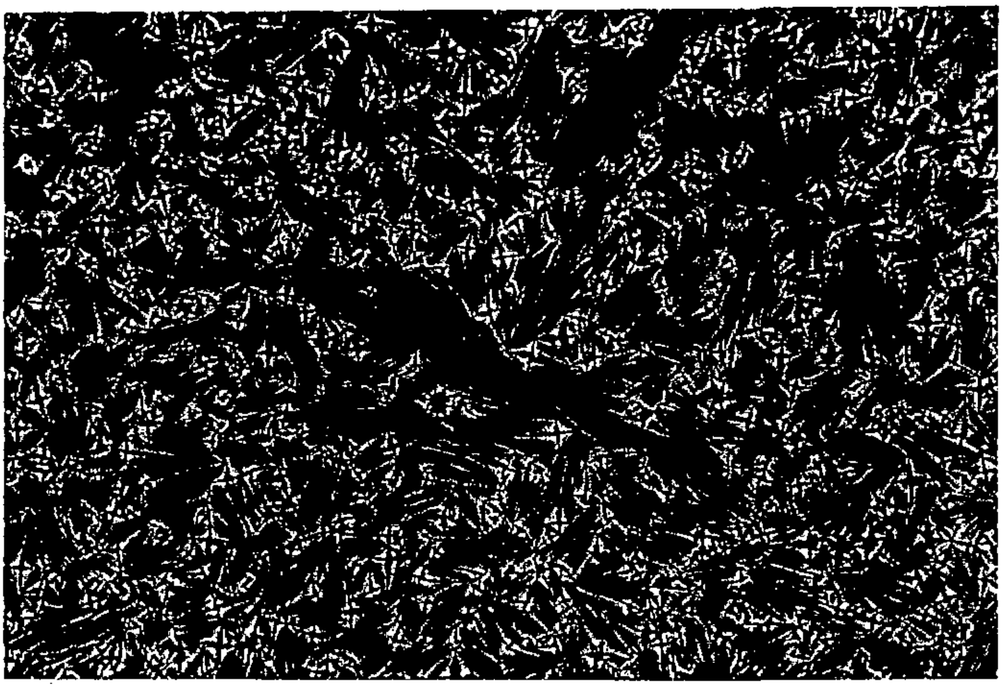
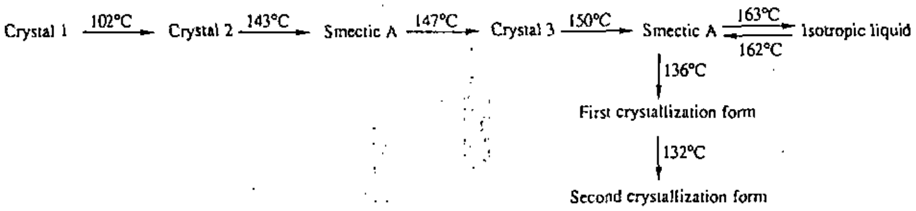


Fig. 4. *Representative thermal polarized optical micrograph of the focal-conic texture displayed by* **III** (*n* = 12) *in the smectic-A phase upon cooling from the isotropic liquid to 164°* (200 ×)

Scheme 3. *Phase-Transition Temperatures of* **IIr** (*n* = 18)

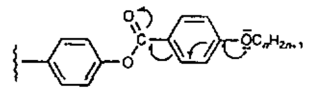


In all cases, the smectic-A phase was identified by means of polarized-light microscopy from the observation of both homeotropic and focal-conic textures. A representative example of a focal-conic texture is given in *Fig. 4*.

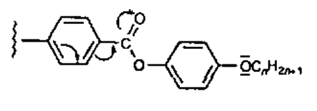
The results reported above clearly demonstrate the strong influence of the central linking ester function on the mesomorphic properties. An explanation of this influence can be attempted on the basis of structural and electronic considerations. By analogy to a 1,1′-disubstituted ferrocene-containing 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.

The organic fragments **A** and **B** are used for constructing **I** and **II**, respectively. Comparison of the two isomeric structures reveals interesting characteristics for each moiety. Firstly, in **A**, electron delocalization can occur from the O-atom of the alkoxy chain to the ester function. Thus, mesomerism takes place in the external part of the organic fragment. However, in **B**, electron delocalization appears in the interior of the organic core and in the opposite direction. Consequently, the O-atom of the ether group is more polar in **A** than in **B**. Secondly, examination of CPK models indicate that rotation could occur around some C–C bonds: in **B**, the rotation is probably more restricted than in **A** as it requires the motion of a larger molecular fragment.

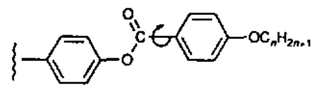
A combination of both electron delocalization (electrostatic interactions) and rotational motion (rigidity of the organic rod) presented above is probably at the origin of the



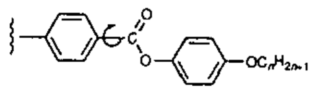
A



B



A



B

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.

We acknowledge Prof. *J. W. Goodby*, University of Hull, England, for invaluable discussions and for his help in the characterization of compounds **IIe** and **IIr**. We thank *Ciba-Geigy SA*, Switzerland, for financial support to *J.-L. M.* and for the elemental analyses, and *Veba Oel AG*, Germany, for a generous gift of ferrocene-1,1′-dicarboxylic acid.

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 N_2. Optical studies: *Zeiss-Axioscop* polarizing microscope equipped with a *Linkam-THMS-600* variable-temperature stage; under N_2. ^1H-NMR Spectra: *Bruker-AMX-400* spectrometer at 400 MHz: in $CDCl_3$ 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], **I** [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 $SOCl_2$ (16 g) was heated at reflux for 2 h. The excess of $SOCl_2$ was removed under vacuum. The acyl chloride **1b** was esterified with hydroquinone monobenzyl ether (**2**; 4.95 g, 24.7 mmol) in dry CH_2Cl_2 (50 ml) under reflux for 2 h in the presence of Et_3N (2.28 g, 22.5 mmol). The soln. was cooled to r.t., washed with sat. $NaHCO_3$ soln. and sat. NaCl soln., dried ($MgSO_4$), and evaporated. Purification of the resulting residue by CC (hexane/AcOEt 2:1) and by crystallization from CH_2Cl_2/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*, PhCH_2); 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. *Ph*CH_2); 8.15 (*d*, 2 arom. H). Anal. calc. for $C_{21}H_{18}O_4$ (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 CH_2Cl_2/EtOH 1:5 (150 ml) was shaken overnight under H_2 (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 $SOCl_2$ (15 g) was stirred under reflux. After 2 h, the excess of $SOCl_2$ 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

