Université de Neuchâtel
Faculté des Sciences

CRISTAUX LIQUIDES THERMOTROPES DU FERROCENE :

ETUDE SYSTEMATIQUE DE L'INFLUENCE DE PARAMETRES STRUCTURAUX SUR LES PROPRIETES MESOMORPHES ET EXTENSION AUX COMPOSES POLYMERIQUES

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par

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Cristaux liquides thermotropes du ferrocène :
Etude systématique de l'influence de paramètres
structuraux sur les propriétés mésomorphes
et extension aux composés polymériques

de Monsieur Jean-Luc Marendaz

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FACULTÉ DES SCIENCES

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

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autorise l'impression de la présente thèse.

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Le doyen :

A. Robert

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Liste des publications

- R. Deschenaux and J.-L. Marendaz, '**Novel 1,1' and 1,3 Disubstituted Ferrocene-containing Thermotropic Liquid Crystals : A Remarkable Isomeric Effect.**' *J. Chem. Soc., Chem. Commun. 1991*, 909.

- R. Deschenaux, J.-L. Marendaz and J. Santiago, '**1,1'-Disubstituted Ferrocene-Containing Thermotropic Liquid Crystals of Structure $[Fe\{(\eta^5-C_5H_4)COOC_6H_4xC_6H_4OC_nH_{2n+1})_2]$ (x = OOC or COO). Influence of the Orientation of the Center Ester Function on the Mesogenic Properties.**' *Helv. Chim. Acta* 76, *1993*, 865.

- R. Deschenaux, I. Kosztics, J.-L. Marendaz and H. Stoeckli-Evans, '**1,3-Disubstituted Ferrocene-Containing Thermotropic Liquid Crystals: Synthesis, Mesomorphic Properties and the Crystal and Molecular Structure.**' *Chimia* 47, *1993*, 206.

Novel 1,1′- and 1,3-Disubstituted Ferrocene-containing Thermotropic Liquid Crystals: A Remarkable Isomeric Effect

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Comparison of results obtained from 1,1′- and 1,3-disubstituted ferrocenes clearly demonstrates the influence of structural isomerism on the mesomorphic properties.

There is currently considerable interest in metallomesogens owing to their unique properties[1] and potential applications[2] in electronic technology. Among all the metal-containing liquid crystals reported thus far, little attention has been focused on thermotropic metallocenes.[3] This is surprising since metallocenes have a high thermal stability and are very soluble in common organic solvents, making their characterization straightforward. In addition, they possess a 3-dimensional structure which offers multiple possibilities of forming derivatives for fine tuning of the mesomorphic properties.

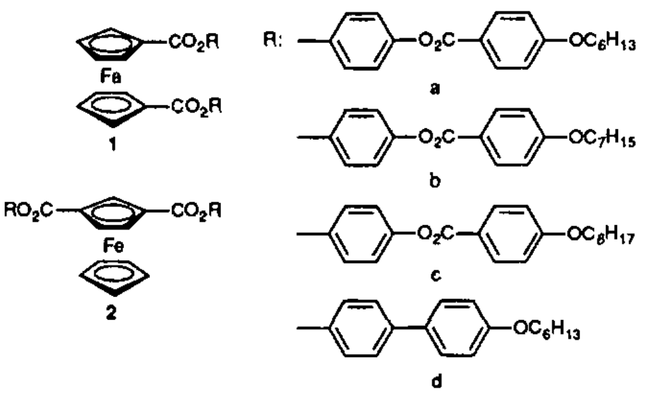
We report herein the preparation and mesogenic behaviour of ferrocenes substituted in the 1,1′- and 1,3-positions. To our knowledge, 1,3-disubstituted ferrocene-containing thermotropic liquid crystals have not previously been described. Compounds **1a–c** and **2a–d** were obtained by condensing either the ferrocene 1,1′-diacid chloride[4] or the ferrocene 1,3-diacid chloride[5] with various phenol derivatives [4-(4′-n-alkoxybenzoyloxy)phenol[6] and 4′-n-hexyloxybiphenyl-4-ol].[7]

The syntheses were performed in CH_2Cl_2 at reflux, in the presence of triethylamine. Crystallization from CH_2Cl_2–MeOH afforded the pure solids in 75–80% yield. The ^1H NMR spectra and microanalyses for all these new compounds are in agreement with the proposed structures. The transition temperatures and enthalpies are presented in Table 1.

Table 1 Transition temperatures of complexes **1** and **2**

Complex	Transition[a]	T/°C	ΔH/kJ mol^{-1} [b]
1a[d]	C → I	172	40.8
	(I → N)[c]	(153)	(3.0)
1b	C → I	169	46.0
1c	C → I	167	63.3
2a[d]	C → N	184	40.5
	N → I	248	4.8
2b[d]	C → N	183	53.5
	N → I	217	4.3
2c[d]	C → N	172	42.1
	N → I	206	3.8
2d[d]	C → N	204	58.5
	N → I	235	3.4

[a] Observed on a Zeiss Axioscopo polarizing microscope equipped with a Linkam THMS 600 variable temperature stage. [b] Measured on a Mettler DSC-30 from the second heating cycle at a rate of 10 °C min^{-1}. [c] Monotropic transition. [d] Nematic droplets were observed near the I → N transition on cooling slowly (5 °C min^{-1}) from the isotropic melt.



None of the 1,1′-disubstituted compounds **1a–c** exhibited liquid crystal properties on heating. They clearly and directly melted into an isotropic liquid. However, a monotropic nematic phase was observed for **1a**. Insufficient supercooling of the isotropic melt probably prevented **1b** and **1c** from forming mesophases.

Remarkable thermotropic properties resulted from the 1,3-isomeric structures. Indeed, ferrocene derivatives **2a–c** not only showed enantiotropic behaviour, but they also gave rise, in each case, to a wide nematic phase: 64 °C (**2a**), 34 °C (**2b**) and 34 °C (**2c**). Compound **2d**,† containing a biphenyl system, also led to a stable enantiotropic nematic phase (31 °C). This demonstrates that the capability of the 1,3-disubstituted structure for forming thermotropic materials could be generalized to a variety of rigid organic moieties.

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† The corresponding 1,1′-isomer[3b] gave a monotropic S_c transition associated with a very narrow anisotropic range (7 °C).

