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

Robert Deschenaux* and Jean-Luc Marendaz

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

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.

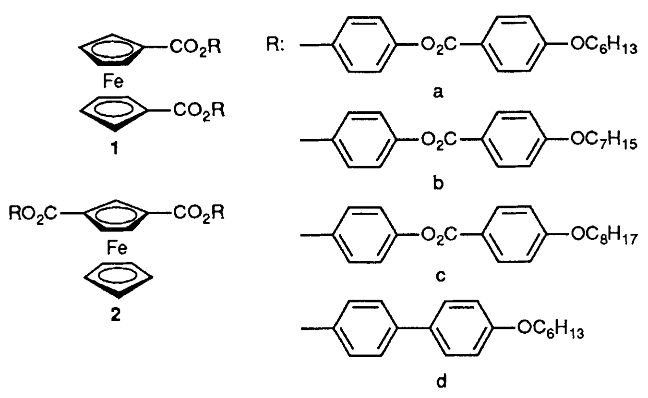
We report herein the preparation and mesogenic behaviour of ferrocenes substituted in the 1,1′- and 1,3-positions. To our knowledge, 1,3-disubstituted ferrocene-containing thermotropic liquid crystals have not previously been described. Compounds **1a–c** and **2a–d** were obtained by condensing either 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).