	n	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

	n	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

K_2CO_3 soln., and filtered. Purification by CC (hexane/AcOEt 3:1) and crystallization from CH_2Cl_2/EtOH afforded **4m** ($n = 13$; 1.35 g, 58%). White solid. R_f (hexane/AcOEt 2:1) 0.44. M.p. 113°. ^{1}H-NMR: 0.88 (*t*, Me); 1.27 (*m*, $(CH_2)_9(CH_2)_3O$); 1.47 (*m*, $CH_2(CH_2)_2O$); 1.82 (*m*, CH_2CH_2O); 4.04 (*t*, CH_2O); 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 $C_{26}H_{36}O_4$ (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-methoxybenzoyloxy)phenyl] Ferrocene-1,1'dicarboxylate (**Ia**, $n = 1$). A soln. of ferrocene-1,1'-dicarbonyl dichloride (50 mg, 0.16 mmol), **4a** ($n = 1$; 94 mg, 0.38 mmol), dry Et_3N (14 mg, 0.32 mmol), and dry CH_2Cl_2 (5 ml) was heated at reflux for 2 h. The soln. was cooled to r.t., washed with sat. $NaHCO_3$ soln., dried ($MgSO_4$), and evaporated. The resulting residue was purified by CC (CH_2Cl_2/AcOEt 50:1) and crystallization from CH_2Cl_2/EtOH: **Ia** (86 mg, 75%). Orange solid. R_f (CH_2Cl_2/AcOEt 24:1) 0.59. ^{1}H-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 **Ib–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**), $SOCl_2$ (13 ml), DMF (1 drop), and dry CH_2Cl_2 (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 CH_2Cl_2 (5 ml) and added, dropwise, to a soln. of 4-ethoxyphenol (**7**, $n = 2$; 3.02 g, 21.9 mmol), dry Et_3N (2.22 g, 21.9 mmol), and a cat. amount of 4-pyrrolidinopy-

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

	n	Calculated		I		II			n	Calculated		I		II	
		%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}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 $C_{22}H_{20}O_4$ (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}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 (CH_2Cl_2/AcOEt 10:1) and crystallization from EtOH/CH_2Cl_2: **IIb** (183 mg, 86%). Orange solid. R_f (CH_2Cl_2/AcOEt 10:1) 0.78. ^{1}H-NMR: 1.43 (*t*, 2 Me); 4.04 (*q*, 2 CH_2O); 4.66 (*t*, 4 HCp); 5.10 (*t*, 4 H, 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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Disubstituted Ruthenocene-containing† Thermotropic Liquid Crystals: A Novel Family of Metallomesogens

Robert Deschenaux* and Julio Santiago
Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2000 Neuchâtel, Switzerland

The synthesis and mesomorphic behaviour of the first family of 1,1′-disubstituted ruthenocene-containing liquid crystals are reported.

Keywords: *Metallomesogen*; *Liquid crystal*; *Thermotropic*

Intense research activity has been devoted to metallomesogens.[1] The search for original structures possessing unique properties has been the main motivation for these studies. However, little attention has been focussed on metallocene-containing liquid crystals. The few known examples are derived from the ferrocene unit, the derivatization of which leads to thermotropic monosubstituted[2] and 1,1′-disubstituted[3] compounds. The monosubstituted ferrocenes exhibited only nematic mesophases.[2] However, the 1,1′-disubstitution led to smectic C[3a,d] and nematic[3e] or smectic A[3e] liquid crystals. The stability of the mesophases strongly depended on the structures of the compounds. In some cases,[3b,c] the textures could not be identified. Recently, we prepared the first 1,3-disubstituted ferrocene-containing liquid crystals and demonstrated the strong influence of structural isomerism on the mesogenic properties.[4] While the 1,1′-disubstituted ferrocenes indeed exhibited either monotropic nematic or non-mesogenic behaviour, their 1,3-isomeric analogues, owing to their highly anisometric structure, gave rise to large enantiotropic nematic mesophases.

To investigate further and rationalize the capability of metallocenes for forming thermotropic materials, the design and study of new structures is of prime importance. We report herein the synthesis and mesomorphic behaviour of ruthenocenes substituted in the 1,1′ positions. To our knowledge, ruthenocene-containing thermotropic liquid crystals have not been described previously.

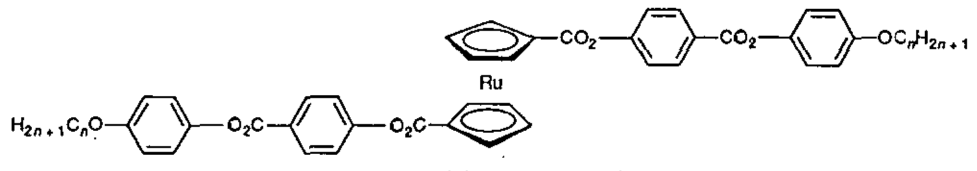
Compounds **1a–f** were prepared by esterification of 1,1′-ruthenocene diacid chloride (by an analogous method to that of 1,1′-ferrocene diacid chloride[5]) with the appropriate phenol derivative.[6] The syntheses were performed in CH_2Cl_2, under reflux, in the presence of triethylamine and catalytic amounts of pyrrolidinopyridine. Purification by column chromatography (silica gel, CH_2Cl_2–AcOEt 50 : 1) and crystallization from EtOH–CH_2Cl_2 afforded the pure compounds, as pale-yellow solids (50–55% yield). The structures were confirmed by ^1H NMR spectroscopy and elemental analyses. The mesomorphic properties were investigated by a combination of differential scanning calorimetry (DSC) and polarized optical microscopy. Reproducible thermograms were obtained except for some crystal-to-crystal transitions which disappeared after the first heating–cooling cycle. These modifications will be discussed in the subsequent full report. The main transition temperatures and enthalpy changes are summarized in Table 1.

Table 1 Phase-transition temperatures and enthalpy changes of ruthenocene derivatives 1a–f

compound	transition[a]	T/°C	ΔH^b/kJ mol^{-1}
1a	C→I	173	68.4
	(I→S$_A$)[c]	(161)	*d*
1b	C→I	169	68.0
	(I→S$_A$)[c]	(164)	(8.3)
1c	C→S$_A$	167	*d*
	S$_A$→I	169[e]	*d*
1d	C→S$_A$	166	*d*
	S$_A$→I	170	*d*
1e	C→S$_A$	165	45.5
	S$_A$→I	173	11.0
1f	C→S$_A$	161	51.8
	S$_A$→I	174	12.4

[a] Observed on a Zeiss Axioscop polarizing microscope equipped with a Linkam THMS 600 variable temperature stage. [b] Measured on a Mettler DSC-30 at a rate of 10 °C min^{-1} under a flow of nitrogen. [c] Monotropic transition. [d] Not measurable owing to peak overlap. [e] Observed by means of polarized-light microscopy only.

