

Planar chirality: a fascinating symmetry breaking which leads to ferroelectricity in ferrocenyl liquid crystals

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We describe the synthesis, characterization and properties of the first optically-active 1,3-unsymmetrically disubstituted ferrocene derivative which is to exhibit smectic C* and smectic A* phases.

Symmetry breaking operations and chirality have held centre stage in the fundamental investigations and applications of liquid crystals.^{1,2} Furthermore, recent studies on mesogens with banana-shaped molecular structures have shown that chiral induction in self-organizing systems is possible even though the materials are themselves achiral.^{3,4} The search for new chiral effects in mesomorphic systems prompted us to synthesize unsymmetrically 1,3-disubstituted ferrocene-containing liquid crystals,⁵ where the different substituents at the 1- and 3-positions generate structures with planar chirality (Fig. 1). A representative example is illustrated by compound **1** (see Scheme 1); the two substituents are differentiated by the length of the alkyl chains and the orientation of the outer ester groups. Homologues of this material were prepared in racemic form from (±)-**2**⁵ (see Scheme 1). Over the entire range of the compounds studied, smectic C (SmC) and smectic A (SmA) phases were observed, and in some cases an additional nematic phase was detected.

The presence of the SmC phase in this family of compounds provided a unique challenge to make the materials optically active (SmC*) and thereby ferroelectric. Of course symmetrically 1,3-disubstituted ferrocene derivatives have the potential to exhibit ferro- or antiferro-electricity if the packing constraints of the molecules within the layers induce a restricted rotation of

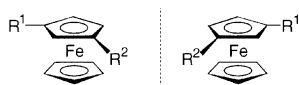
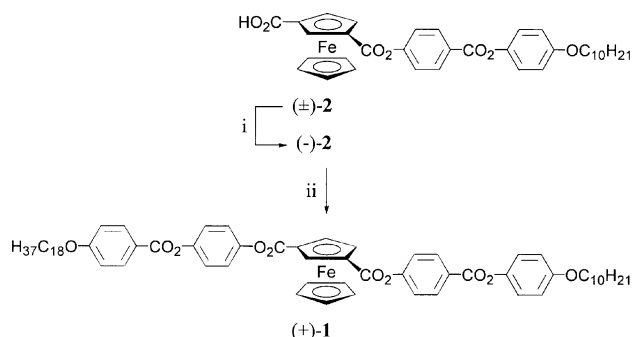


Fig. 1 Planar chirality in unsymmetrically 1,3-disubstituted Fc derivatives. Planar chirality: chirality resulting from the arrangement of out-of-plane groups with respect to a reference plane, called the 'chiral plane'.⁶



Scheme 1 Reagents and conditions: i, (+)-phenylethylamine [(+)-PEA], CH₂Cl₂; ii, (a) oxalyl chloride, pyridine, CH₂Cl₂, reflux, 3 h; (b) 4-hydroxyphenyl 4-(octadecyloxy)benzoate,¹⁰ triethylamine, CH₂Cl₂, reflux, 3 h.

the molecules about their long axes. Within this packing constraint, the V-shaped molecules will pack together to give a non-symmetric arrangement thereby leading to the induction of non-linear properties.

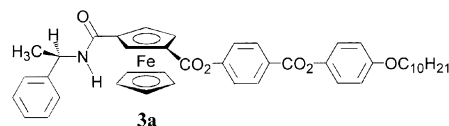
Ferroelectric liquid crystals are of considerable interest in switchable, half-wave plate, bistable light-valves. For ferrocenyl liquid crystals, SmC* phases have been reported only for two mono-substituted derivatives.^{7,8} Chirality was introduced into the peripheral side-chain by means of asymmetric carbon atoms, but for the two materials no ferroelectric behavior was described.

