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Preliminary Communication

Chiral butadiene-tricarbonyliron liquid crystal complexes: racemates and enantiomers[†]

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Mesogenic butadiene-tricarbonyliron complexes **6** and **7** have been obtained in optically active forms and they exhibit columnar, cholesteric, smectic A and smectic C* properties. Both smectic mesophases can potentially be used in switchable bistable electro-optic devices and all the mesogenic enantiomers can act as dopants by inducing ferroelectric properties when dissolved in a non-chiral smectic A or C phase.

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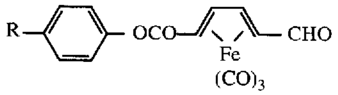
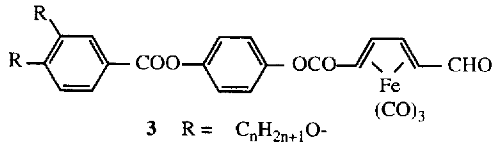
During the past few years, intense research activity has been devoted to the synthesis of ferroelectric liquid crystal materials such as chiral smectic C (S_C*) materials, suitable for use in switching bistable electro-optic display devices [2]. In connection with this topic, we have recently described a new class of potentially ferroelectric metallomesogens, namely racemic butadiene-tricarbonyliron complexes [3], which have the double advantage of possessing a rigid chiral unit with a not insignificant lateral dipole. As a matter of fact, it turns out that a conformationally rigid stereo-polar unit may favour short electro-optic response times linked with high polarization density [4]. Moreover, it is of interest to assess the effect of axial chirality upon the spontaneous polarization [5]. Finally, some metallomesogens display high polarizabilities and birefringences [6].

We describe herein the syntheses and mesomorphic properties of the enantiomerically pure mesogenic complex **6**, previously reported as a racemic mixture [3], and the new four chain metallophasmids **7**, prepared in order to obtain S_C and S_C* properties with the racemates and enantiomers, respectively, as is the case with biforked smectogens [7]. The ^{1}H NMR spectra and microanalyses are in agreement with the structures of all new compounds, i.e. (+)-**2**, racemates and enantiomers, **3**, (-)-**6**, and racemates and enantiomers **7**. The transition temperatures and enthalpies are given in tables 1–3. Racemates **7** ($6 < n < 10$) were not prepared.

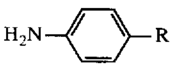
Mesogenic aldehydes **2** and **3**[‡] are key intermediates in the preparation of the mesogenic optically active Schiff's bases **6** and **7**. The starting chiral complex **1a** was obtained by resolution using fractional crystallization of diastereoisomeric oxazolidine derivatives [8] and its optical purity was ascertained by ^{1}H NMR using $Eu(hfc)_3$[§]. The figure shows the absolute configuration of (+)-**1a** [9] and the measured rate of thermal racemization in benzene solution was $2{\cdot}37 \times 10^{-4}\ \mathrm{min}^{-1}$, giving $\Delta G^{\#}$ close to $130\ \mathrm{kJ\ mol}^{-1}$ [10].



2 R = $C_{10}H_{21}O$-



3 R = $C_nH_{2n+1}O$-



4 R = $C_{10}H_{21}O$-

[†] Presented in part at the 15th International Liquid Crystal Conference, 3–8 July 1994. Budapest, Hungary.

[*] Author for correspondence. Fax (33) 140 51 06 36.

[‡] An unidentified smectic phase was occasionally observed.

[§] Racemic complex **1a** exhibits a clear splitting of both the methoxy singlet and the aldehydic doublet in the presence of 0·08 equiv. of $Eu(hfc)_3$. This splitting is not observed in pure optically active **1a** under the same conditions (i.e. ≥99%). No significant racemization was observed for optically active derivatives **2**, **3**, **6** and **7**.

