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1,3-Disubstituted Ferrocene-Containing Thermotropic Liquid Crystals: Synthesis, Mesomorphic Properties and the Crystal and Molecular Structure

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Abstract. Two families of 1,3-disubstituted ferrocene derivatives have been synthesized and their liquid-crystal behavior investigated. Compounds of series I, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_3)\text{-1,3-(COOC}_6\text{H}_4\text{OOC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1})_2]$ ($n = 1\text{--}14, 16, 18$), exhibited remarkable mesomorphic properties. Indeed, nematic and/or smectic C phases, associated with large anisotropic domains, were observed. Derivatives of series II, $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}[(\eta^5\text{-C}_5\text{H}_3)\text{-1,3-(COOC}_6\text{H}_4\text{OC}_n\text{H}_{2n+1})_2]$ ($n = 1\text{--}9$), were found to be non-mesogenic. The crystal and molecular structure of **Ih** ($n = 8$) was determined by means of X-ray analysis. The crystallographic data confirmed both a highly anisometric structure for **Ih** and a compact arrangement of the molecules in the crystal. The present results have shown that a critical length/depth ratio of *ca.* 5–7 must be passed for obtaining liquid-crystal properties.

Introduction

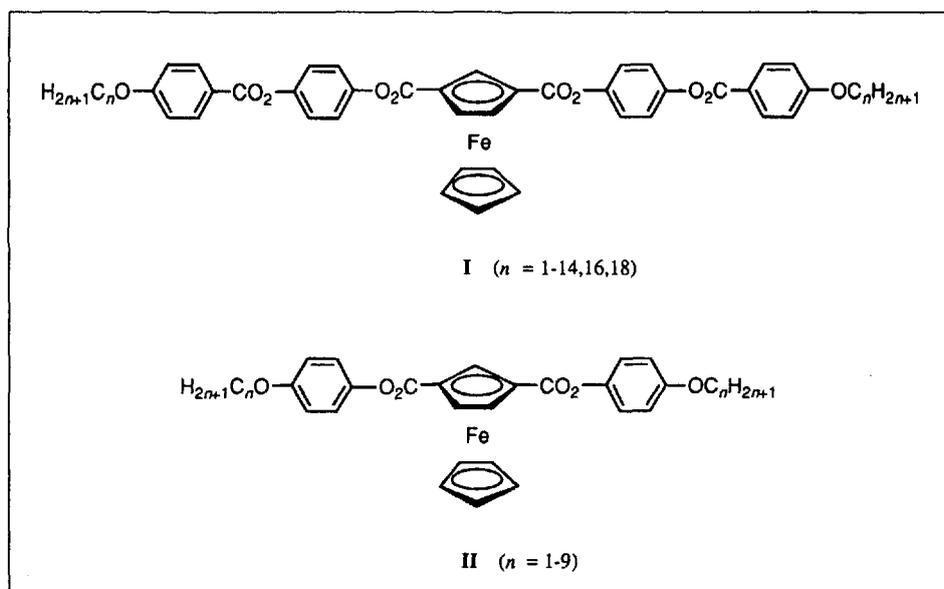
In the last few years, increasing attention has been paid to 1,1'-disubstituted ferrocene-containing liquid crystals [1]. The possibility of studying metallomesogens possessing a novel three-dimensional organometallic unit mainly motivated these investigations. However, most of the compounds studied thus far showed only limited mesomorphic properties. Indeed, either monotropic smectic A or C phases [1a], or narrow enantiotropic smectic C domains [1d] were obtained. In other cases, the textures could not be identified [1b,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.



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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 $\text{CH}_2\text{Cl}_2/\text{EtOH}$ afforded the desired compounds as orange solids. The structures were confirmed by $^1\text{H-NMR}$ 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 ($T_{\text{C/N}}$) increased slightly from **Ia** ($T_{\text{C/N}} 246^\circ$) to **Ic** ($T_{\text{C/N}} 254^\circ$), then decreased rapidly as far as **If** ($n = 6$) ($T_{\text{C/N}} 184^\circ$), and finally fluctuated around $175-180^\circ$. Compound **II** ($n = 12$) 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 [$^\circ\text{C}$]^{a)} and Enthalpy Changes [kJ/mol] of Ferrocene Derivatives **I** and **II** during the Second Heating-Cooling Cycle

<i>n</i>	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	IIIi	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	II	-	(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.