In addition to the investigation of the dependency of ferroelectricity on planar chirality, this study allowed us to probe the influence of the chiral unit, which is embedded in the central region of the molecular structure, on the self-organization process and mesophase formation. In metallomesogens, planar chirality was elegantly exploited by Malthête and coworkers who reported optically-active butadiene-tricarbonyliron liquid crystal complexes.⁹ The spontaneous polarization of one of the complexes was determined, and a value of 32 nC cm⁻² was obtained (response time: 9 ms).^{9b}

We report, herein, the synthesis, mesomorphic behavior and ferroelectric properties of the liquid-crystalline Fc derivative (+)-**1** (Scheme 1). The latter structure was selected because the corresponding racemic analogue gave the broadest SmC range among the family of homologues studied.⁵

The preparation of (+)-**1** is shown in Scheme 1. Optical resolution of acid (±)-**2** with (+)-phenylethylamine [(+)-PEA] gave (–)-**2**.[†] Treatment of (–)-**2** with oxalyl chloride gave the corresponding acid chloride derivative, which was condensed with 4-hydroxyphenyl 4-(octadecyloxy)benzoate¹⁰ to furnish (+)-**1**.[‡]

Derivatization of the acid (–)-**2** with (+)-PEA gave the amide **3a**,[§] which served for the determination of the enantiomeric excess (ee) of (–)-**2** by ¹H NMR and HPLC techniques. We assumed that the reactions used to prepare **3a** and (+)-**1** did not alter the optical purity of (–)-**2**. Therefore, the determination of the diastereomeric excess (de) of **3a** is a measure of the ee of (–)-**2** and, consequently, of (+)-**1**. The 1:1 diastereomeric mixture of **3a**:**3b** synthesized from (±)-**2** and (+)-PEA was used to fix the analytical conditions. The ¹H NMR and HPLC characteristics of diastereoisomer **3b** [from (+)-**2** and (+)-PEA] were deduced by comparing the data of the 1:1 diastereomeric mixture with that of **3a**.



In the ¹H NMR spectrum of the 1:1 diastereomeric mixture, each diastereoisomer gave well separated signals for the five protons of the unsubstituted cyclopentadienyl (Cp) ring (**3a**:

4.28 ppm; **3b**: 4.33 ppm) and the two Cp protons *ortho* to the amide function (**3a**: 5.70 and 5.19 ppm; **3b**: 5.65 and 5.24 ppm). For these signals, the five Cp protons gave two sharp singlets with baseline resolution, and appeared to be suitable for the determination of the de of **3a**. HPLC analysis (column Nucleosil 120 RP-C₁₈ (250 × 4 mm) equipped with a precolumn Nucleosil 120 RP—C₁₈ (30 × 4 mm); solvent, acetonitrile–water (80:20); elution rate, 1.5 ml min⁻¹) of the 1:1 diastereomeric mixture furnished two peaks (**3a**: 40.2 min; **3b**: 38.0 min) with almost baseline resolution. Both techniques led to reliable and reproducible results.

Optical resolution of (±)-**2** by (+)-PEA proved to be efficient: ¹H NMR and HPLC methods gave a de of 98% for **3a**, leading to an ee value of 98% for (+)-**1**.

The absolute configuration of the Fc in (+)-**1**, (–)-**2** and **3a** is shown arbitrarily. So far, crystallization of the salt (+)-PEA/(–)-**2** and amide **3a** failed to give crystals suitable for X-ray analysis.

The liquid-crystalline properties were investigated by differential scanning calorimetry (DSC, 10 °C min⁻¹, under N₂) and polarized optical microscopy.¶ Ferrocene (+)-**1** gave enantiotropic SmC* and SmA* phases (Cr → SmC*: 170 °C; SmC* → SmA*: 198 °C; SmA* → I: 202 °C; onset point, first heating run). The SmC* to SmA* phase transition was not detected by DSC (second order transition). No decomposition or racemization was observed for (+)-**1**. Similar transition temperatures were obtained for racemic (±)-**1** (Cr → SmC: 166 °C; SmC → SmA: 198 °C; SmA → I: 200 °C).⁵ No mesomorphic behavior was observed for the acid (–)-**2** and amide **3a**.

Fig. 2 shows the value of the spontaneous polarization as a function of temperature.∥ At the Curie point, the spontaneous polarization increased rapidly to a value of ca. 1.36 nC cm⁻², at which point it increased almost linearly as the temperature was lowered. At a temperature of 30 °C below the Curie point, a value of only 2.8 nC cm⁻² was reached (response time: ca. 200 ms).

