Columnar Phases from Covalent and Hydrogen-Bonded Liquid-Crystalline Ferrocene Derivatives

Preliminary Communication

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The synthesis and liquid-crystalline properties of tetracatenar covalent and H-bonded bis-ferrocene derivatives **1** and **2**, respectively, are reported. Both compounds gave rise to enantiotropic columnar liquid-crystalline behavior with a hexagonal molecular organization. To explore the possibility to obtain also calamitic liquid-crystalline phases from H-bonded ferrocene-containing liquid crystals, a rod-shaped ferrocene mesogen **3** was synthesized, which gave rise to enantiotropic smectic C and smectic A phases. For the first time, a rational synthetic design at the ferrocene level led to ferrocene-based liquid-crystals with columnar behavior and to H-bonded metallomesogens.

Introduction. – Current efforts oriented towards the development of ferrocene-based mesomorphic materials led to the synthesis of ferrocene-containing side-chain liquid-crystalline polymers [1], ferrocene-containing liquid-crystalline dendrimers [2], and a liquid-crystalline mixed [60]fullerene-ferrocene derivative [3]. These structures are promising candidates to construct switchable anisotropic materials. We demonstrated that electron transfer can be used to generate mesomorphism in the ferrocene-ferrocenium redox system [4].

To further explore the *structure/supramolecular organization* relationship in the case of ferrocene-containing mesomorphic molecular units, the study of novel structures is required. Mesomorphic ferrocenes exhibiting columnar liquid-crystalline phases would be of particular interest: No such examples have been reported [5–7]¹). Because of the bulky, three-dimensional structure of the ferrocene core, the primary influence of which is to reduce the intermolecular interactions (resulting in a lowering of the liquid-crystalline tendency in comparison with the ferrocene-free analogues) [5], the design of such compounds represents both a conceptual and synthetic challenge. Ultimately, owing to its redox activity, the incorporation of ferrocene units into columnar phases may open the doors to new supramolecular wires [9].

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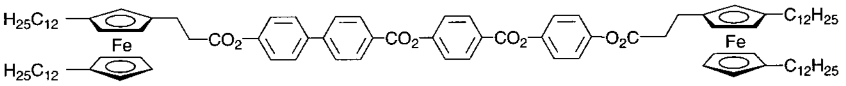
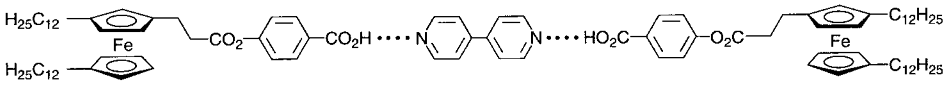
¹) A liquid-crystalline ferrocenyl-phthalocyanine derivative (the ferrocene unit is located at the end of one alkyl chain) showing a discotic phase was described [8]; even if the discotic phase was induced by the phthalocyanine core, this example is important as it shows that ferrocene can accomodate to discotic phases.

We report, herein, the synthesis and liquid-crystalline properties of the tetracatenar ferrocene derivatives **1** and **2**. A tetracatenar system was selected to design ferrocene derivatives showing columnar phases in view of successful investigations made for organic liquid crystals [10]. Furthermore, to explore the possibility to use H-bonds to design ferrocene-containing thermotropic liquid crystals exhibiting calamitic liquid-crystalline phases, the rod-like-shaped H-bonded ferrocene complex **3** was synthesized. Compounds **2** and **3** represent the first H-bonded metallomesogens described so far [5–7]. Note that the H-bonds were elegantly used to elaborate ferrocene-based sensors [11].



1



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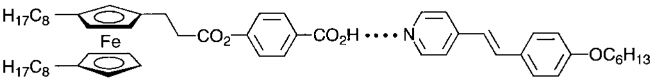

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Results and Discussion. – The syntheses of **1**–**3** are illustrated in *Schemes 1–3*, respectively(2). The preparation of **1** (and of the ferrocene intermediates) required an esterification-deprotection sequence. The H-bonded complexes **2** and **3** were prepared by reacting the appropriate acid and pyridine derivatives in THF at room temperature. The formation of H-bonds was confirmed by FT-IR spectroscopy [13]. The structure and purity of all compounds were confirmed by NMR spectroscopy and elemental analysis.