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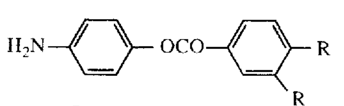
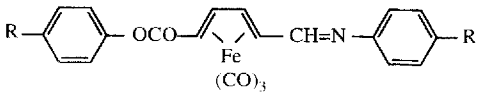
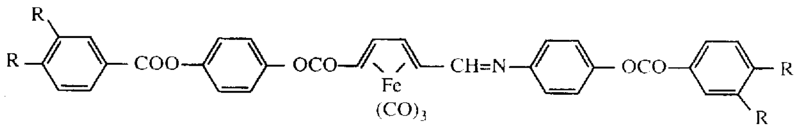


5 R = $C_nH_{2n+1}O$-



R = $C_{10}H_{21}O$-

6



R = $C_nH_{2n+1}O$-

7

Mesogenic complexes stemmed from (±)-**1a**, (+)-**1a** and (−)-**1a** in the same way. Ester **1a** was saponified with KOH in aq. MeOH via the diethyl acetal derivative **1b** to afford the acid **1c** (scheme [8, 11]). Complex (±)-**6** was prepared by reaction of *p*-n-decyloxyaniline **4** with the aldehyde (±)-**2** in absolute ethanol (15 min heating under reflux). After removing the solvent, the yellow solid was purified by crystallization from absolute ethanol (60–80% yield from **2**) [3]. Complexes (±)-**7** were prepared from aldehydes (±)-**3** by combination with the appropriate *p*-aminophenyl 3,4-di-n-alkyloxybenzoates **5** in CH_2Cl_2 in the presence of *p*-toluenesulfonic acid and 3 Å molecular sieves. The yellow crude solid was purified by crystallization from an $MeOH/Et_2O$ (8:2) mixture (40–70% yield from **3**). Aldehydes **3** were prepared by esterification of acid **1c** with 1 equiv. of the corresponding *p*-hydroxyphenyl 3,4-di-n-alkyloxybenzoate in CH_2Cl_2 in the presence of dicyclohexylcarbodiimide and 4-pyrrolidinopyridine (30–60% yield).

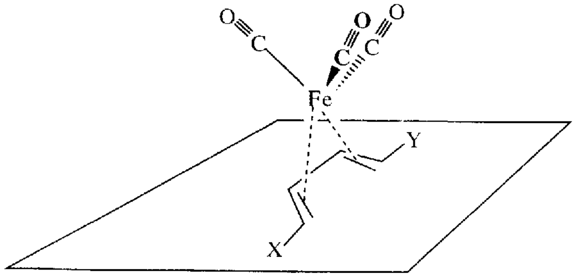
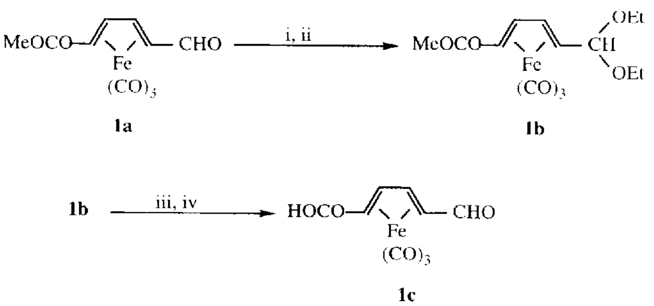


Figure. Complex (+)-**1a** ($X = CO_2Me$, $Y = CHO$).



Scheme. Reagents and conditions: (i) triethyl orthoformate, *p*-toluenesulfonic acid in $EtOH/CH_2Cl_2$ (3:1); (ii) $NaHCO_3$; (iii) KOH in aq. MeOH; (iv) HCl.

Complex (−)-**6** ($R = C_{10}H_{21}O$) was obtained from aldehyde (+)-**2** derived from acid (+)-**1c** and its precursor methyl ester (+)-**1a**. Complexes (+)-**7** ($n = 6$) and (−)-**7** ($7 \leq n \leq 16$) came from (−)-**3**, (−)-**1c**, (−)-**1a** and (+)-**3**, (+)-**1c**, (+)-**1a**, respectively.

Complex (−)-**6** ($[\alpha]_D$ −219°, $[\alpha]_{578}$ −241°, c.0·80 in CH_2Cl_2, 25°C) exhibits a smectic A phase, as does the corresponding racemic mixture (±)-**6**, and a cholesteric phase in place of the nematic. Transition enthalpies and temperatures are similar except for the melting points (table 1).

The observed polymesomorphism of complexes **7** (tables 2 and 3), as for simple four-chain phasmids [7], depends on the curvature between the aromatic core and the aliphatic parts: owing to the increase of the main area per aliphatic chain, the long chain homologues exhibit a hexagonal columnar mesomorphism, whereas a S_C (S_C*) and/or a nematic (cholesteric) phase(s) appear for shorter chains which act to the detriment of the hexagonal 2D order.