Separatum
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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

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(12.XI.92)

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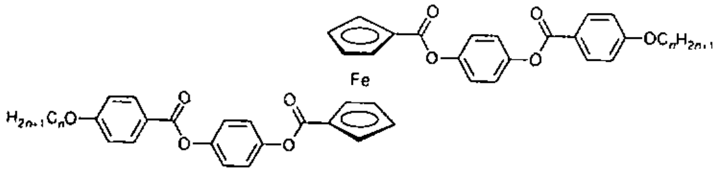
[1]) Part of Ph.D. Thesis of *J.-L. M.* and of *J. S.*

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.

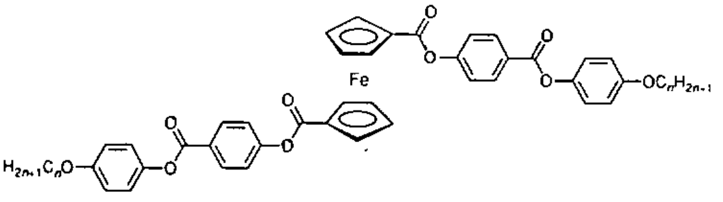
To further investigate the importance of structural parameters on the liquid-crystal behavior, we decided to examine the influence of the functional groups present in the rigid organic part. It was already known, from studies performed on organic liquid crystals, that the nature and the stability of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

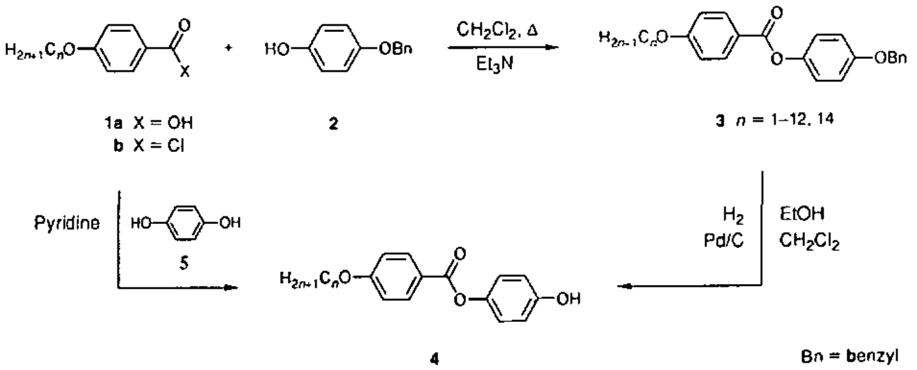


IIb–l,n,p,r

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]

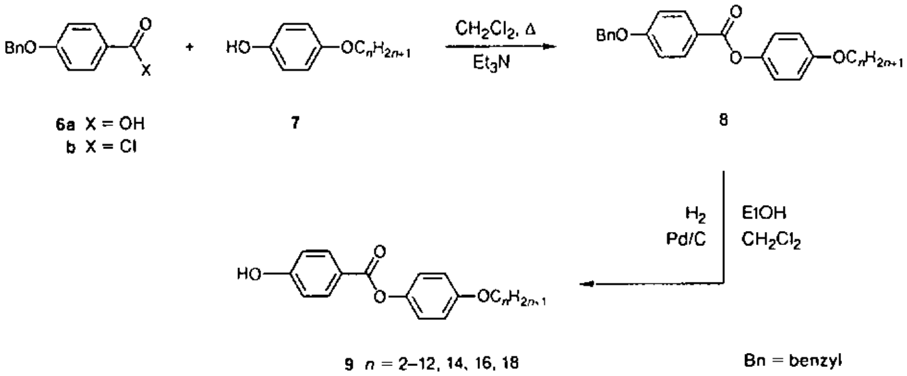


[a] Esters **4** with $n = 1–12, 14$ were prepared following the protection/deprotection route *via* **3**, and esters **4** with $n = 13, 16, 18$ were prepared by the direct route.

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_2Cl_2 under reflux in the presence of Et_3N and catalytic 4-pyrrolidinopyridine gave esters **8** ($n = 2–12$, 14, 16, 18). Removal of the benzyl protecting group (H_2, Pd/C, $EtOH/CH_2Cl_2$) 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 (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*

	n	*T* (*ΔH*) for transitions							
		C_1/C_2b)	C_{1-2}/I	C_{1-2}/S_A	S_A/N	S_A/I	C_{1-2}/N	N/I	Recryst.
IIb	2	–	186 (51.5)	–	–	–	–	177c) (3.1)	155
IIc	3	–	182 (66.3)	–	–	–	–	144c)(d))	141
IId	4	–	164 (55.5)	–	–	–	–	157c) (3.2)	123
IIe	5	–	–	–	–	–	154(d))	156c)	124
IIf	6	151f) (8.6)	167 (51.7)	–	148c)e)	–	–	161c) (4.0)	135
IIg	7	–	165 (68.3)	–	–	154c) (5.9)	–	–	136
IIh	8	–	164 (73.8)	–	–	157c) (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.

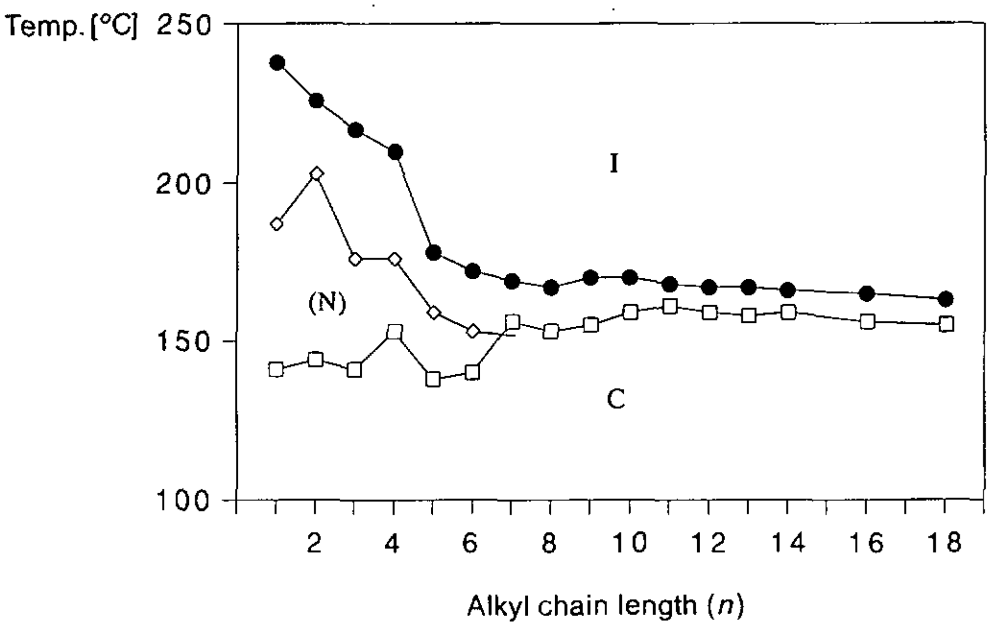


Fig. 1. *Phase diagram of ferrocenes* **I**.
●: Melting point; ◇: isotropic liquid/nematic transition; □: recrystallization.
C = crystal; I = isotropic liquid; N = nematic phase.