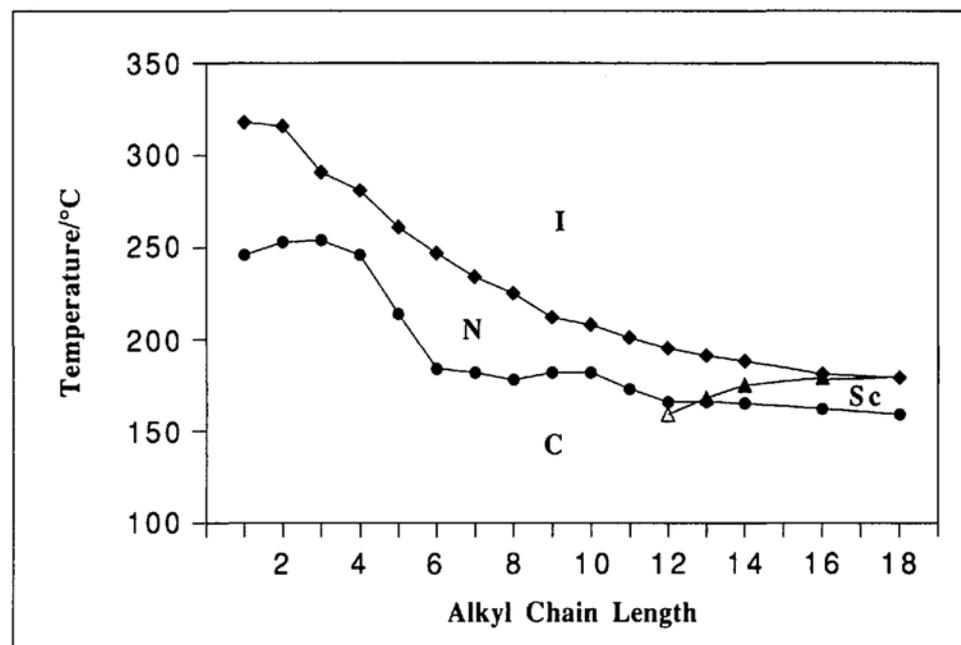


Fig. 1. Phase diagram of ferrocenes **I**. ●: melting point; ◆: clearing point; ▲: smectic C/nematic transition; △: nematic/smectic C transition. C = crystal; I = isotropic liquid; N = nematic phase; Sc = smectic C phase.

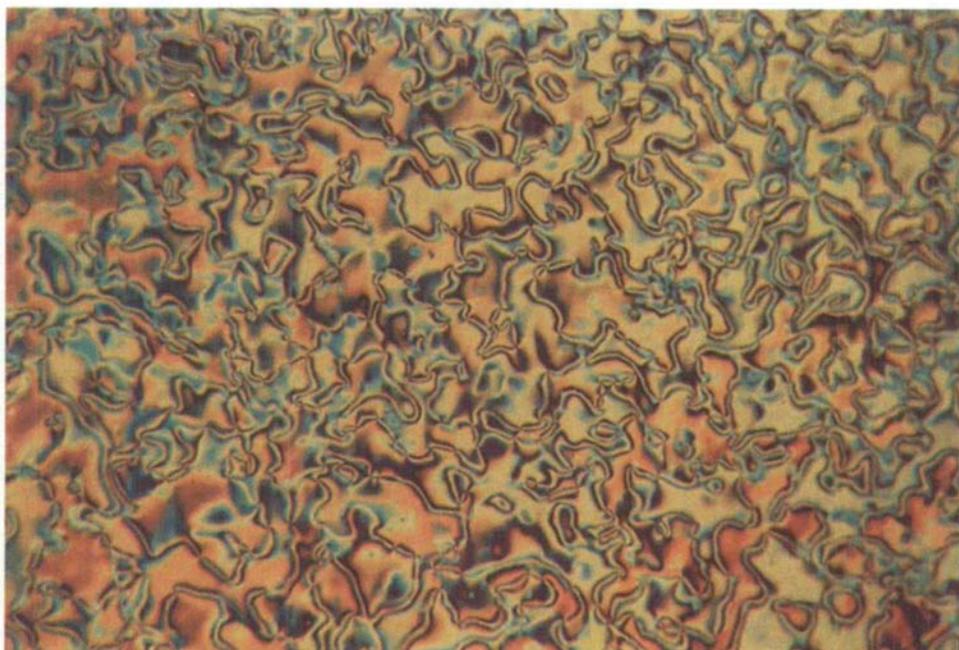


Fig. 2. Representative thermal polarized optical micrograph of the smectic C Schlieren texture displayed by **In** ($n = 14$) upon cooling from the nematic phase to 168°

