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

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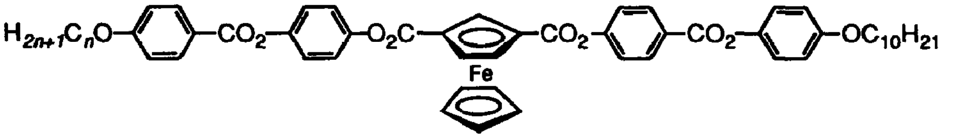
Abstract: The synthesis and mesomorphic properties of the first family of unsymmetrically-1,3-disubstituted ferrocene-containing thermotropic liquid crystals are presented. The title compounds exhibited enantiotropic liquid crystalline phases (nematic and/or smectic A and smectic C phases) associated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

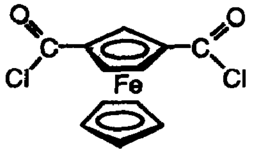
Recently, we reported the first symmetrically 1,3-disubstituted ferrocene-containing thermotropic liquid crystals.[5] These compounds presented interesting liquid crystals properties. Indeed, enantiotropic mesophases associated with broad anisotropic ranges were obtained. These mesomorphic properties 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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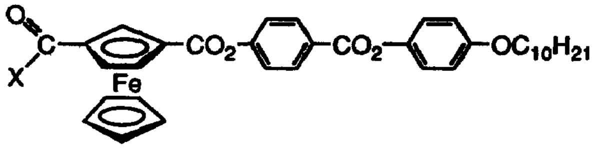
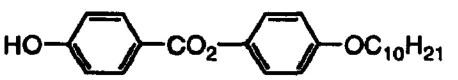


4 **a**: X=OH
b: X=Cl



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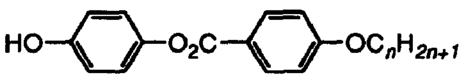

5 n=10-14, 16, 18

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-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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10. Elemental analytical data of ferrocene derivatives **1a-g** .
    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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