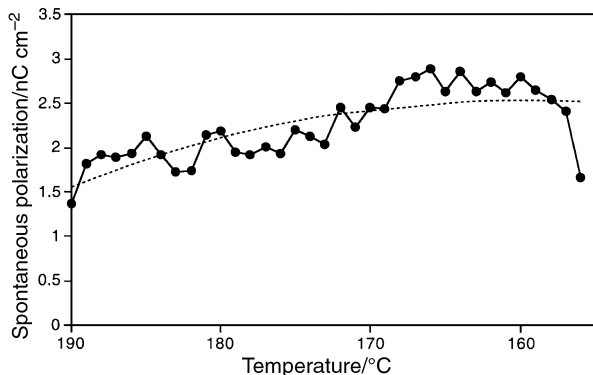


Fig. 2 The spontaneous polarization measured as a function of temperature from the Curie point for (+)-**1**.

An appreciable scatter in the data was observed because of the weak ferroelectric properties. The results obtained indicate firstly that planar chirality can induce ferroelectric properties, and secondly the induced effects are weak, revealing a poor coupling between the chirality associated with the Fc moiety at the centre of the molecular structure, the strongly polar functional groups in the material, and the liquid-crystalline environment. The weak ferroelectric properties are probably linked to the fact that the two arms attached to the Fc unit are not greatly different in length or polarity.

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Notes and references

† Optical resolution of (±)-**2**: to a warm solution of (±)-**2**⁵ (1.45 g, 2.31 mmol) in dry CH₂Cl₂ (130 ml), was added a solution of (+)-PEA (140 mg,

1.16 mmol) in dry CH₂Cl₂ (15 ml). The solution was allowed to stand overnight at room temperature. The salt was recovered by filtration, dried (743 mg), and crystallized in a 1:1 mixture of dry CH₂Cl₂–acetone (75 ml); yield: 554 mg. A mixture of the salt (554 mg), CH₂Cl₂ (40 ml) and 5 M HCl (40 ml) was vigorously shaken and the layers were separated. The organic layer was washed (water), dried (MgSO₄), and evaporated to dryness. Crystallization (CH₂Cl₂–hexane) of the solid residue gave (–)-**2** (327 mg, 45% with respect to the desired enantiomer) of ee = 98%. Mp 170 °C. [α]_D²⁰ –18 (c 0.45, CH₂Cl₂). δ_H(200 MHz, acetone-*d*₆) 8.27 (d, 2 H, arom.), 7.52 (d, 2 H, arom.), 7.22 (d, 2 H, arom.), 7.01 (d, 2 H, arom.), 5.52 (t, 1 H, Cp), 5.19 (dd, 1 H, Cp), 5.14 (dd, 1 H, Cp), 4.44 (s, 5 H, Cp), 4.03 (t, 2 H, OCH₂), 1.80 (m, 2 H, OCH₂CH₂), 1.60–1.20 [m, 14 H, O(CH₂)₂(CH₂)₇], 0.89 (t, 3 H, CH₃). Anal. Calc. for C₃₅H₃₈O₇Fe (626.53): C, 67.10; H, 6.11. Found: C, 67.08; H, 6.27%.