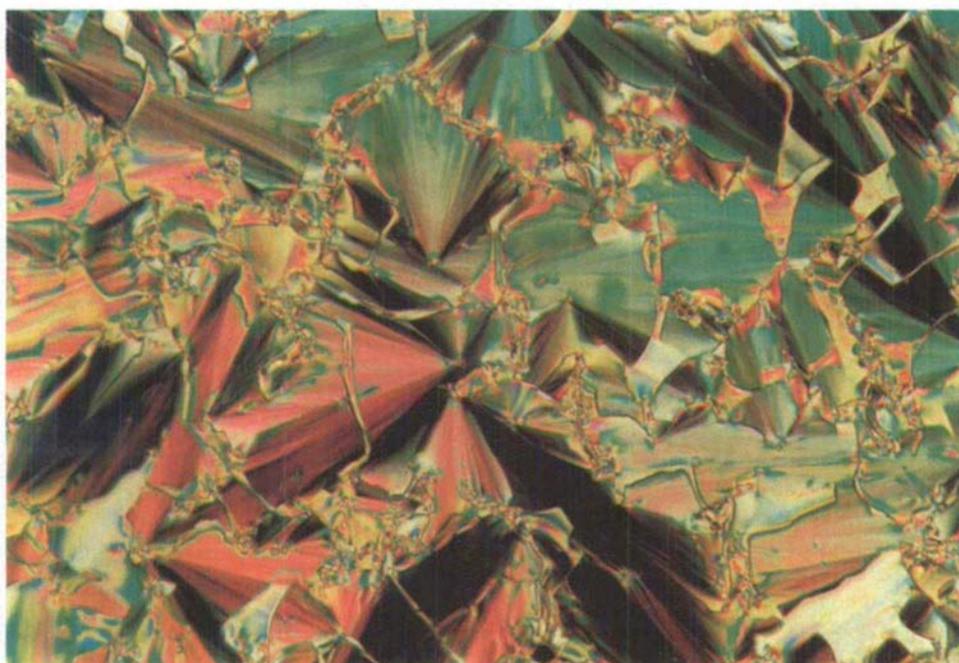


Fig. 3. Representative thermal optical micrograph of the focal conic texture displayed by **Ir** ($n = 18$) upon cooling from the isotropic liquid to 165°

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 $107.2(10)^\circ$, 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 $14.9(9)^\circ$ is observed between the Planes 1 and 3. The dihedral angle of $90.8(6)^\circ$ 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 $35.0(6)^\circ$. Finally, the small torsion angle ($7.4(11)^\circ$) 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-

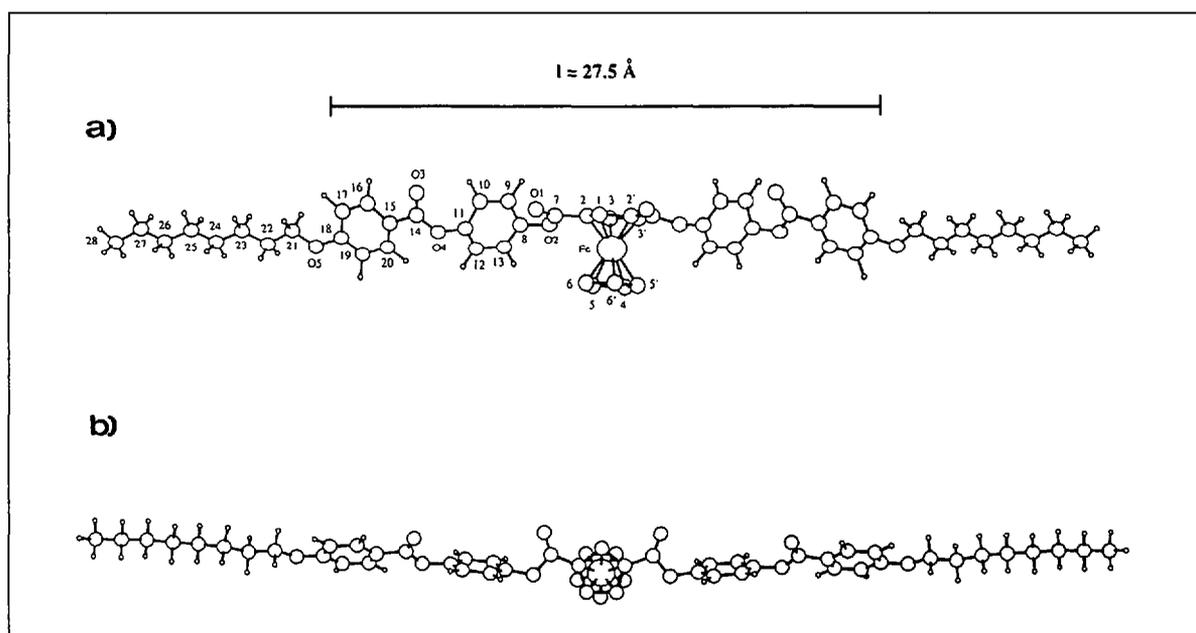


Fig. 4. PLUTO plot [15] of **1h**, showing a) the atom-numbering scheme, and b) a projection onto the Cp rings