Besides some large differences in crystal–mesophase temperatures and enthalpies between racemates and

Table 1. Transition temperatures (°C) and enthalpies ($kJ\,mol^{-1}$, in italics) for compound **6** (racemate and enantiomer). Cr = crystal; S_A = smectic A phase; N = nematic phase.

	Cr		S_A		N		I
(±)	•	78·5 *47·7*	•	91·5 *0·8*	•	96·5 *1·3*	•
(−)	•	84 *40·5*	•	92 *1·0*	•[a]	97 *1·8*	•

[a] Cholesteric phase.

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Table 2. Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in italics) for compounds (±) – **7** (racemates); Φ_h = hexagonal columnar mesophase.

n	Cr		S_C		Φ_h		N		I
6	●	101·5 *59·8*	—		—		●	144·5 *0·2*	●
(...)									
10	●	72 *42·9*	●	104·5 *2·7*	—		●	124 *0·5*	●
11	●	69 *51·9*	●	100·5 *2·4*	—		●	108·5 *0·6*	●
12	●	59 *51·9*	—		●	110 *3·7*	—		●
13	●	60·5 *41·9*	—		●	100·5 *3·5*	—		●
14	●	63 *53·2*	—		●	104·5 *3·3*	—		●
15	●	70 *61·7*	—		●	100·5 *2·9*	—		●
16	●	85 *142·9*	—		●	111 *3·9*	—		●

Table 3. Transition temperatures (°C) and enthalpies (kJ mol^{-1}, in italics) for compounds **7** (enantiomers). S_C^* = chiral smectic C phase; N* = cholesteric phase.

n	Cr		S_C^*		Φ_h		N*		I
6(+)	●	84 *18·1*	—		—		●	139 *0·9*	●
7(–)	●	71·5 *38·1*	●	94·5 *2·9*	—		●	146 *0·6*	●
8(–)	●	84·5 *61·8*	●	94·5 *2·9*	—		●	130·5 *0·6*	●
9(–)	●	68·5 *45·3*	●	82 *2·2*	—		●	100·5 *0·4*	●
10(–)	●	73·5 *18·4*	●	109 *2·3*	—		●	127 *0·6*	●
11(–)	●	52·5 *28·7*	●	111 *2·3*	—		●	119 *0·3*	●
12(–)	●	60·5 *33·5*	—		●	112·5 *3·1*	—		●
13(–)	●	64·5 *59·8*	—		●	103·5 *2·8*	—		●
14(–)	●	88·5 *78·1*	—		●	94 *3·2*	—		●
15(–)	●	71 *69·0*	—		●	106 *2·4*	—		●
16(–)	●	89·5 *87·1*	—		●	103·5 *3·8*	—		●

enantiomers **7** (see compounds with *n* = 6, 11, 14 and *n* = 6, 10, 11, 14, 16 respectively), all the data are similar.

Compound (–)-**7** (*n* = 8) ($[\alpha]_D$ –113°, $[\alpha]_{578}$ –125°, c.0·65 in CH_2Cl_2, 25°C) was confined between two ITO coated glasses. In spite of covering the glasses with a rubbed film of polyvinylalcohol, good planar alignment could not be obtained, due among other causes to the small cholesteric pitch (0·43 µm at 113°C). The thicknesses of the cells used were 2–5 µm. A classical electro-optical set-up was used for measuring switching current, electric response time and apparent tilt angle. Nevertheless, at 90°C in some S_C* domains, using a field around 10 V µm^{-1}, it was possible to access the spontaneous polarization (32 nC cm^{-2}), response time (9 ms) and tilt angle (47°). X-ray diffraction on an oriented S_C sample of (±)-**7** (*n* = 10) gave a tilt angle of 42°.

The results reported above confirm that the butadienetricarbonyliron moiety can be favourably inserted into a phasmidic mesogenic structure to induce ferroelectric properties. It remains to be proved whether more dissymmetric chiral iron complexes—i.e. with a butadienetricarbonyliron moiety in a non-central position and a core terminated with four or three paraffinic chains—may lead to higher spontaneous polarisations. Additionally, the study of other mesogenic chiral metal complexes is in progress.

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