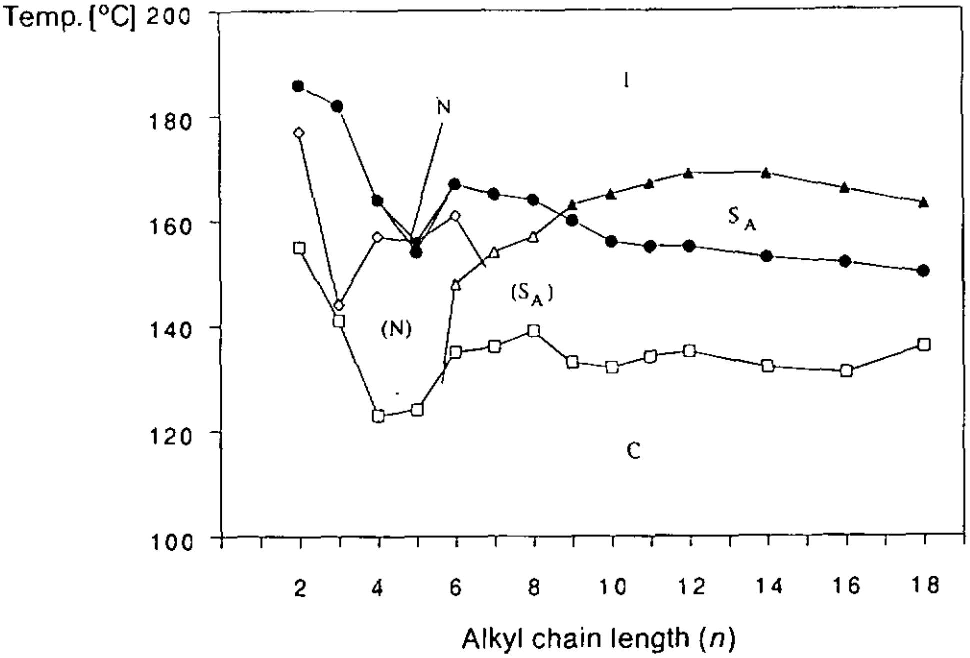


Fig. 2. *Phase diagram of ferrocenes* **II**. ●: Melting point; ◆: nematic/isotropic liquid transition; ▲: smectic-A/isotropic liquid transition; ◇: isotropic liquid/nematic transition; △: isotropic liquid or nematic/smectic-A transition; □: recrystallization. C = crystal; I = isotropic liquid; N = nematic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

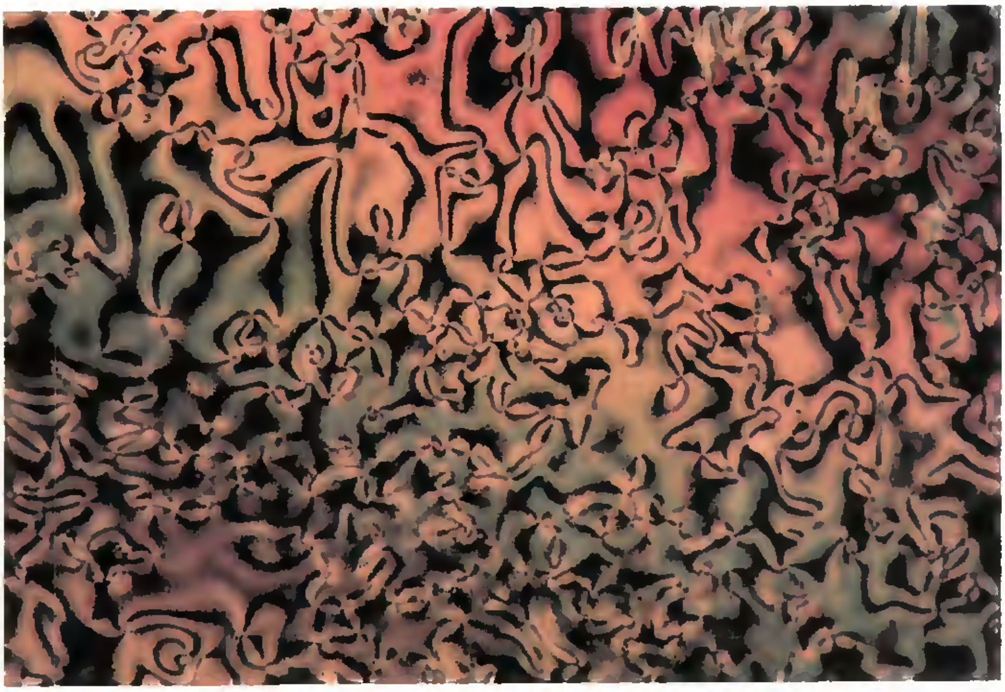
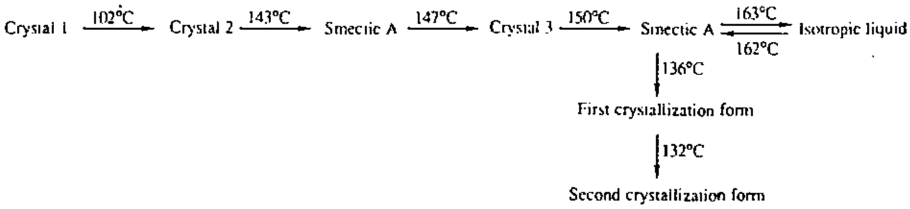


Fig. 3. *Representative thermal polarized optical micrograph of the nematic* schlieren *texture displayed by* **Ic** (*n* = 5) *upon cooling from the isotropic liquid to 159°* (100 ×)

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)

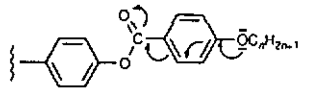


In all cases, the smectic-A phase was identified by means of polarized-light microscopy from the observation of both homeotropic and focal-conic textures. A representative example of a focal-conic texture is given in *Fig. 4*.