When heated, compounds **1a** and **b** melted directly into an isotropic liquid. As expected, the melting point decreased as the number of carbon atoms in the alkyl chain increased. When they were cooled from the isotropic state, they both gave rise to a monotropic smectic A phase. More interesting mesomorphic properties resulted for **1c–f**. Indeed, these latter compounds had an enantiotropic smectic A phase. The anisotropic domain was narrow for **1c** (2 °C) and **1d** (4 °C), but broadened rapidly for **1c** (8 °C) and **1f** (13 °C). In all



1a n = 8, **b** n = 9, **c** n = 10
d n = 11, **e** n = 12, **f** n = 14

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† Ruthenocene = bis(η-cyclopentadienyl)ruthenium(II).

cases, the smectic A phases could be identified from the observation of both homeotropic and focal-conic textures.[7]

Comparison of the mesogenic properties of **1a–f** with those of the analogous ferrocenes[6] shows that both series give rise to smectic A mesophases. The ruthenocene derivatives melt at higher temperatures (*ca.* 10 °C) than the ferrocene analogues. On the other hand, the clearing points appear in both families at similar temperatures. Consequently, the anisotropic domains of the ruthenocene derivatives are shorter than those of the corresponding ferrocenes. However, this tendency attenuates as the alkyl chain length increases. In conclusion, we have demonstrated that the ruthenocene framework is a valuable organometallic unit for the design of stable metallomesogens.

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Unsymmetrically 1,1'-Disubstituted Ferrocene-containing Thermotropic Liquid Crystals.

Robert Deschenaux,* Mafalda Rama, and Julio Santiago.

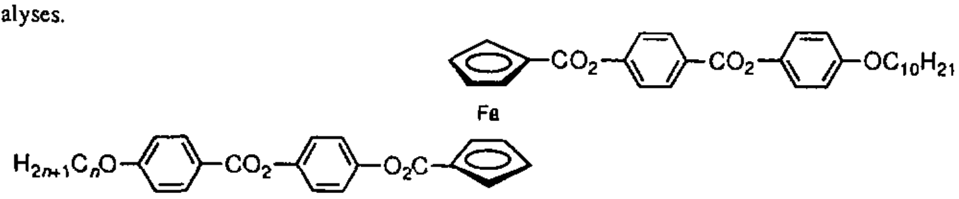
Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2000 Neuchâtel, Switzerland.

Abstract: The synthesis and mesomorphic properties of the first family of unsymmetrically 1,1'-disubstituted ferrocene-containing liquid crystals are reported.

Metallocene-containing liquid crystals have recently been shown to be a valuable class of metallomesogens. Indeed, we[1], and others[2], described the first 1,1'-disubstituted ferrocene-containing liquid crystals which exhibited broad nematic and/or smectic A mesophases. Extension of our investigations to other metallocenes led to the first 1,1'-disubstituted ruthenocene-containing liquid crystals[3]. These latter compounds, and their ferrocene analogues[1], showed similar mesogenic properties. Remarkable mesomorphic behaviour arose from ferrocene substituted in the 1,3-positions[4] as large enantiotropic nematic and/or smectic C phases were observed in each case. Thermotropic liquid crystals exhibiting smectic C phases are of interest for the development of electro-optical devices[5].

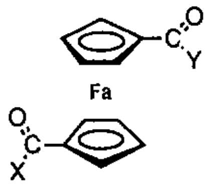
All disubstituted thermotropic metallocene derivatives studied thus far are symmetrically derivatized. Therefore, we thought that a non-symmetrical structure would be of interest to investigate further the *structure-mesogenic properties* relationship.

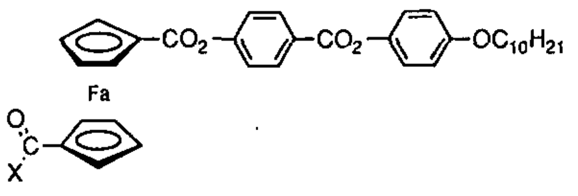
We describe herein the synthesis and mesomorphic behaviour of compounds **1a-f**, which constitute the first family of unsymmetrically disubstituted ferrocene-containing liquid crystals. The structures of all new compounds, i.e. **1a-f**, **2c,d** and **4a-c**, were confirmed by ^{1}H-NMR spectroscopy and elemental analyses.



1 a: n=11, b: n=12, c: n=13
d: n=14, e: n=15, f: n=16

Ferrocene-1,1'-dicarboxylic acid, **2a**, was converted into the diacid chloride, **2b**, following a literature procedure[6]. Treatment of **2b** with benzylalcohol in CH_2Cl_2, at reflux, in the presence of Et_3N gave, after purification by column chromatography (silicagel, CH_2Cl_2/AcOEt/AcOH 8:2:0.1), the monoprotected intermediate **2c** (51%, m.p. = 146-148°C). The monoacid **2c** was transformed into the acid chloride **2d** (97%, m.p. = 68-69°C) by reaction with oxalylchloride (CH_2Cl_2, Et_3N, reflux). Esterification of **2d** with 4-(decyloxy)phenyl 4-hydroxybenzoate[1], **3**, (CH_2Cl_2, Et_3N, reflux) led to **4a** (56%, m.p.=107-109°C). Removal of the benzyl protecting group under standard reaction conditions (EtOH/CH_2Cl_2, H_2/Pd-C) gave **4b** (83%, m.p. = 174-177°C), which was subsequently transformed into the acid chloride **4c** (96%, m.p. = 108-111°C), applying the procedure used for the preparation of **2d**. Finally, condensation of **4c** with 4-hydroxyphenyl 4-(alkyloxy)benzoate[1], **5**, (*n* = 11-16) (CH_2Cl_2, Et_3N, reflux) gave the targeted molecules **1a-f** (65-70%), as orange solids[7].

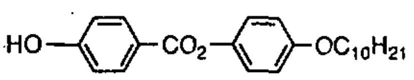




2 a: X=Y=OH
b: X=Y=Cl
c: X=OBn, Y=OH
d: X=OBn, Y=Cl

4 a: X=OBn
b: X=OH
c: X=Cl

Abbreviation: Bn = benzyl



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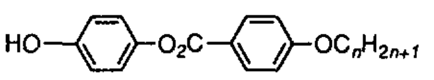

5 *n*=11-16

The thermal properties of **1a-f** were investigated by a combination of differential scanning calorimetry (DSC) and polarized optical microscopy. The transition temperatures and enthalpy changes are reported in the Table. All complexes presented smectogenic properties. Ferrocene derivative **1a** exhibited only an enantiotropic smectic A phase. Compound **1b** gave an enantiotropic smectic A phase, and a monotropic smectic C one. Further increase of the alkyl chain length led to enantiotropic smectic C and smectic A phases and to broad anisotropic domains, as shown by **1d** (17°C), **1e** (19°C) and **1f** (21°C). However, the smectic C range increased (7°C for **1d**, 13°C for **1e** and 16°C for **1f**), and, inversely, the smectic A one attenuated (10°C for **1d**, 6°C for **1e** and 5°C for **1f**).

