97. Crystal Smectic-B Phase from a Mesomorphic Ferrocene Derivative

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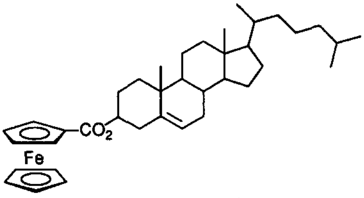
The thermal properties of two ferrocene derivatives, substituted by either one or two cholesteryloxycarbonyl units, were investigated. While the monosubstituted ferrocene derivative **1** was found to be non-mesomorphic, the disubstituted ferrocene derivative **2** exhibited a crystal smectic-B phase. This result shows that ferrocene-containing thermotropic liquid crystals, despite the bulkiness of the metallocene core, are not limited to disordered calamitic phases.

Introduction. – Ferrocene was successfully used to design thermotropic metallomesogens [1]. Careful transformation of the metallocene core led to materials which showed enantiotropic mesomorphism associated with a broad anisotropic domain [1]. Owing to its bulky three-dimensional structure (the distance between the two cyclopentadienyl rings is *ca.* 3.3 Å [2]) it was clearly established that the ferrocene unit reduces the intermolecular interactions in comparison with analogous metal-free derivatives, the consequence of which is the formation of liquid crystals exhibiting weakly ordered mesophases, namely nematic, smectic-A, and smectic-C phases. A chiral smectic-C phase was also observed for an optically active ferrocene derivative [3].



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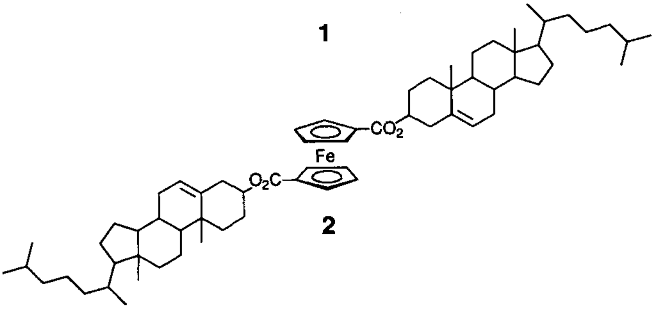

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The obtention of a ferrocene derivative giving rise to a soft crystal phase ($B_{(cryst)}$, E, J, G, H, and K) would be of fundamental interest to further understanding of the supramolecular organization of ferrocene-containing molecular units within the mesomorphic state. Indeed, such a result would prove that, despite the bulkiness of the metallocene core, liquid-crystalline ferrocene derivatives are not limited to fluid-like calamitic mesophases but can organize into more ordered molecular systems.

We describe, herein, the thermal properties of ferrocenyl steroids **1** and **2** and the first observation of a crystal smectic-B phase from a mesomorphic ferrocene derivative. The synthesis and redox properties of **2** were already described as part of a study devoted to the design of redox-switched molecular aggregates [4].

Results and Discussion. – The thermal behavior of **1**[1]) and **2**[1]) was examined by a combination of differential scanning calorimetry (DSC) and polarized optical microscopy[2]) under N_2 to avoid decomposition. No liquid-crystalline behavior was obtained from monosubstituted ferrocene derivative **1**. Heating of the sample led to the formation of an isotropic melt at 179° which crystallized on cooling.

Interesting mesogenic properties resulted from compound **2**. During the first heating run, three endotherms were obtained, at 223, 265, and 276°. From polarized optical microscopy, the first transition was attributed to a crystal-to-crystal modification. The second transition showed an important morphological change of the sample, but an unambiguous interpretation of this observation, *i.e.*, crystal-to-mesophase or crystal-to-crystal transition, could not be given. As for the third transition, it clearly corresponded to the formation of an isotropic fluid.

On cooling from the isotropic melt, two transitions were detected by DSC, at 268 and 247°, which indicated the formation of a mesomorphic state. Polarized optical microscopy confirmed the DSC data: a texture characterized by lancets with mosaic patterns and homeotropic areas (*Fig.*) developed before the sample crystallized. Microscopy also revealed a long-range three-dimensional positional order of the molecules as seen from the formation of mosaic twins and sharp grain boundaries. From the optical observations, the mesophase was identified as a crystal smectic-B phase (rather than a hexatic-B phase).

The fact that **1** does not show liquid-crystalline behavior, whereas cholesteryl benzoate does [6], is most likely due to the bulkiness of the metallocene unit. The latter acts as a spacer, separating the molecules from each other. Consequently, intermolecular interactions are too weak to generate mesomorphism. This result is in agreement with literature data reported for other ferrocene derivatives [1].