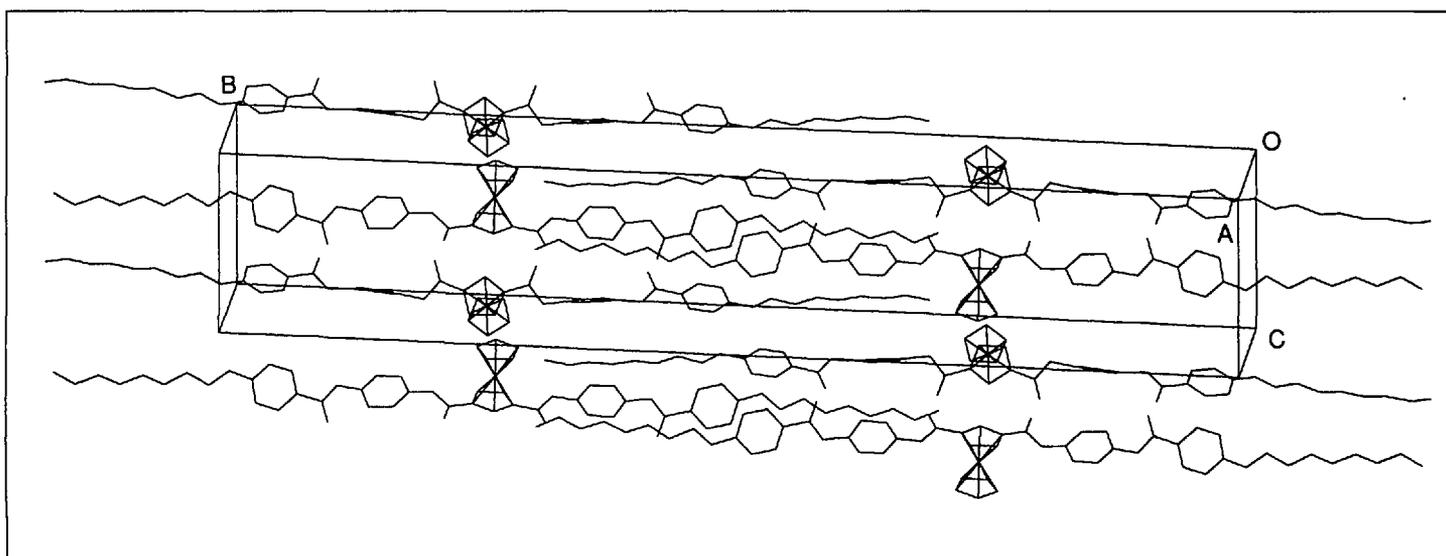


Fig. 5. Crystal packing diagram [16] of **1h**

Table 2. Elemental Analytical Data of Ferrocenes I and II

n	I				II			
	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 Et₃N, and CH₂Cl₂ (5 ml) was heated at reflux for 2 h. The soln. was cooled to r.t. and washed with a sat. NaHCO₃ soln. The org. layer was separated, dried (MgSO₄), and evaporated. Purification of the resulting residue by CC (silica gel, CH₂Cl₂/AcOEt 50:1 for Ia-e, and for IIa-i, and 100:1 for II-n, p, r) and crystallization from CH₂Cl₂/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. C₅₄H₅₈O₁₀Fe, M_r = 922.9, orthorhombic, Pnma, a = 7.602(1), b = 57.538(3), c = 10.760(1) Å, V = 4706.5 Å³, Z = 4, D_x = 1.302 g·cm⁻³, λ = 0.71073 Å, μ = 3.8 cm⁻¹, F(000) = 1952, 3074 unique reflections, 1401 observed [I > 2σ(I)], R = 0.102, R_w = 0.132, k = 0.006, S = 1.53. Max shift/sigma ratio 0.126, residual density (e/Å³) max. 0.83, min -0.56.

Intensity data were collected at r.t. on a Stoe AED24-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) Å²). The non-hydrogen atoms were refined anisotropically using weight-

ed full-matrix least-squares, where w = 1/[σ²(F_o) + k(F_o²)]. 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 be obtained from H. St.-E.

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