Table. Phase-transition temperatures and enthalpy changes of the ferrocene derivatives **1a-f**.

Compound	*n*	Transition[a]	T/°C	ΔH^b/kJ·mol^{-1}
1a	11	C-S_A	144	41.0
		SA-I	149	9.6
1b	12	C-S_A	143	42.0
		(S_A-S_C)[c,d]	(138)	
		S_A-I	150	9.9
1c	13	C-S_C	140	[e]
		S_C-S_A[d]	144	[e]
		S_A-I	151	10.5
1d	14	C-S_C	135	35.9
		S_C-S_A[d]	142	
		S_A-I	152	11.0
1e	15	C-S_C	132	37.7
		S_C-S_A[d]	145	
		S_A-I	151	11.0
1f	16	C-S_C	132	38.7
		S_C-S_A[d]	148	
		S_A-I	153	11.6

[a] Observed on a Zeiss Axioscop polarizing microscope equipped with a Linkam THMS 600 variable temperature stage; C: crystal, N: nematic, S_A: smectic A, S_C: smectic C, I: isotropic liquid. [b] Measured on a Mettler DSC-30 at a rate of 10°C·min^{-1} under a flow of nitrogen. [c] Monotropic transition. [d] Observed by means of polarized optical microscopy. [e] Not measurable owing to peak overlap.

The results reported above demonstrate that introduction of a dissymmetry had two effects on the thermal properties. Firstly, in comparison with the ferrocene derivatives symmetrically substituted in the 1,1'-positions[1], a depression of the melting point was observed. Secondly, ferrocene-containing liquid crystals which exhibited smectic C and smectic A phases were obtained for the first time. In conclusion, fine tuning of the mesomorphic properties for 1,1'-disubstituted ferrocene-containing liquid crystals has become feasible.

Acknowledgments: We thank the Swiss National Science Foundation for financial support.

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7. Elemental analytical data of ferrocene derivatives **1a-f**.
   1a: anal. calc. for $C_{59}H_{68}O_{10}Fe$ (993.04): C 71.36, H 6.90; found: C 71.31, H 6.93.
   1b: anal. calc. for $C_{60}H_{70}O_{10}Fe$ (1007.07): C 71.56, H 7.01; found: C 71.45, H 7.12.
   1c: anal. calc. for $C_{61}H_{72}O_{10}Fe$ (1021.09): C 71.75, H 7.11; found: C 71.75, H 7.19.
   1d: anal. calc. for $C_{62}H_{74}O_{10}Fe$ (1035.12): C 71.94, H 7.21; found: C 71.88, H 7.17.
   1e: anal. calc. for $C_{63}H_{76}O_{10}Fe$ (1049.15): C 72.13, H 7.30; found: C 71.72, H 7.35.
   1f: anal. calc. for $C_{64}H_{78}O_{10}Fe$ (1063.18): C 72.30, H 7.39; found: C 72.26, H 7.43.

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1,3-Disubstituted Ferrocene-containing Thermotropic Liquid Crystals of Form $(\eta^5\text{-}C_5H_5)Fe[(\eta^5\text{-}C_5H_3)\text{-}1,3\text{-}(CO_2C_6H_4CO_2C_6H_4OC_nH_{2n+1})_2]$

Robert Deschenaux,[*a] **Julio Santiago,**[a] **Daniel Guillon**[b] **and Benoît Heinrich**[b]
[a] *Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2000 Neuchâtel, Switzerland*
[b] *Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, 67 rue du Loess, 67037 Strasbourg Cedex, France*

The title compounds have been synthesized and their liquid-crystal properties investigated. The reported ferrocene derivatives exhibited enantiotropic nematic and/or smectic A phases associated with broad anisotropic domains. The molecular arrangement within the smectic A phases was studied by X-ray diffraction. The experimental data, compared to the values obtained from CPK models, suggested a monolayer molecular organization with a pronounced chain disorganization for the medium- and long-chain derivatives.

The mesomorphic properties of ferrocene-containing thermotropic liquid crystals have recently been reviewed.[1] Among the structures reported so far,[1] 1,3-disubstituted ferrocene-containing liquid crystals[2] are of particular interest. Indeed, 1,3-substitution led to thermotropic materials which exhibited remarkable liquid-crystalline properties compared with those obtained for the 1,1′- and 1,2-isomeric analogues: the 1,3-disubstituted ferrocene derivatives showed enantiotropic nematic and/or smectic C phases,[2] while their 1,1′-isomeric analogues (series I in ref. 3) gave only monotropic nematic phases (for the short-chain derivatives) and their 1,2-isomeric analogues (structure 18 in ref. 1) were found to be non-mesomorphic.

The origin of the strong liquid-crystalline character resulting from 1,3-disubstitution can be explained on the basis of structural considerations. First, the two substituents, located on each side of the cyclopentadienyl ring, are disposed in a coplanar arrangement. Such a situation, provided that the rigid rod is sufficiently long, can thwart the unfavourable steric effect of the bulky ferrocene core, which strongly decreases the mesomorphic behaviour (with respect to the ferrocene-free material) when incorporated into a mesogenic structure. The tendency of the ferrocene unit in decreasing the liquid-crystalline properties, was also clearly established in the case of 1,1′-disubstituted ferrocene derivatives.[4] Secondly, the X-ray crystal structure determined for one derivative[2a] revealed a highly anisotropic structure for the 1,3-disubstituted ferrocene derivatives, so allowing favourable intermolecular attractions.

More information is required to understand fully the structure–mesomorphic properties relationship for the 1,3-disubstituted ferrocene derivatives, particularly concerning their supramolecular organization in liquid-crystalline states. Therefore, to explore further the capability of such structures for forming liquid-crystalline materials, we describe the preparation, mesomorphic properties and X-ray diffraction studies of the new ferrocene derivatives I. These compounds differ from those previously reported[2] by the orientation of the external ester functions.

Results and Discussion

Syntheses

Ferrocene derivatives I were prepared by reaction of the ferrocene 1,3-diacid chloride[5] with the 4-alkoxyphenyl 4-hydroxybenzoates[3] (n = 5–8, 10, 12, 14, 16, 18) in dry CH_2Cl_2, at reflux, in the presence of Et_3N. Purification by column chromatography (Silica gel; CH_2Cl_2–AcOEt, 50:1 v/v) and crystallization from CH_2Cl_2–EtOH gave the desired compounds in 70% yield. The structures were confirmed by ^1H NMR spectroscopy and elemental analysis.

Mesomorphic Properties

The transition temperatures and enthalpy changes were determined by differential scanning calorimetry (DSC) and are reported in Table 1. The mesophases were identified by a combination of thermal polarized optical microscopy and X-ray diffraction. The phase diagram of compounds I is illustrated in Fig. 1.