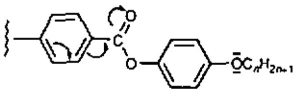
The results reported above clearly demonstrate the strong influence of the central linking ester function on the mesomorphic properties. An explanation of this influence can be attempted on the basis of structural and electronic considerations. By analogy to a 1,1'-disubstituted ferrocene-containing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



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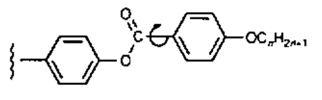
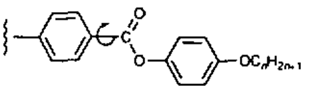


A



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 *Vebo 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. ^{1}H-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°. ^{1}H-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°). ^{1}H-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°. ^1H-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 **Ia** (*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. ^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 **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*, *Ph*CH_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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,3-Disubstituted Ferrocene-Containing Thermotropic Liquid Crystals: Synthesis, Mesomorphic Properties and he Crystal and Molecular Structure

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d Helen Stoeckli-Evans

stract. Two families of 1,3-disubstituted ferrocene derivatives have been synthe-
ed and their liquid-crystal behavior investigated. Compounds of series **I**, (η^5-
H_5)Fe[(η^5-C_5H_3)-1,3-($COOC_6H_4OOCC_6H_4OC_nH_{2n+1})_2$] ($n$ = 1–14, 16, 18), exhibit-
remarkable mesomorphic properties. Indeed, nematic and/or smectic C phases,
ociated with large anisotropic domains, were observed. Derivatives of series **II**, (η^5-
H_5)Fe[(η^5-C_5H_3)-1,3-($COOC_6H_4OC_nH_{2n+1})_2$] (n = 1–9), were found to be non-
sogenic. The crystal and molecular structure of **Ih** (n = 8) was determined by means
X-ray analysis. The crystallographic data confirmed both a highly anisometric
ucture for **Ih** and a compact arrangement of the molecules in the crystal. The present
ults have shown that a critical length/depth ratio of *ca.* 5–7 must be passed for
taining liquid-crystal properties.

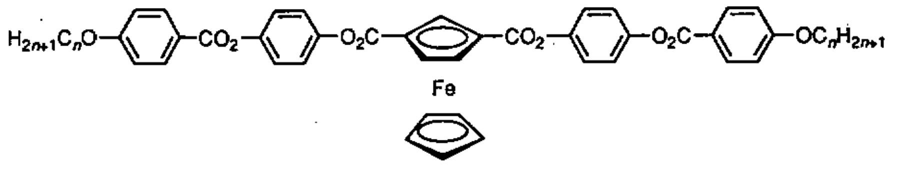
troduction

In the last few years, increasing atten-
n has been paid to 1,1'-disubstituted
rocene-containing liquid crystals [1].
e possibility of studying metallomes-
ens possessing a novel three-dimen-
nal organometallic unit mainly moti-
ted these investigations. However, most
the compounds studied thus far showed
ly limited mesomorphic properties. In-
ed, either monotropic smectic A or C
ases [1a], or narrow enantiotropic smec-
C domains [1d] were obtained. In other
ses, the textures could not be identified
),c].

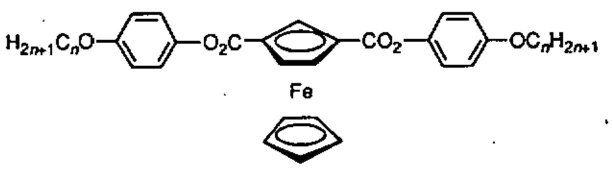
Recently, we [2] and others [1e] reported the first two series of 1,1'-disubstituted ferrocene derivatives which exhibited broad enantiotropic nematic and/or smectic A phases. These results clearly proved that the ferrocene framework is a valuable organometallic unit for forming metallomesogens having stable mesophases, which prompted us to extend our investigations to other metallocenes. This led us to design the first 1,1'-disubstituted ruthenocene-containing liquid crystals [3]. These latter compounds and their ferrocene analogues, series **II** in [2], exhibited similar mesomorphic behavior [2][3] but different electronic spectra and redox potentials [4]. This is of particular interest for the tuning of optical and electrochemical properties in organized molecular assemblies built up from metallomesogen-containing building blocks.

To explore the influence of substitution on the liquid-crystal properties, we have synthesized, for the first time, some ferrocene derivatives substituted in the 1,3-positions [5]. Remarkable mesomorphic behavior resulted from these structures. Indeed, the latter gave rise to large enantiotropic nematic phases, while their 1,1'-isomeric analogues [5], and series **I** in [2], exhibited either monotropic or non-mesogenic properties. Undoubtedly, the 1,3-disubstituted ferrocene derivatives are interesting compounds and warrant special attention. Therefore, following our preliminary investigations [5], we decided to study their *structure-mesomorphic properties* relationship in more depth.

We report herein two series of homologous 1,3-disubstituted ferrocene derivatives which contain either two (series **I**) or one (series **II**) aromatic ring(s) on each side of the substituted cyclopentadienyl nucleus. Comparison of their thermal properties, in addition to information obtained by means of X-ray diffraction for derivative **Ih** (n = 8), allowed us to propose some structural requirements which must be satisfied for designing thermotropic 1,3-disubstituted ferrocene derivatives.



I (n = 1-14,16,18)



II (n = 1-9)

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Part of the Ph.D. Thesis of *J.-L. M.*

Results and Discussion

Syntheses. The ferrocene derivatives **I** and **II** were prepared by esterification of the ferrocene-1,3-diacid chloride [6] with the 4-hydroxyphenyl 4-(alkyloxy)benzoates (n = 1–14, 16, 18) [2], and the 4-alkyloxyphenols (n = 1–9) [7], respectively. The syntheses were carried out in dry CH_2Cl_2 at reflux in the presence of Et_3N. Purification by column chromatography (see *Exper. Part*) and crystallization from CH_2Cl_2/EtOH afforded the desired compounds as orange solids. The structures were confirmed by ^{1}H-NMR spectroscopy and elemental analysis.