The introduction of a second cholesteryloxycarbonyl unit (→ **2**), firstly, led to an elevation of the melting point and, secondly, generated mesomorphism. Undoubtedly,

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[1]) Synthesized from the corresponding ferrocene carbonyl chloride and cholesterol (*Fluka AG*) following [4]. Purification by column chromatography (silica gel *60*, 0.060–0.200 mm, *SDS*, hexane/AcOEt 2:1) and crystallization (CH_2Cl_2/EtOH) led to pure materials. Selected analytical data: *Cholest-5-en-3β-yl ferrocene-1-carboxylate* (**1**; 45%): ^{1}H-NMR: 0.69–2.43 (43 H, Chol); 4.20 (*s*, 5 H, Cp); 4.38 (*t*, 2 H, Cp); 4.78 (*m*, CHO of Chol); 4.80 (*t*, 2 H, Cp); 5.43 (*m*, C=CH of Chol). Anal. calc. for $C_{38}H_{54}FeO_2$ (598.70): C 76.24, H 9.09; found: C 76.36, H 9.08. *Bis(cholest-5-en-3β-yl) ferrocene-1,1′-dicarboxylate* (**2**; 46%): Anal. calc. for $C_{66}H_{98}FeO_4$ (1011.36): C 78.38, H 9.77; found: C 78.37, H 9.81.

[2]) For instrumentation, see [5].

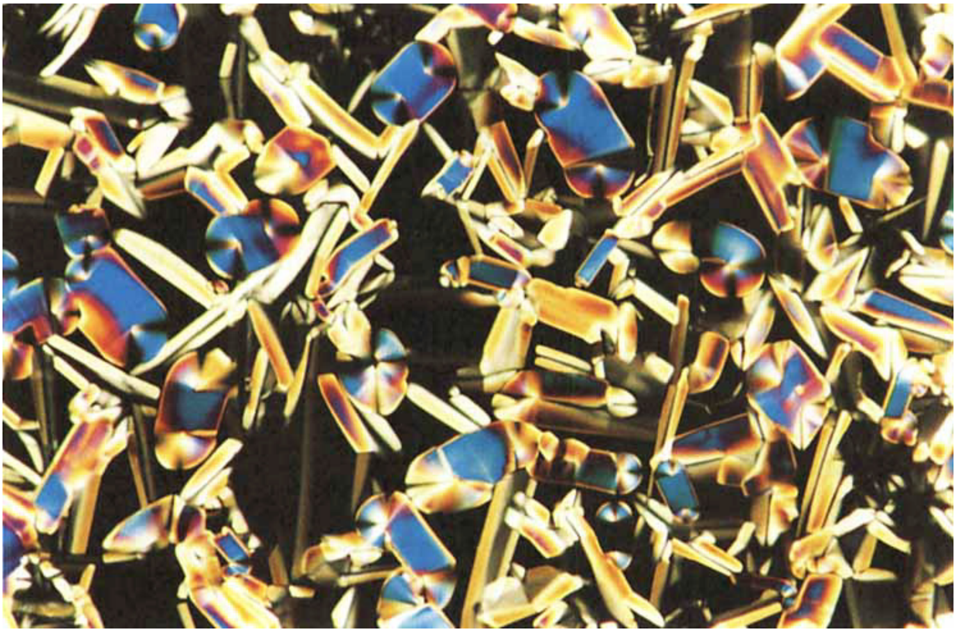

Figure. *Polarized optical micrograph of the crystal smectic-B phase displayed by* **2** *upon cooling from the isotropic liquid to 260°*

both effects arose from an increase in the intermolecular interactions. This result further confirms literature data [1], *i.e.*, disubstitution is more favorable than monosubstitution for generating mesomorphism.

The supramolecular organization of **2** into a crystal smectic-B phase (the molecules are oriented orthogonally to the layers and packed in a hexagonal array [7]) is essentially due to the lack of polarity of the molecule (around the mesogenic cholesteryl group) coupled with a non-flexible structure. It is well-known that non-polar liquid crystals, which have terminal aliphatic chains, are more likely to form crystal smectic-B phases [7].

Finally, depending on the conformation of the ferrocene derivative **2**, two different molecular arrangements can be envisaged within the mesophase. In the *cis*-conformation (the cholesteryloxycarbonyl units point in the same direction), the molecules form individual large cylinders which can only pack hexagonally. Such a molecular disposition is not so favorable for maintaining long-range order. In the *trans*-conformation (the cholesteryloxycarbonyl units are oriented in opposite directions), however, the molecules adopt a 'step-like' structure which would force them to pack in a certain way, so that the 'kinks' overlap to give long-range positional order.

Conclusions. – We reported the first mesomorphic ferrocene derivative showing a long-range three-dimensional positional order of the molecules, in the present case, a crystal smectic-B phase. This result is of general interest in the field of metallomesogens [8], as it shows that ferrocene-containing thermotropic liquid crystals, despite the bulkiness of the metallocene core, are not limited to disordered calamitic phases. The design of ferrocene-containing thermotropic liquid crystals showing any kind of mesophases may be feasible.

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