All ferrocene derivatives I exhibited a strong liquid-crystalline character. The first member of the series, I (n = 5), showed an enantiotropic nematic phase associated with a broad liquid-crystal range (62 °C). On cooling from the isotropic state, a monotropic smectic A phase formed after the nematic phase. Owing to the high clearing temperature, slight decomposition was detected in the isotropic liquid. The ferrocene derivatives I (n = 6) and I (n = 7) exhibited two

Table 1 Phase-transition temperatures/°C[a] and enthalpy changes/kJ mol^{-1} of ferrocene derivatives I

n	C–S_A	S_C–S_A	C–N	S_A–N	S_A–I	N–I
5	—	—	186	(178)[b,c]	—	248
			32.6			2.6
6	191	—	—	219[c]	—	239
	47.1					3.2
7	190	—	—	228	—	233
	41.3			1.0		3.4
8	190	—	—	—	228	—
	45.0				7.4	
10	185	—	—	—	227	—
	44.9				10.5	
12	178	—	—	—	223	—
	43.3				11.6	
14	174	—	—	—	219	—
	43.8				12.4	
16	171	—	—	—	213	—
	40.4				13.7	
18	168	(163)[b,c]	—	—	208	—
	43.2				13.0	

[a] C = crystal; N = nematic phase; S_A = smectic A phase; S_C = smectic C phase; I = isotropic liquid. [b] Monotropic transition. [c] Observed by polarized optical microscopy only.

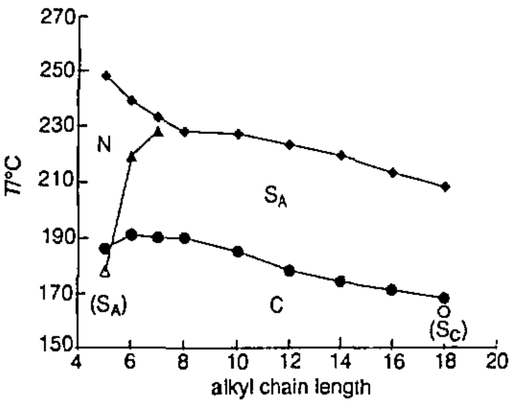


Fig. 1 Phase diagram of ferrocenes I. ●, Melting point; ◆, clearing point; ▲, smectic A–nematic transition; ○, smectic A–smectic C transition; △, nematic–smectic A transition.

enantiotropic mesophases, a smectic A phase and a nematic phase. Compounds I ($n=8$, 10, 12, 14, 16) gave rise to enantiotropic smectic A phases with large anisotropic domains. Finally, the last member of the family, I ($n=18$), showed two mesophases, a broad enantiotropic smectic A phase and a monotropic smectic C phase.

Typical textures were observed by means of polarized optical microscopy. When I ($n=5$–7) were cooled from the isotropic liquid, the nematic phases appeared either in the *schlieren* texture or in the homeotropic one. In the latter case, bright flashes were observed when the preparation was touched with a spatula. The nematic to smectic A transition was clearly detected by polarized optical microscopy and in one case, *i.e.* for I ($n=7$), also by DSC. When ferrocene derivatives I ($n=8$, 10, 12, 14, 16, 18) were cooled from the isotropic liquid, focal–conic fan textures and, in several cases, homeotropic zones, both characteristic of the smectic A phases, were observed. For I ($n=18$), the smectic A to smectic C transition was identified by the formation of a *schlieren* texture from the previous homeotropic zones, and by the transformation of the focal–conic fan texture (Plate 1) into the broken focal–conic fan texture (Plate 2).

To strengthen the interpretation given from the observations obtained by polarized optical microscopy, and to gain information about the molecular organization within the liquid-crystalline states, the smectic phases of the ferrocene derivatives I ($n=6$, 8, 10, 18) were analysed by X-ray diffraction. The nature of the smectic A phases was thus clearly confirmed. Each of these compounds gave similar data, *i.e.* X-ray patterns presenting a sharp ring in the low-angle region and a diffuse one in the wide-angle region. The monotropic smectic C phase of I ($n=18$), which crystallized during experiment owing to its short existence range (S_A–S_C, 163 °C; S_C–C, 158 °C), could not be characterized by X-ray diffraction.

The layer spacing, d, obtained by X-ray diffraction, the molecular length, L, measured from CPK models, and the corresponding d/L ratio are reported in Table 2. For the ferrocene derivatives I ($n=6$) and I ($n=8$), the d/L ratio ranged between 0.9 and 1.0 and indicated a monolayer arrangement of the molecular units in the smectic A phases. On increasing the alkyl chain length, *i.e.* for compounds I ($n=10$) and I ($n=18$), the d/L ratio decreased to 0.78 [I ($n=18$)]. The discrepancy between the layer spacing and the molecular length can be attributed to the pronounced disorganized state of the long alkyl chains which can fold easily owing to the lateral bulkiness of the ferrocene moiety. However, we cannot exclude that the low d/L values may also originate from intensive orientational fluctuations or from pre-existing smectic C correlations in the smectic A phase. These results are in agreement with literature data reported for other metallomesogens.[6]

Table 2 Layer spacing of ferrocene derivatives I

n	d^a/Å	T/°C	L^b/Å	d/L
6	42.1	200	46	0.92
8	50.1	200	51	0.98
10	49.6	200	57	0.87
18	59.9	190	77	0.78

[a] From X-ray diffraction. [b] From CPK models in the fully extended conformation.