The liquid-crystalline properties of **1** and **2** were examined by a combination of differential scanning calorimetry (DSC), polarized optical microscopy (POM), and

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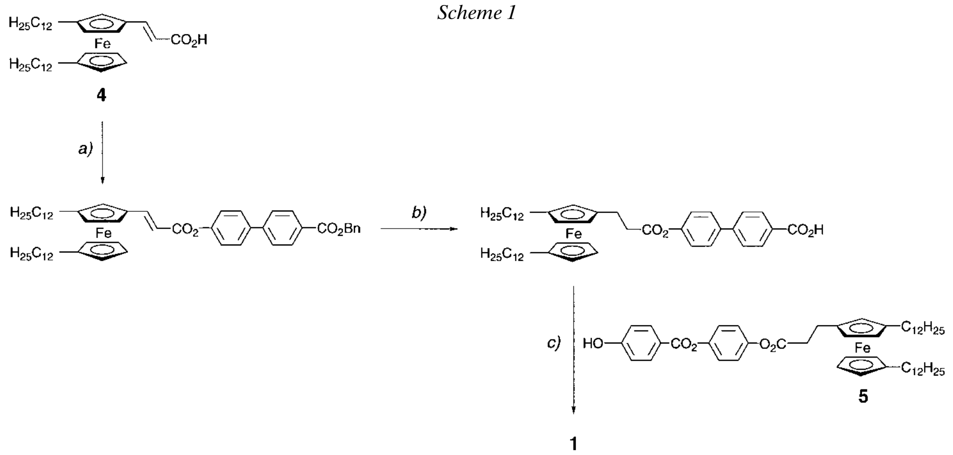
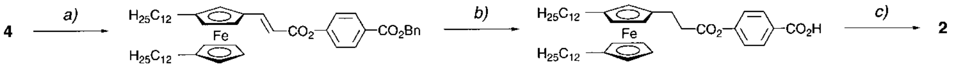
(2) Ferrocene derivatives **4** and **5** were prepared analogously to their dioctyl homologues [1a]. Compounds **6** [1a] and **7** [12] were synthesized as published. Benzyl 4′-hydroxy-[1,1′-biphenyl]-4-carboxylate (*Step a* in *Scheme 1*) was obtained from 4′-hydroxy-[1,1′-biphenyl]-4-carboxylic acid and benzyl bromide (MeCN, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 70°, 5 h; yield 78%; purification by column chromatography; (silica gel, CH_2Cl_2) and crystallization from acetone/hexane). Benzyl 4-hydroxybenzoate (*Fluka*, $\geq$98%), 4,4′-bipyridyl (*Fluka*, $\geq$99%), and 4′-hydroxy-[1,1′-biphenyl]-4-carboxylic acid (*Aldrich*, 99%) were used as received.

Scheme 1



a) Benzyl 4′-hydroxy-[1,1′-biphenyl]-4-carboxylate, *N*,*N*′-dicyclohexylcarbodiimide (DCC), 4-(pyrrolidin-1-yl)pyridine (4-ppy), CH_2Cl_2, r.t., 3 h; 74%; purification by column chromatography (CC; silica gel, CH_2Cl_2). *b*) H_2, 10% Pd/C, CH_2Cl_2, r.t., 16 h; 90%; purification by CC (silica gel, Et_2O). *c*) DCC, 4-ppy, CH_2Cl_2, r.t., 3 h; 89%; purification by CC (silica gel, CH_2Cl_2).

Scheme 2



a) Benzyl 4-hydroxybenzoate, DCC, 4-(dimethylamino)pyridine (DMAP), CH_2Cl_2, r.t., overnight; 87%; purification by CC (silica gel, CH_2Cl_2). *b*) H_2, 10% Pd/C, CH_2Cl_2, r.t., 1 h; 73%; purification by dissolution in hexane and precipitation in MeOH. *c*) 4,4′-Bipyridine, THF, r.t., 0.5 h; 80%; purification by trituration with hexane, filtration, and washing with hexane.

X-ray diffraction (XRD)[3]). The mesomorphic behavior of **3** was investigated by DSC and POM. The thermal and liquid-crystalline data of **1**–**3** are reported in *Table 1*.

Both compounds **1** and **2** gave rise to birefringent fluids as detected by POM. Slow cooling of **1** from the isotropic fluid revealed the formation of spherulites and linear birefringent defects; a similar texture was observed for **2**. From these observations, the mesophases displayed by **1** and **2** were identified as columnar phases.

Compound **3** showed enantiotropic smectic C and smectic A phases which were identified from their textures: The smectic C phase gave rise to focal-conic and *schlieren* textures; as for the smectic A phase, a focal-conic texture and homeotropic areas were observed. The mesomorphic behavior of **3** is similar to that observed for an analogous covalent ferrocene derivative [1a].

The XRD confirmed the columnar nature of the liquid-crystalline phases of **1** and **2**. In both cases, a broad diffuse halo was observed for a scattering angle of 20°. This diffuse halo characterized the molten state of the alkyl chains and the lateral

