

## A Liquid Crystalline Ferrocene Derivative with a Chiral Smectic C Phase

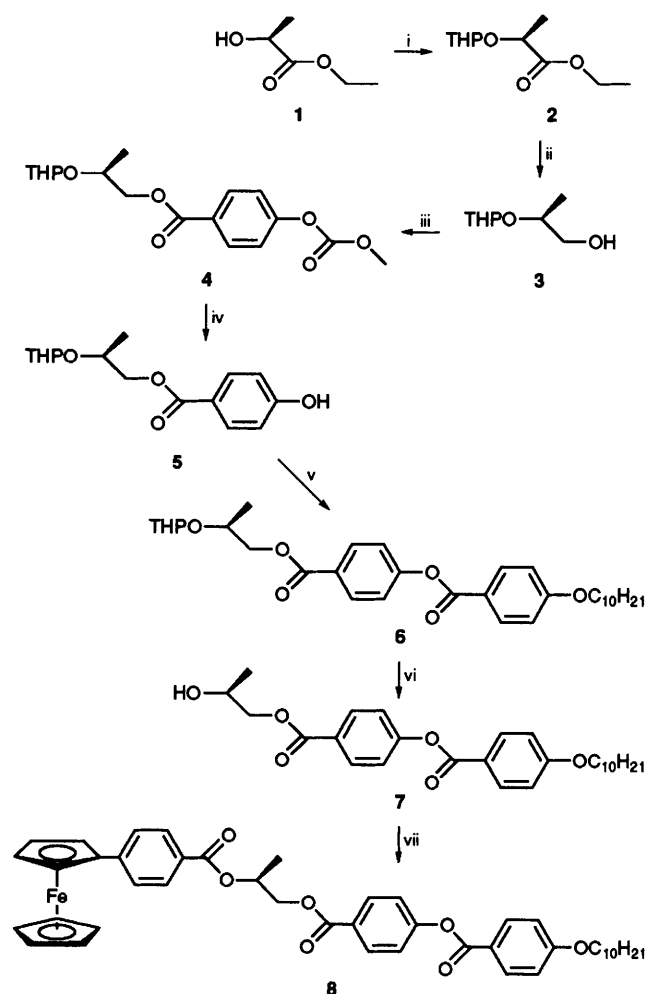
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The synthesis of the first liquid crystalline derivative of ferrocene with a chiral smectic C phase is reported.

Liquid crystalline materials containing transition metals are attracting special attention because of the ability of the transition metal centre to impart unique optical, magnetic and electrical properties.<sup>1</sup> Attention is presently shifting from achiral to optically active metallomesogens and compounds containing Pd, Cu, or V with one or more stereocentres have been prepared and their ferroelectric properties investigated.<sup>2</sup> Generally in these complexes the metal is in a planar environment if considered within the context of the surrounding aromatic rings. The use of the ferrocenyl group in constructing liquid crystals with novel molecular geometries has recently led to much discussion,<sup>3,4</sup> although these efforts usually involved disubstituted ferrocenes. Our interest in investigating the effect of attaching the bulky ferrocenyl unit to a single mesogenic unit stems from our discovery that the ferrocenyl group can lower the temperature at which the compound is liquid crystalline.<sup>4</sup> This led to the design of the monosubstituted ferrocene compound incorporating a single stereocentre described here.



**Scheme 1** Reagents and conditions: i, dihydropyran; ii, LAH, Et<sub>2</sub>O, reflux; iii, DEAD, PPh<sub>3</sub>, THF; iv, NH<sub>3</sub>, EtOH; v, DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>; vi, Dowex X8, MeOH; vii, DCC, DMAP, CH<sub>2</sub>Cl<sub>2</sub>

The molecule was constructed by starting with versatile (*S*)-ethyl lactate **1** (Scheme 1). Alcohol **3**, suitably protected as the THP ether, was used to attach the organic mesogenic component, while deprotection of **6** permitted introduction of the 4-carboxyphenylferrocene. All of the reactions employed are based on well-known procedures. The ferrocene derivative was purified by column chromatography (CH<sub>2</sub>Cl<sub>2</sub>) followed by repeated recrystallization.