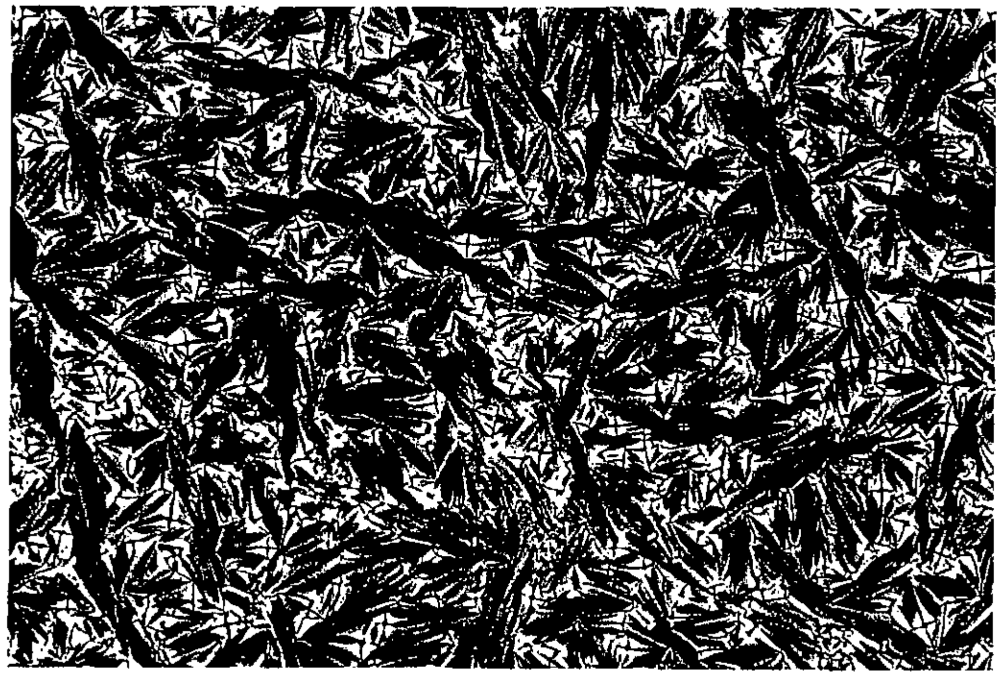


Plate 1 Thermal optical micrograph of the focal–conic fan texture displayed by I($n=18$) in the smectic A phase upon cooling from the isotropic liquid to 204.7 °C

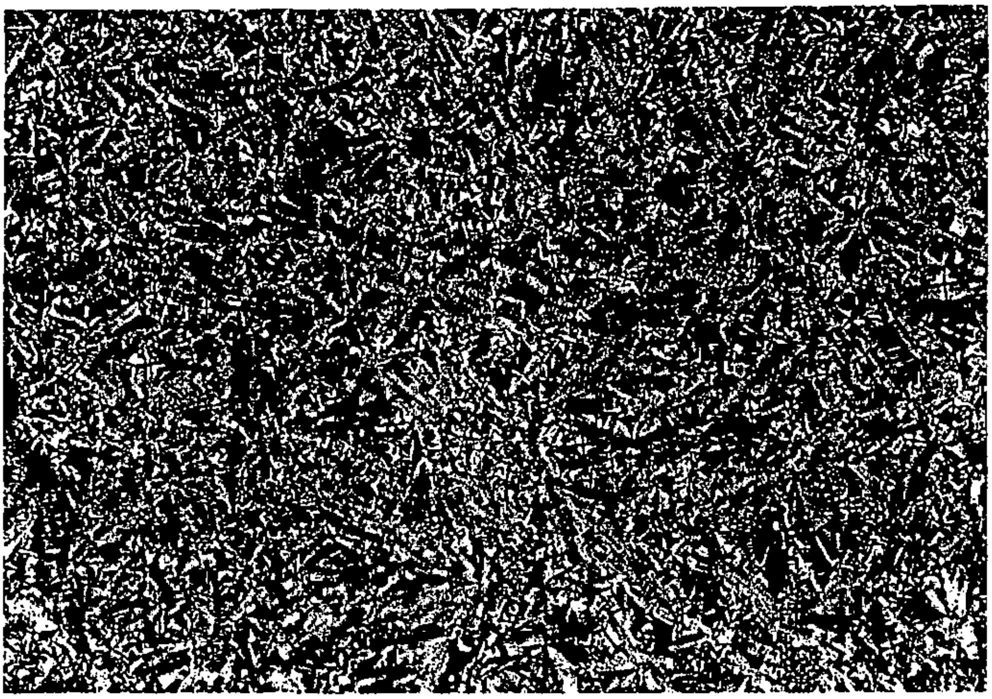
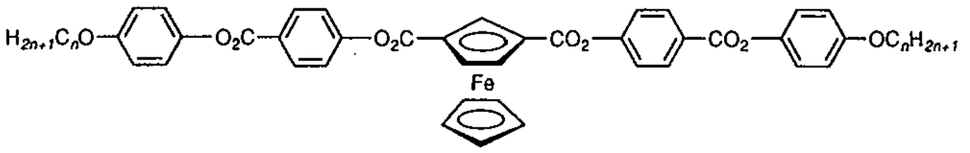


Plate 2 Thermal optical micrograph of the broken focal-conic fan texture displayed by I($n=18$) in the smectic C phase upon cooling from the smectic A phase (see Plate 1) to 154.8 °C



I (n=5-8,10,12,14,16,18)

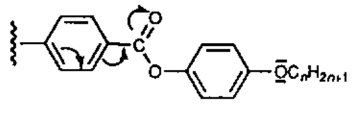
The strong liquid-crystal character shown by ferrocene derivatives I can be interpreted on the basis of structural features. In fact, in a previous report,[2a] by comparing the thermal properties of two families of ferrocene derivatives substituted in the 1,3-positions, we demonstrated that mesomorphism develops from an l/l' ratio$>$5–7 (l=length of the rigid rod; l'=distance between the two cyclopentadienyl rings of the ferrocene unit). In the present study, the length l of the rigid segment in I was found to be *ca.* 27.5 Å (in the most extended conformation) from CPK molecular models. The depth l' of the ferrocene core being *ca.* 3.3 Å,[7] an l/l' ratio of 8.3–8.4 is obtained. Therefore, this value confirms that ferrocene derivatives I possess the required structural characteristics for exhibiting pronounced mesomorphism.

The ferrocene derivatives I and those reported in ref. 2 differ in the orientation of the external ester functions. It is interesting to point out that, whereas compounds I exhibit smectic A and nematic phases, their isomeric structures gave smectic C and nematic phases.[2] These observations, which show the strong influence of the organic substituents on the nature and stability of the mesophases, can be explained in terms of electronic effects. Owing to the C_S symmetry of compounds I (and of their isomeric analogues[2]), local effects can be considered.

The organic fragments 1 and 2 were used for constructing ferrocene derivatives I and their isomeric analogues,[2] respectively. In structure 1, electron delocalization takes place in the interior of the organic fragment. In structure 2, electron delocalization occurs in the opposite direction, from the O atom of the alkoxy chain to the ester function. Consequently, (1) electron delocalization is more extended in 2 than in 1, and (2) the O atom of the ether group is more polar in 2 than in 1.

The electron delocalization presented above which leads to different intermolecular interactions for each organic fragment is, most likely, at the origin of the different mesomorphic behaviour observed between the two isomeric series. Such results, which were also observed for isomeric 1,1′-disubstituted ferrocene derivatives,[3] are in agreement with literature data reported for wholly organic liquid crystals.[8]

Finally, the liquid-crystal ranges reported herein, and those exhibited by the first family of 1,3-disubstituted ferrocene derivatives,[2] represent the largest anisotropic domains observed to date in case of ferrocene-containing thermotropic liquid crystals.