‡ Synthesis of (+)-**1**: first step: a mixture of (–)-**2** (250 mg, 0.441 mmol), oxalyl chloride (670 mg, 5.29 mmol), pyridine (5 drops) and dry CH₂Cl₂ (15 ml) was heated under reflux for 3 h, and evaporated to dryness. The solid residue was extracted with hot light petroleum (bp 60–90 °C) until the extracts remained colorless. Evaporation of the solvent gave the acid chloride derivative (273 mg, 96%), which was used in the next step without further purification. δ_H(400 MHz, CDCl₃) 8.29 (d, 2 H, arom.), 7.33 (d, 2 H, arom.), 7.13 (d, 2 H, arom.), 6.94 (d, 2 H, arom.), 5.74 (t, 1 H, Cp), 5.34 (dd, 1 H, Cp), 5.21 (dd, 1 H, Cp), 4.50 (s, 5 H, Cp), 3.97 (t, 2 H, OCH₂), 1.79 (m, 2 H, OCH₂CH₂), 1.60–1.20 [m, 14 H, O(CH₂)₂(CH₂)₇], 0.89 (t, 3 H, CH₃). Second step: a solution of the above acid chloride derivative (250 mg, 0.39 mmol), 4-hydroxyphenyl 4-(octadecyloxy)benzoate¹⁰ (188 mg, 0.39 mmol), triethylamine (40 mg, 0.39 mmol) in dry CH₂Cl₂ (15 ml) was heated under reflux for 3 h, cooled to room temperature, and evaporated to dryness. Purification of the solid residue twice by column chromatography (CC) [first CC: silica gel, CH₂Cl₂–AcOEt (50:1); second CC: silica gel, CH₂Cl₂–AcOEt (100:1)], and crystallization (CH₂Cl₂–EtOH) gave (+)-**1** (232 mg, 54%) of ee = 98%. [α]_D²⁰ +3 (c 0.42, CH₂Cl₂). δ_H(200 MHz, CDCl₃) 8.29 (d, 2 H, arom.), 8.15 (d, 2 H, arom.), 7.35 (d, 2 H, arom.), 7.27 (d, 4 H, arom.), 7.12 (d, 2 H, arom.), 6.98 (d, 2 H, arom.), 6.94 (d, 2 H, arom.), 5.79 (t, 1 H, Cp), 5.27 (br s, 2 H, Cp), 4.47 (s, 5 H, Cp), 4.06 (t, 2 H, OCH₂), 3.97 (t, 2 H, OCH₂), 1.80 (m, 4 H, OCH₂CH₂), 1.60–1.20 (m, 44 H, aliph.), 0.89 (2 × t, 6 H, CH₃). Anal. Calc. for C₆₆H₈₂O₁₀Fe (1091.21): C, 72.65; H, 7.57. Found: C, 72.79; H, 7.77%.

§ **3a**: prepared analogously to the synthesis of (+)-**1**, from (–)-**2** (3.00 mg) and (+)-PEA. Purification by column chromatography [silica gel, CH₂Cl₂–AcOEt (98:2)] gave the desired product of de = 98%. δ_H(200 MHz, acetone-*d*₆) 8.26 (d, 2 H, arom.), 7.74 (d, 1 H, NH), 7.56–7.27 (m, 5 H, arom.), 7.48 (d, 2 H, arom.), 7.21 (d, 2 H, arom.), 7.01 (d, 2 H, arom.), 5.70 (t, 1 H, Cp), 5.28 (qut., 1 H, CHCH₃), 5.19 (dd, 1 H, Cp), 5.10 (dd, 1 H, Cp), 4.28 (s, 5 H, Cp), 4.03 (t, 2 H, OCH₂), 1.84–1.73 (m, 2 H, OCH₂CH₂), 1.57 (d, 3 H, CHCH₃), 1.55–1.25 [m, 14 H, O(CH₂)₂(CH₂)₇], 0.89 (t, 3 H, CH₃). Anal. Calc. for C₄₃H₄₇NO₆Fe (729.69): C, 70.78; H, 6.49, N, 1.92. Found: C, 70.60; H, 6.61, N, 1.90%.

¶ For instrumentation, see: B. Dardel, R. Deschenaux, M. Even and E. Serrano, *Macromolecules*, 1999, **32**, 5193.

∥ Electro-optic studies on the ferroelectric properties were carried out using homogeneously aligned cells (Linkam) which were constructed from ITO coated glass, treated with antiparallel-buffed polyimide (PI) coated layers so as to give sites for planar, homogeneous growth of the liquid-crystalline state. The cell gap (ca. 5 μm) maintained by glass spacers was verified by UV–VIS interferometry. The effective electrode areas of the cells used were 0.9 cm². The cells were filled by capillary action at atmospheric pressure with (+)-**1** in the isotropic phase. Good alignment was achieved by cooling slowly (<0.1 °C min⁻¹) from the isotropic liquid into the liquid-crystalline state. The spontaneous polarization was determined using the triangular wave method.

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