Mesogenic Properties. The thermal properties of **I** and **II** were investigated by a combination of differential scanning calorimetry (DSC) and polarized optical microscopy. The transition temperatures and enthalpy changes are reported in *Table 1*, and the phase diagram of **I** is illustrated in *Fig. 1*. The mesomorphic properties of **If–h** (n = 6–8) have recently been reported [5].

The ferrocene derivatives **Ia–k** (n = 1–11) displayed enantiotropic nematic phases. Due to their high clearing temperatures, the first members of the series, **Ia–c** (n = 1–3), started to decompose when they reached the isotropic state. An increase in the alkyl chain length led to a regular decrease of the isotropization temperature. The crystal-to-nematic transition ($T_{C/N}$) increased slightly from **Ia** ($T_{C/N}$ 246°) to **Ic** ($T_{C/N}$ 254°), then decreased rapidly as far as **If** (n = 6) ($T_{C/N}$ 184°), and finally fluctuated around 175–180°. Compound **Il** (n = 12) presented a monotropic smectic C phase, and an enantiotropic nematic one. The nematic-to-smectic C modification was observed by DSC as well as by polarized optical microscopy. Ferrocene derivatives **Im, n, p** (n = 13, 14, 16) gave two enantiotropic mesophases, a smectic C phase, and a nematic one. The smectic C range broadened rapidly and, inversely, the nematic one narrowed rapidly from **Im** to **Ip**. This evolution was further confirmed by **Ir** (n = 18), which exhibited only a large smectic C phase (20°).

The mesophases were identified by observation of the textures in the different liquid crystal states. The nematic phases led to typical *Schlieren* textures [8]. In some cases, nematic droplets [8] could be observed when the compounds were cooled slowly from the isotropic liquid. On cooling from the nematic phase, the S_C phases appeared in the *Schlieren* form. A representative example is shown in *Fig. 2*. In the case of **Ir**, on cooling from the isotropic state, either a *Schlieren* texture or a

Table 1. *Phase-Transition Temperatures* [°C][a]) *and Enthalpy Changes* [kJ/mol] *of Ferrocene Derivatives* **I** *and* **II** *during the Second Heating-Cooling Cycle*

n	Compd.	C/S_C	S_C/N	S_C/I	C/N	N/I	Recryst.	Compd.	C/I	Recryst.
1	**Ia**	–	–	–	246	318[b])	125	**IIa**	210	125
					52.6	*5.1*			*52.0*	
2	**Ib**	–	–	–	253	316[b])	190	**IIb**	233	117
					72.8	*6.1*			*59.2*	
3	**Ic**	–	–	–	254	291[b])	190	**IIc**	193	117
					66.5	*5.4*			*55.5*	
4	**Id**	–	–	–	246	281	200	**IId**	153	112
					67.8	*5.7*			*41.3*	
5	**Ie**	–	–	–	214	261	175	**IIe**	135	100
					69.2	*6.1*			*35.7*	
6	**If**	–	–	–	184	247	144	**IIf**	125	104
					53.2	*4.8*			*36.3*	
7	**Ig**	–	–	–	182	234	154	**IIg**	126	103
					51.9	*4.2*			*39.7*	
8	**Ih**	–	–	–	178	225	151	**IIh**	123	100
					52.8	*4.0*			*39.0*	
9	**Ii**	–	–	–	182	212	152	**IIi**	121	102
					69.5	*3.0*			*43.2*	
10	**Ij**	–	–	–	182	208	152			
					74.0	*3.6*				
11	**Ik**	–	–	–	173	201	152			
					63.8	*3.3*				
12	**Il**	–	(159)[c])	–	166	195	151			
			2.0		*42.8*	*3.6*				
13	**Im**	166	169	–	–	191	150			
		39.5	2.9			*3.8*				
14	**In**	165	175	–	–	188	147			
		35.9	3.8			*4.1*				
16	**Ip**	162	179	–	–	181	141			
		34 3	[d])			[d])				
18	**Ir**	159	–	179	–	–	141			
		33.6		*15.2*						

[a]) C: crystal, N: nematic, S_C: smectic C, I: isotropic liquid. [b]) Slow decomposition. [c]) Monotropic transition. [d]) Not measurable due to peak overlap.

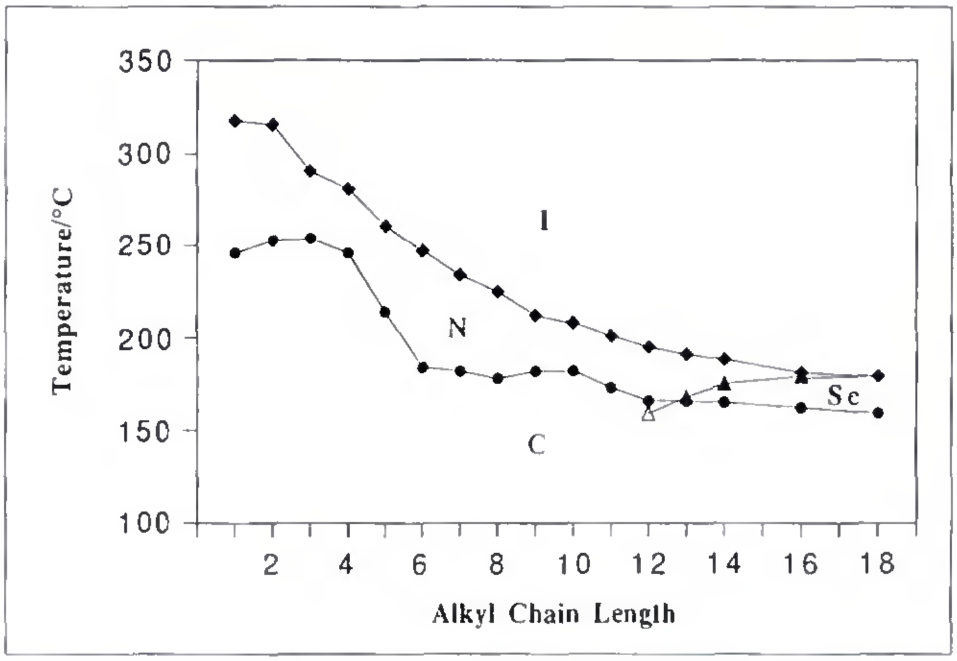

Fig. 1. *Phase diagram of ferrocenes* **I**. ●: melting point; ◆: clearing point; ▲: smectic C/nematic transition; Δ: nematic/smectic C transition. C = crystal; I = isotropic liquid; N = nematic phase; Sc = smectic C phase.