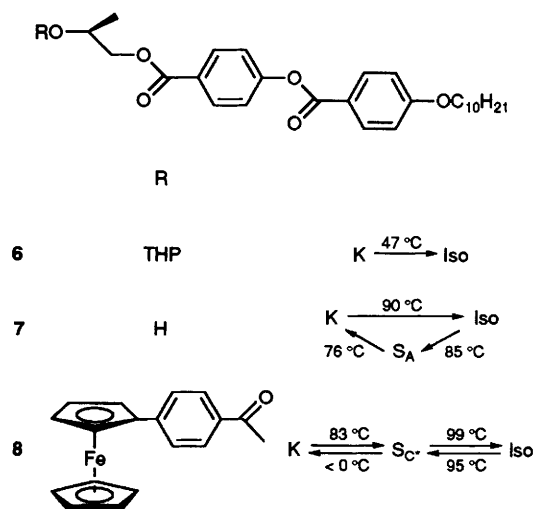
Scheme 2 summarises the phase transition temperatures for the ferrocene derivative **8**, as well as for two of its precursors, **6** and **7**. The smectic A phase exhibited by **7** is thermodynamically unstable and crystallises upon standing within the temperature range. Remarkable therefore is the effect achieved by attaching the 4-carboxyphenylferrocene group; in **8** the smectic A phase of **7** is replaced by a stable chiral smectic C phase, readily identified by its *schlieren* texture (phase transitions were confirmed by DSC). Upon cooling the isotropic liquid, the chiral smectic C phase reappears and supercools to room temperature, where it persists for weeks. Crystallisation to the solid state occurs gradually upon prolonged exposure to subzero temperatures. The smectic C texture is preserved when crystallisation takes place. Rotation of the upper polariser of the microscope reveals a right-handed helical structure<sup>5</sup> in the phase, confirmed by its miscibility with a compound having a similar helical arrangement.

Compound **8**<sup>†</sup> is the first ferrocene derivative which exhibits a chiral smectic C liquid crystal phase and the preparation of derivatives thereof is in progress.

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### Footnote

<sup>†</sup> Yield 61% (Anal. found: C, 70.96; H, 6.56; C<sub>44</sub>H<sub>48</sub>FeO<sub>7</sub> requires C, 70.97; H, 6.50). IR (KBr) ν/cm<sup>-1</sup> 2924, 1720, 1713, 1606, 1513, 1267, 1165, 1113, 764. NMR <sup>1</sup>H (δ, CDCl<sub>3</sub>) 0.87 (t, 3H, CH<sub>3</sub>), 1.20–1.40 [m, 14H, (CH<sub>2</sub>)<sub>7</sub>], 1.47 (2 × d, 3H, Me), 1.80 (q, 2H, CH<sub>2</sub>), 4.01 (s, 5H,



**Scheme 2**

C<sub>5</sub>H<sub>5</sub>), 4.02 (t, 2H, OCH<sub>2</sub>), 4.36 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 4.50 (m, 2H, CH<sub>2</sub>), 4.68 (t, 2H, C<sub>5</sub>H<sub>4</sub>), 5.52 (m, 1H, \*CH), 6.94 (m, 2H, ArH), 7.27 (m, 2H, ArH), 7.48 (m, 2H, ArH), 7.93 (m, 2H, ArH), 8.10 (m, 4H, ArH); the presence of the chiral centre manifests itself on the spectra of compounds **2** to **8** in the form of complex signals for the *vicinal* methylene protons around 4.5 ppm. <sup>13</sup>C (δ, CDCl<sub>3</sub>) 14.08, 16.75, 22.66, 25.97, 29.08, 29.30, 29.34, 29.53, 31.88, 66.84 (2C, ferrocenyl), 66.68 (2C, ferrocenyl), 68.40, 68.71, 69.81, 69.82 (5C, ferrocenyl), 83.38 (1C, ferrocenyl), 114.41, 121.06, 121.90, 125.67, 127.30, 127.37, 129.80, 131.31, 132.38, 145.32, 155.01, 163.80, 164.35, 165.60, 165.98.

## References

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