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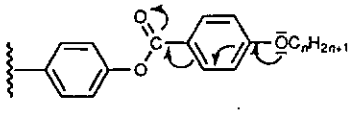

2

Conclusions

The synthesis and characterization of the second family of homologous 1,3-disubstituted ferrocene-containing thermotropic liquid crystals are described. Ferrocene derivatives I exhibited broad enantiotropic smectic A and/or nematic phases. X-Ray investigations suggested a molecular organization into monolayers with an important chain disorganization for the medium and long-chain derivatives ($n=10$, 18) within the smectic A phases. The present results, and those recently described,[2] clearly show that 1,3-disubstituted ferrocene-containing thermotropic liquid crystals, owing to their high thermal stability and pronounced mesomorphic character, are valuable metallomesogens.[9] Furthermore, the electrochemical characteristics of the ferrocene unit,[7] which can be reversibly oxidized into the ferrocenium species, combined with the mesomorphic properties of the 1,3-disubstituted ferrocene derivatives, make such compounds interesting candidates for elaborating liquid-crystalline materials from electroactive molecular units.

Experimental

General

Ferrocene-1,3-diacid chloride,[5] and the 4-alkoxyphenyl 4-hydroxybenzoates[3] were prepared as in the literature. Column chromatography (CC) used Silicagel 60 (0.063–0.200 mm, Merck) and TLC used Silicagel plates (Merck). Transition temperatures and enthalpies were determined with a differential scanning calorimeter (Mettler DSC 30) connected to a Mettler-TA 3000 system, rate 10 °C min^{-1} under N_2. Optical studies were conducted using a Zeiss-Axioscop polarizing microscope equipped with a Linkam-THMS-600 variable temperature stage under N_2. A Bruker AMX 400 spectrometer at 400.13 MHz was used for ^{1}H NMR spectra. X-Ray diffraction patterns of powder samples in Lindemann capillaries were recorded photographically at several temperatures using a Guinier focusing camera equipped with a bent quartz monochromator (Cu-Kα_1 radiation from a Philips PW-1009 generator) and an electrical oven. Elemental analyses were conducted by Ciba SA, Marly, Switzerland.

Syntheses

The general synthetic procedure of bis[4-(4-alkoxyphenoxycarbonyl)phenyl] ferrocene-1,3-dicarboxylates I is exemplified by the preparation of bis[4-(4-pentyloxyphenoxycarbonyl)phenyl] ferrocene-1,3-dicarboxylate I ($n=5$). A mixture of ferrocene-1,3-diacid chloride (0.1 g, 0.32 mmol), 4-pentyloxyphenyl 4-hydroxybenzoate (0.194 g, 0.65 mmol), Et_3N (66 mg, 0.65 mmol), a catalytic amount of 4-pyrrolidinopyridine and CH_2Cl_2 (10 cm^3) was heated at reflux for 3 h. The solution was cooled to room temperature and evaporated. Purification of the resulting residue by CC (Silica gel, CH_2Cl_2–AcOEt 50:1, v/v) and crystallization from CH_2Cl_2–EtOH gave the desired compound in 70% yield. ^{1}H NMR ($CDCl_3$, TMS) δ_H: 0.94 (6 H, t, $2\times CH_3$), 1.42 [8 H, m, $2\times(CH_2)_2$], 1.80 (4 H, m, $2\times CH_2CH_2O$), 3.97 (4 H, t, $2\times CH_2CH_2O$), 4.48 (5 H, s, Cp), 5.28 (2 H, d, Cp), 5.80 (1 H, t, Cp), 6.94 (4 H, d, 2 × 2H-arom.), 7.13 (4 H, d, 2 × 2H-arom.), 7.35 (4 H, d, 2 × 2H-arom.), 8.29 (4 H, d, 2 × 2H-arom.). IR (KBr) ν_{max}/cm^{-1}: 3132, 2933, 2869, 1733, 1604, 1467, 1415, 1120, 1103, 869, 834, 814. Found: C, 68.76, H, 5.59; calc. for $C_{48}H_{46}O_{10}Fe$ (838.74): C, 68.74, H, 5.53%.

Table 3 Elemental analytical data of ferrocene derivatives I (calculated values in parentheses)

n	C(%)	H(%)
5	68.76(68.74)	5.59(5.53)
6	69.06(69.29)	5.58(5.81)
7	69.87(69.80)	6.14(6.08)
8	70.27(70.28)	6.42(6.34)
10	70.86(71.16)	6.87(6.80)
12	71.84(71.94)	7.30(7.21)
14	72.55(72.65)	7.39(7.57)
16	73.22(73.28)	7.78(7.91)
18	73.87(73.86)	8.06(8.21)

Ferrocene derivatives I ($n=6$–8, 10, 12, 14, 16, 18) gave analytical data which were in agreement with their structure (Table 3).

One of the authors (R.D.) acknowledges Ciba S.A, Marly, Switzerland, for the elemental analyses, Chemische Betriebe Pluto/Veba Oel AG, Germany, for a generous gift of acetyl ferrocene used to prepare ferrocene-1,3-dicarboxylic acid, and the Swiss National Science Foundation for financial support.

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Unsymmetrically-1,3-Disubstituted Ferrocene-containing Thermotropic Liquid Crystals: A New Family of Chiral Metallomesogens.

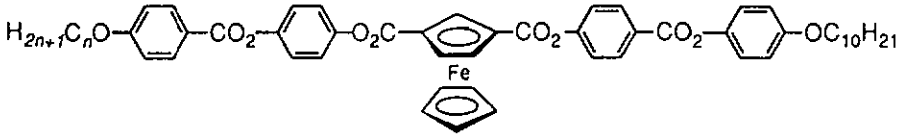
Robert Deschenaux* and Julio Santiago

Université de Neuchâtel, Institut de Chimie, Av. de Bellevaux 51, 2000 Neuchâtel, Switzerland

Abstract: The synthesis and mesomorphic properties of the first family of unsymmetrically-1,3-disubstituted ferrocene-containing thermotropic liquid crystals are presented. The title compounds exhibited enantiotropic liquid crystalline phases (nematic and/or smectic A and smectic C phases) associated with large anisotropic domains.

Despite the increasing interest devoted to chirality in liquid crystals,[1] little attention has been focused on optically active metallomesogens: racemic mesogenic butadiene iron-tricarbonyl derivatives[2] (nematic and/or smectic A phases), optically active palladium-containing liquid crystals[3] (diverse mesophase sequences from the combination of cholesteric, smectic A and chiral smectic C phases) and monosubstituted ferrocene derivatives containing the cholesteryl moiety[4] (mesophases not identified) were described. In several cases, ferroelectric properties were investigated.[3b-d]

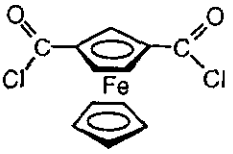
Recently, we reported the first symmetrically 1,3-disubstituted ferrocene-containing thermotropic liquid crystals.[5] These compounds presented interesting liquid crystals properties. Indeed, enantiotropic mesophases associated with broad anisotropic ranges were obtained. These mesomorphic properties prompted us to consider liquid crystalline ferrocene derivatives unsymmetrically substituted on the 1,3-positions as a new family of metallomesogens. Such compounds, which lack symmetry, are chiral, and, consequently, of interest with the view to developing new electro-optical liquid crystal devices.[6]



1 a: *n*=10, b: *n*=11, c: *n*=12
d: *n*=13, e: *n*=14, f: *n*=16, g: *n*=18

We describe, herein, the syntheses and mesomorphic properties of compounds 1a-g, which constitute the first family of unsymmetrically-1,3-disubstituted ferrocene-containing thermotropic liquid crystals.[7] The structures of all new compounds, i.e. 1a-g and 4a,b, were confirmed by ^{1}H-NMR spectroscopy and elemental analyses.