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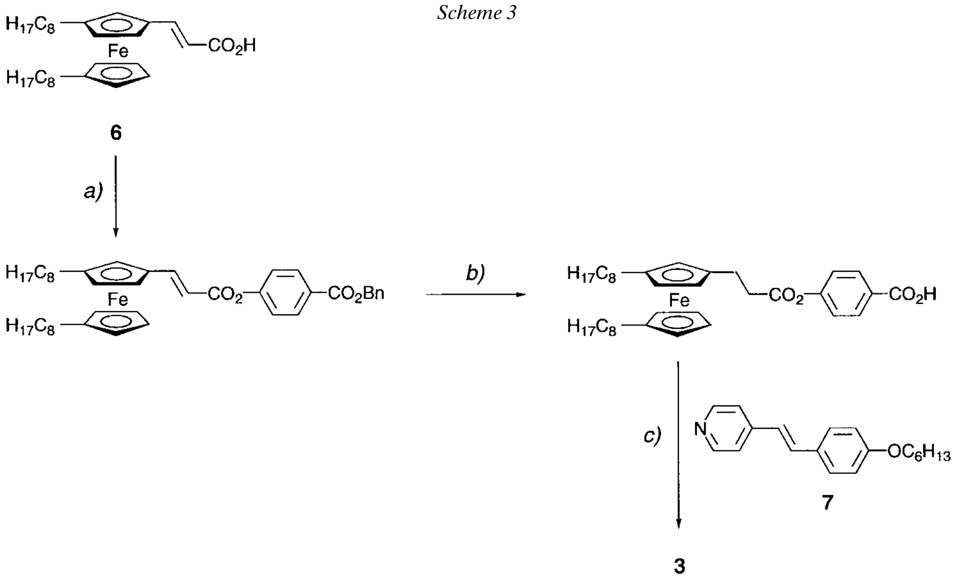
[3]) Instrumentation and techniques, see [14]. X-Ray diffraction experiments were performed using a monochromatic CuK_α beam with a section of *ca.* 0.25 mm^2. The sample temperature was maintained within ±0.2 K. The imaging-plate detector was read out by a molecular-dynamic system, and the detector to sample distance varied between 65 and 300 mm.

Scheme 3



a) Benzyl 4-hydroxybenzoate, DCC, 4-ppy, CH_2Cl_2, r.t., overnight, 95%; purification by CC (silica gel, CH_2Cl_2). *b*) H_2, 10% Pd/C, CH_2Cl_2, r.t., 2 h; 89%; purification by CC (silica gel, CH_2Cl_2/MeOH 99:1). *c*) THF, r.t., 0.5 h; 80%; purification by trituration with hexane, filtration, and washing with hexane.

Table 1. *Phase Transitions and Enthalpy Changes of Compounds* **1**–**3**

	Phase transition[a])	T [°C][b])	ΔH [kJ mol^{-1}]
1	K→Col$_h$	52	65
	Col$_h$→I	84	2.8
2	K→Col$_h$	66	91
	Col$_h$→I	72	3.0
3	K→S$_C$	55	64
	S$_C$→S$_A$[c])	84	–
	S$_A$→I	101	7.9

[a]) K, crystalline state; Col$_h$, hexagonal columnar phase; S$_C$, smectic C phase; S$_A$, smectic A phase; I, isotropic liquid. [b]) Onset transition determined during the first heating run (10° min^{-1}, under N_2). [c]) Determined by polarized optical microscopy.

organization of the rod-like cores. For compound **1**, three sharp rings were seen at low angles corresponding to lattice spacings in $1:\sqrt{3}:2$ ratios. These three sharp rings revealed a hexagonal organization with a lattice constant $a = 49.8$ Å (*Table 2*). The structure of compound **2** is very similar to the one of **1**, but the mesophase growed in large domains so that the innermost ring was made of less than ten dinstinct spots. At larger angles, one could see spots corresponding to the 110 or 200 positions of a hexagonal lattice. However, only two or three spots of weak intensity were seen for each kind. Interestingly, both compounds **1** and **2** gave exactly the same lattice constant (*Table 2*).

Table 2. Bragg *Reflections, Lattice Constant* a [Å] *and Observed and Calculated* d *Spacings* [Å]

			Compound **1**			Compound **2**		
h	*k*	*l*	*a*	d_{obs} [a])	d_{calc}	*a*	d_{obs} [a])	d_{calc}
1	0	0	49.8	43.2	43.1	49.8	42.9	42.9
1	1	0		25.0	24.9		24.8	24.8
2	0	0		21.4	21.5		21.5	21.5

[a]) Recorded at 60°.

As for phasmidic compounds [15], the organization of the molecules in a column was more like that of lyotropic molecules in a cylinder, rather than like that of disc-like molecules stacked one above the other. There were five to six molecules in a slice of column 4.5 Å thick. Finally, the large lattice constant was in agreement with the length of the rigid core.

Conclusion. – The results presented in this report are of interest for three reasons. Firstly, ferrocene-containing thermotropic liquid crystals showing columnar phases are obtained. This finding, associated with data we already described [1–5], establishes that structural engineering at the ferrocene level can be exploited for tuning the molecular organization of ferrocene-based mesomorphic molecular units within the liquid-crystalline state. Secondly, the elaboration of metallomesogens through H-bonds opens unique opportunities for exploiting the properties of metals in novel supramolecular liquid-crystalline materials [16]. Finally, oxidation of one ferrocene unit in **1** or **2** will lead to mixed ferrocene-ferrocenium metallomesogens which will be sensitive to both oxidation and reduction processes. New properties and behavior are expected from such systems.

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