Fig. 2. *Representative thermal polarized optical micrograph of the smectic C* Schlieren *texture displayed by* **In** (n = 14) *upon cooling from the nematic phase to 168°*

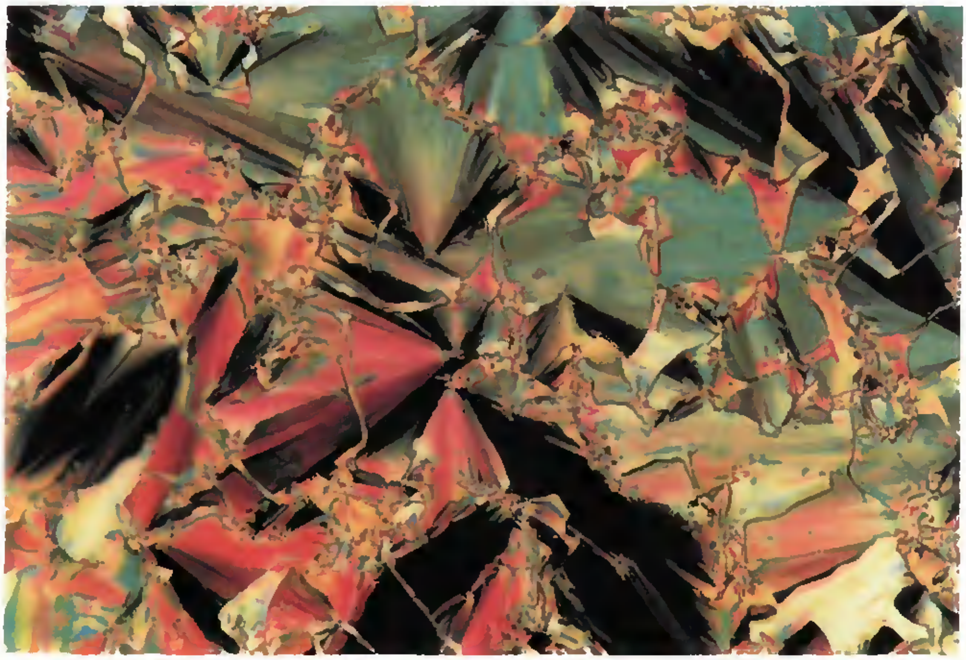

Fig. 3. *Representative thermal optical micrograph of the focal conic texture displayed by* **Ir** (*n* = 18) *upon cooling from the isotropic liquid to 165°*

focal-conic one was observed. A photomicrograph of the *focal-conic* texture is presented in *Fig. 3*.

None of the ferrocene derivatives ***II*** exhibited liquid crystal behavior. When heated they clearly and directly melted into an isotropic state; on cooling from the isotropic liquid, a supercooling was observed (see *Table 1*), but they all gave isotropic liquid-to-crystal state transitions. As expected, the melting point was higher for the first members of the series, but decreased as the alkyl chain length increased. No sign of decomposition was detected, even for the high-melting derivatives.

Structure. Crystals of **Ih** (*n* = 8) suitable for X-ray analysis were grown at a CH_2Cl_2/benzene 1:5 interface. Two different views of the molecular structure are presented in *Fig. 4*, with the atom numbering scheme given in *Fig. 4a*. The planes are defined as follows: disubstituted cyclopentadienyl ring: Plane 1; unsubstituted cyclopentadienyl ring: Plane 2; C(7), O(1), O(2): Plane 3; C(8)–C(13): Plane 4; C(14), O(3), O(4): Plane 5; C(15)–C(20): Plane 6. To our knowledge, this is the first X-ray crystal-structure analysis of a ferrocene derivative substituted in the 1,3-positions with such extremely long substituents.

The X-ray structure confirmed the 1,3-substitution, with the two organic molecular halves presenting identical structural features as the molecule possesses crystallographic C_s symmetry. The dihedral angle of 1.2° between Planes 1 and 2 indicates that the two cyclopentadienyl (Cp) rings are almost parallel to one another. From *Fig. 4b*, it can be seen that the Cp rings are in a staggered conformation. These observations are in agreement with literature data [9].

The average bond length and bond angle in the Cp rings, 1.443(10) Å and 107.2(10)°, respectively, are normal within experimental error. The average metal to C(Cp) distance of 2.050(13) Å is the same, within experimental error, as that observed in ferrocene, 2.04 Å [9].

In contrast to a structure determined for a 1,1'-disubstituted ferrocene-containing liquid crystal [10], the carboxyl groups are not coplanar with the Cp rings. Indeed, an angle of 14.9(9)° is observed between the Planes 1 and 3. The dihedral angle of 90.8(6)° shows that the first aromatic ring (Plane 4) is perpendicular to the first ester function (Plane 3). As for the two aromatic rings (Planes 4 and 6), they form a dihedral angle of 35.0(6)°. Finally, the small torsion angle (7.4(11)°) defined by C(17)–C(18)–O(5)–C(21) and the all-*trans* conformation of the alkyl chain indicate that the molecule is in the most extended conformation.

The crystal packing of **Ih** is presented in *Fig. 5*. As the molecules are in the most extended conformation (see above), they are almost as long as the **b** axis of the crystal unit. The molecules assemble in pairs with a head-to-tail arrangement of the ferrocene frameworks. Interestingly, the space between the Cp rings of a ferrocene core is occupied by an organic moiety of another molecule. This organization allows maximal occupation of the space leading to a highly compact packing of the molecules in the crystal.

The 1,3-disubstituted ferrocene derivatives **I** gave rise to remarkable mesomorphic behavior. Indeed, for the first time, a family of homologous ferrocene-containing liquid crystals exhibited broad enantiotropic domains within the entire series.

An explanation of the thermal properties of compounds **I** can be formulated taking into account the crystallographic data obtained for **Ih**. Firstly, despite an angle of 142° between the two substituents, compound **Ih** showed a linear shape with a highly anisometric structure (*Fig. 4*). Secondly, the crystal packing indicates that a molecular arrangement, allowing strong intermolecular interactions, is possible. Undoubtedly, these findings demonstrate that ferrocene derivative **Ih**, and it homologues, have the required structural characteristics for exhibiting stable mesophases.