Ferrocene-1,3-diacid chloride[8] 2 was treated with 4-(decyloxy)phenyl 4-hydroxybenzoate[9] 3 in benzene, at reflux for 3 days, in the presence of pyridine. Purification by column chromatography (silicagel, CH_2Cl_2/AcOEt 10:1 and CH_2Cl_2/AcOEt/ AcOH 10:1:0.1) followed by crystallization (CH_2Cl_2/EtOH) yielded 4a (38%, m.p.=186°C). This latter mono-acid intermediate was converted into the acid chloride 4b (68%) by reaction with oxalyl chloride in CH_2Cl_2, at reflux, in the presence of pyridine. Finally, condensation of 4b with 4-hydroxyphenyl 4-(alkyloxy)benzoates[9] 5 (n=10-14,16,18) (CH_2Cl_2, Et_3N, reflux) gave, after purification by column chromatography (silicagel, CH_2Cl_2/AcOEt 50:1) and crystallization (CH_2Cl_2/EtOH), the targeted compounds 1a-g (70-80%).[10]



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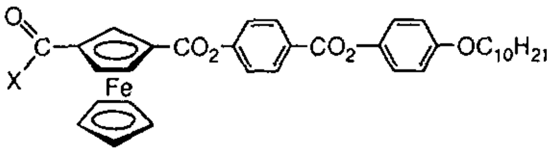
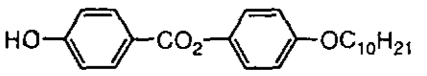
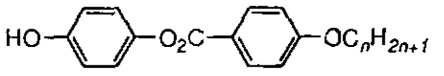


4 **a**: X=OH
b: X=Cl



3



5 *n*=10-14, 16, 18

The thermal properties of 1a-g were investigated by a combination of differential scanning calorimetry and polarized optical microscopy. The transition temperatures and enthalpy changes are reported in Table 1. When heated, the first member of the family, 1a, gave two enantiotropic mesophases, a smectic A phase and a nematic one. On cooling from the isotropic liquid, a monotropic smectic C phase also formed. Compound 1b exhibited three enantiotropic mesophases, two smectic phases (smectic C and smectic A) and a nematic one. Ferrocene derivatives 1c-g presented enantiotropic smectic C and smectic A phases. On increasing the alkyl chain length the smectic C range broadened rapidly (5°C for 1c, 10°C for 1d, 21°C for 1e, 28°C for 1f and 32°C for 1g) and, inversely, the smectic A one shortened (27°C for 1c, 21°C for 1d, 10°C for 1e, 5°C for 1f and 2°C for 1g). It is noteworthy to point out that the derivatization of 2 with substituents 3 and 5 led to liquid crystalline ferrocene derivatives which presented smectic C and smectic A phases, whereas the analogous ferrocene derivatives symmetrically substituted on the 1,3-positions[5] exhibited either a smectic C or a smectic A phase, besides the nematic one.

Table 1.Phase transition temperatures and enthalpy changes of ferrocene derivatives **1a-g** from the second heating-cooling cycle.

Compound	*n*	transition[a]	T/°C	ΔH[b]/kJmol^{-1}
1a	10	C-S_A	177	40.0
		$(S_A\text{-}S_C)^{c,d}$	175	
		S_A-N	205	e
		N-I	210	e
1b	11	C-S_C	176	39.5
		S_C-S_A[d]	178	
		S_A-N	205	e
		N-I	207	e
1c	12	C-S_C	175	41.2
		S_C-S_A[d]	180	
		S_A-I	207	8.3
1d	13	C-S_C	174	41.1
		S_C-S_A[d]	184	
		S_A-I	205	10.2
1e	14	C-S_C	169	33.9
		S_C-S_A[d]	190	
		S_A-I	200	9.0
1f	16	C-S_C	168	35.5
		S_C-S_A[d]	196	
		S_A-I	201	9.8
1g	18	C-S_C	166	37.0
		S_C-S_A[d]	198	
		S_A-I	200	10.9

[a]Observed on a Zeiss Axioscop polarizing microscope equipped with a Linkam THMS 600 variable temperature stage; C: crystal, N: nematic phase, S_A: smectic A phase, S_C: smectic C phase, I: isotropic liquid. [b]Measured on a Mettler DSC-30 at a rate of 10°C.min^{-1} under a flow of nitrogen. [c]Monotropic transition. [d]Observed by means of polarized optical microscopy. [e]Not measurable owing to peak overlap.

The results reported above prove that unsymmetrically 1,3-disubstituted ferrocene-containing thermotropic liquid crystals of structure **1** are valuable metallomesogens. Firstly, enantiotropic phases and broad anisotropic ranges have been observed within the all series. Secondly, the observed smectogenic properties indicate that, in their optically active form, the reported ferrocene derivatives should be interesting candidates for preparing ferroelectric smectic C* materials; furthermore, the smectic A phase could also be used in electro-optical devices by applying the electroclinic effect.[11]

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    1a: anal. calc. for $C_{58}H_{66}O_{10}Fe$ (979.00): C 71.16, H 6.80; found: C 71.32, H 6.93.
    1b: anal. calc. for $C_{59}H_{68}O_{10}Fe$ (993.03): C 71.36, H 6.90; found: C 71.60, H 6.96.
    1c: anal. calc. for $C_{60}H_{70}O_{10}Fe$ (1007.06): C 71.56, H 7.01; found: C 71.85, H 6.97.
    1d: anal. calc. for $C_{61}H_{72}O_{10}Fe$ (1021.08): C 71.75, H 7.11; found: C 71.91, H 7.07.
    1e: anal. calc. for $C_{62}H_{74}O_{10}Fe$ (1035.11): C 71.94, H 7.21; found: C 71.75, H 7.26.
    1f: anal. calc. for $C_{64}H_{78}O_{10}Fe$ (1063.16): C 72.30, H 7.39; found: C 72.15, H 7.34.
    1g: anal. calc. for $C_{66}H_{82}O_{10}Fe$ (1091.22): C 72.65, H 7.57; found: C 72.70, H 7.47.
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