The ferrocene derivatives **II** were synthesized to emphasize the influence of the rigid rod length on the thermal properties. The lowering of the melting points, on going from series **I** to series **II**, is in agreement with literature data obtained for wholly organic liquid crystals, and is attributed to a weakening of the intermolecular attractions [11]. However, the total loss of the liquid crystal properties for all the members of family **II** was unexpected considering the strong mesomorphic character of compounds **I**. Nevertheless, this result is of particular interest for investigating the *structure-liquid crystal properties* relationship as it shows that a limit exists for observing mesogenic behavior in the case of ferrocene derivatives substituted in the 1,3-positions.

It is known that a 1,3-disubstituted cyclopentane, when incorporated into a rigid rod, does not impede the formation of liquid crystals [12]. Thus, in **II**, the ferrocene moiety, due to its depth (*d*), acts as a spacer separating the aromatic rings from each other. As a consequence, the intermolecular attractions become too weak to give rise to mesogenic behavior. Therefore, to thwart the undesired effects induced by the ferrocene core, intensification of the intermolecular attractions is necessary to restore liquid crystal behavior. This can be achieved by increasing the length (*l*) of the rigid rod, *i.e.* by increasing the number of aromatic rings. And indeed, this situation is reflected by compounds **I**, as well as by a ferrocene derivative containing a biphenyl system on either side of the substituted Cp ring, which also exhibited a large enantiotropic nematic phase (see compound **2d** in [5]).

The above considerations indicate that the *l/d* ratio is an important structural parameter for the successful design of 1,3-disubstituted ferrocene-containing liquid crystals. From either crystallographic data or CPK models, the following length values of the rigid segments have been determined: 27.5 Å, 23.7 Å, and 15.1 Å, for **I**, 2d in [5], and **II**, respectively. The depth of the ferrocene being *ca.* 3.3 Å [9], *l/d* ratios of 8.3, 7.2, and 4.6 are obtained for **I**, **2d** in [5], and **II**, respectively. Therefore, these values suggest that liquid crystal behavior develops from a *l/d* ratio > 5–7.

Conclusions

The synthesis of a series of homologous 1,3-disubstituted ferrocene derivatives exhibiting broad enantiotropic mes-

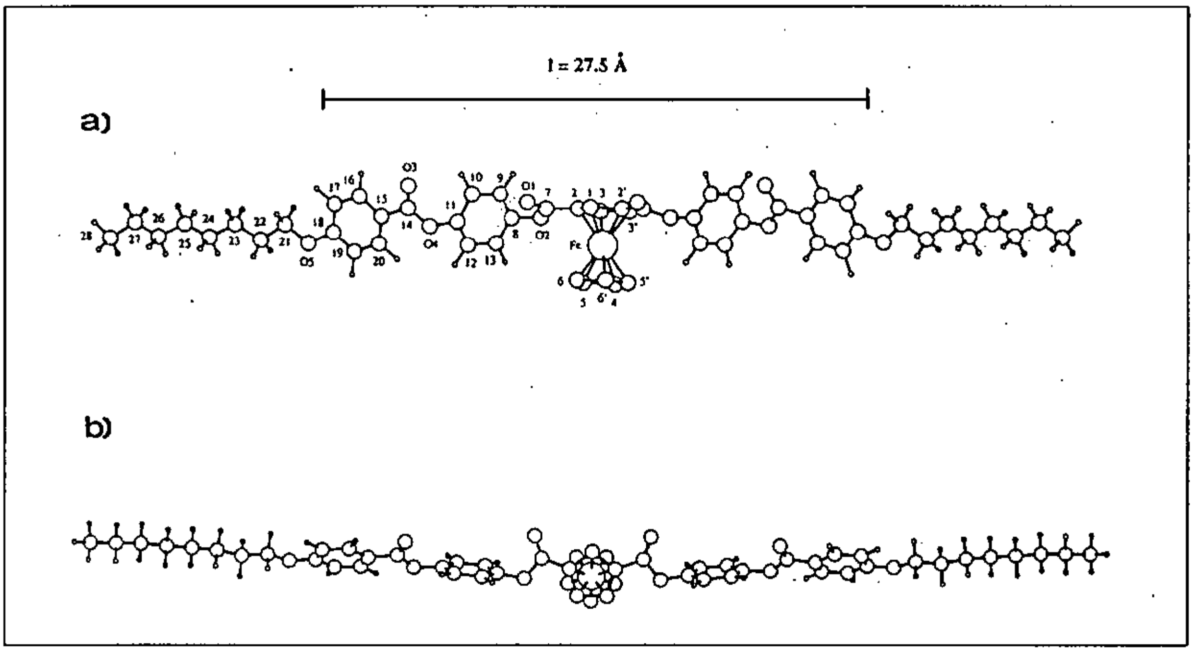

Fig. 4. *PLUTO plot* [15] *of* **Ih**, *showing* a) *the atom-numbering scheme, and* b) *a projection onto the Cp rings*

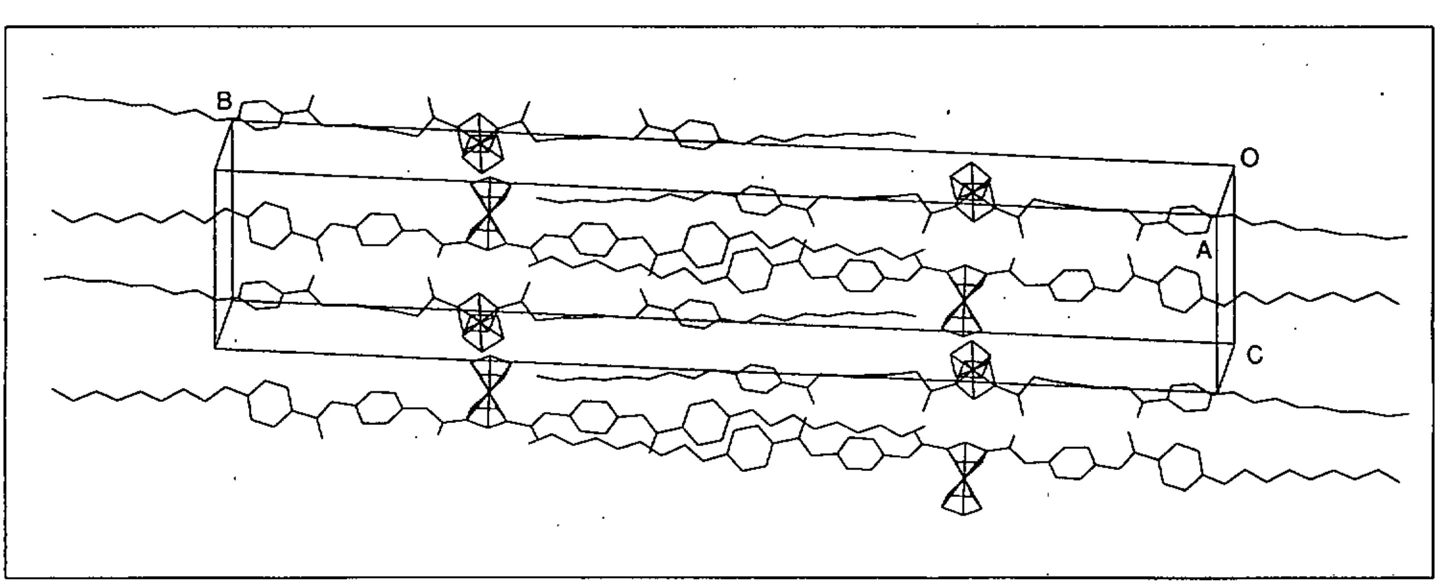

Fig. 5. *Crystal packing diagram* [16] *of* **Ih**

Table 2. *Elemental Analytical Data of Ferrocenes* **I** *and* **II**

	I				**II**			
n	Calculated		Found		Calculated		Found	
	%C	%H	%C	%H	%C	%H	%C	%H
1	66.13	4.16	65.94	4.18	64.22	4.56	63.94	4.55
2	66.85	4.54	66.76	4.48	65.38	5.10	65.03	5.17
3	67.53	4.89	67.60	4.78	66.43	5.57	66.15	5.55
4	68.15	5.22	67.81	5.21	67.14	6.34	66.95	6.10
5	68.74	5.53	68.64	5.53	68.23	6.40	68.24	6.35
6	69.28	5.81	69.11	5.85	69.01	6.76	68.69	6.68
7	69.80	6.08	69.92	6.05	69.72	7.08	69.79	7.19
8	70.28	6.33	70.25	6.44	70.38	7.38	70.15	7.59
9	70.73	6.57	70.65	6.65	70.98	7.66	71.02	7.73
10	71.16	6.80	71.08	6.83				
11	71.56	7.01	71.57	7.05				
12	71.94	7.21	71.94	7.28				
13	72.30	7.39	72.29	7.46				
14	72.65	7.57	72.49	7.79				
16	73.28	7.91	73.07	8.02				
18	73.86	8.21	73.76	8.21				

ophases has been successfully achieved. Rationalization of the *structure-thermal properties* relationship highlighted some important structural features which must be fulfilled in order to obtain liquid crystal behavior. These considerations might be used for other metallomesogens built up from a three-dimensional organometallic unit. Finally, the present results, and those published recently in the case of 1,1'-disubstituted ferrocene- [2] and 1,1'-disubstituted ruthenocene- [3] containing liquid crystals, have shown that sandwich-type transition-metal complexes are valuable organometallic units for the design of metallomesogens.

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Experimental Part

General. See [2].

Ferrocene-1,3-diacid chloride [6], 4-hydroxyphenyl 4-(alkyloxy)benzoate [2] and 4-(alkyloxy)phenol [7] were prepared following published procedures.

Syntheses. Syntheses of bis{4-[4-(alkyloxy)-benzoyloxy]phenyl} ferrocene-1,3-dicarboxylate **I** and bis[4-(alkyloxy)phenyl] ferrocene-1,3-dicarboxylate **II**.

General Procedure. A mixture of ferrocene-1,3-diacid chloride, 2.2 equiv. of the desired phenol derivative, 2.2 equiv. of Et_3N, and CH_2Cl_2 (5 ml) was heated at reflux for 2 h. The soln. was cooled to r.t. and washed with a sat. $NaHCO_3$ soln. The org. layer was separated, dried ($MgSO_4$), and evaporated. Purification of the resulting residue by CC (silica gel, CH_2Cl_2/AcOEt 50:1 for **Ia–e**, and for **IIa–i**, and 100:1 for **If–n, p, r**) and crystallization from CH_2Cl_2/EtOH gave the desired compounds in 70–80% yields. The elemental analytical data of **I** and **II** are reported in *Table* 2.

X-Ray Crystal Structure of **Ih**. $C_{54}H_{58}O_{10}Fe$, $M_r = 922.9$, orthorhombic, *Pnma*, $a = 7.602(1)$, $b = 57.538(3)$, $c = 10.760(1)$ Å, $V = 4706.5$ Å^3, $Z = 4$, $D_x = 1.302$ g·cm^{-3}, $\lambda = 0.71073$ Å. $\mu = 3.8$ cm^{-1}, $F(000) = 1952$. 3074 unique reflections, 1401 observed [$I > 2\sigma(I)$]. $R = 0.102$, $R_w = 0.132$, $k = 0.006$, $S = 1.53$. Max shift/sigma ratio 0.126, residual density (e/Å^3) max. 0.83, min –0.56.

Intensity data were collected at r.t. on a *Stoe AED2* 4-circle diffractometer using MoK_α graphite monochromated radiation. The crystal did not diffract well beyond 35° in 2Θ hence the limited data available for refinement and the rather high *R* factor and poor distances and angles. The structure was solved by *Patterson* and difference *Fourier* syntheses using the NRCVAX [13] system, which was used for all further calculations. Neutral complex-atom scattering factors in NRCVAX [13] are from [14]. The H atoms were included in calculated positions and held fixed ($U_{iso} = (U_{eq}(C) + 0.01)$ Å^2). The non-hydrogen atoms were refined anisotropically using weighted full-matrix least-squares, where $w = 1/[\sigma^2(F_0) + k(F_0^2)]$. Atomic parameters and complete tables of bond distances and angles have been deposited with the *Cambridge Crystallographic Data Centre*, Union Road, Cambridge CB2 1EZ, England. *Figs. 4* and *5* were drawn using the programmes PLUTO [15] and SCHAKAL 88B [16], respectively. Further details may been obtained from *H. St.-E.*

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