

Butadiene Iron-tricarbonyl Liquid Crystal Complexes

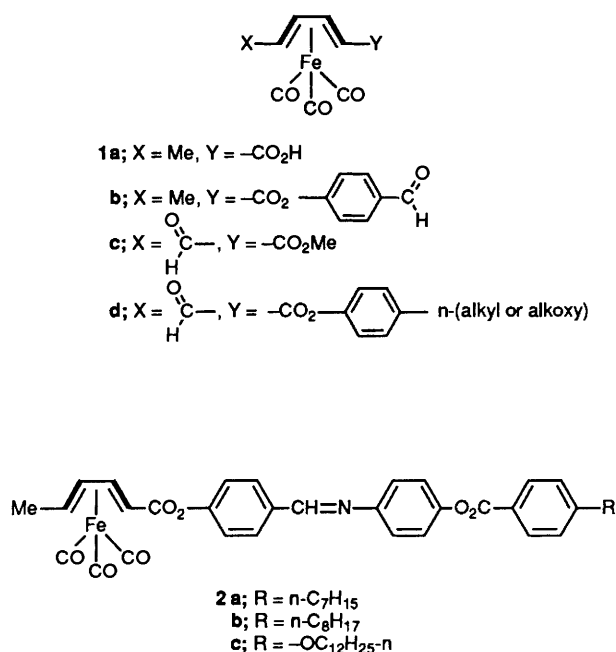
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The first family of butadiene iron-tricarbonyl liquid crystal complexes is described.

Ferroelectric liquid crystals such as chiral smectic C phases¹ are of interest because of their possible application in switching bistable electro-optic devices.² There has been a lot of work done in this area over the past ten years and it has been noted that a large spontaneous polarization is generally

necessary for short switching times. It has also been found that a conformationally rigid stereo-polar unit is important to promote a high polarization density and, in turn, to obtain high speed optical switching liquid crystal materials.³ Nevertheless, to date most of the chiral groups have been introduced



into the flexible paraffinic chains. Some rare examples of mesogens with a chiral rigid part have been described but the results concerning the polarization are not still convincing.⁴

We anticipated that the butadiene iron-tricarbonyl group **1** would be an excellent candidate for building up ferroelectric liquid crystal materials because (i) it is chiral when X and Y are different and the enantiomers are easily available,⁵ (ii) it presents a lateral dipole moment $\pi \rightarrow \text{Fe}(\text{CO})_3$ (about 2D),⁶ (iii) it is rigid and (iv) its two functions X and Y allow it to be inserted into a rod-like mesogenic structure.

We herein describe the mesomorphic behaviour of the racemic butadiene iron-tricarbonyl complexes **2** and **3**. Complexes **2** were prepared from racemic **1a** via the aldehyde **1b** which was condensed with the appropriate *p*-aminophenyl *p*'-n-(alkyl or alkoxy)benzoate in absolute ethanol. Complexes **3** were obtained from racemic **1c** by combination of aldehyde **1d** with the appropriate *p*-n-(alkyl or alkoxy)aniline in absolute ethanol. Complexes **2** and **3** were purified by recrystallization from absolute ethanol (60–80% yield from **1b** and **1d**, respectively; yellow solids). The ¹H NMR spectra and microanalyses are in agreement with the structures of the new complexes. The transition temperatures and enthalpies are given in Table 1.

Table 1 Transition temperatures for complexes **2** and **3**

Complex	Transition ^a	T/ ^o C	$\Delta H/\text{kcal mol}^{-1b}$
2a	C-N	125.5	5.9
	N-I	249.5 ^c	<i>d</i>
2b	C-N	125.5	6.3
	N-I	220.5 ^c	<i>d</i>
2c	C-N	114.5	5.9
	N-I	212.5 ^c	<i>d</i>
3a	C-I	87.5	8.5
	I-N ^e	78	0.2
3b	C-N	109.5	9.9
	N-I	110	0.2
3c	C-I	122	<i>d</i>
	I-N ^e	99	0.15
3d	C-N	91.5	<i>d</i>
	N-S _A ^e	89.5	<i>d</i>
3e	N-I	96.5	0.25
	C-S _A	78.5	11.4
	S _A -N	91.5	0.2
	N-I	96.5	0.3
3f	C-S _A	76	12.2
	S _A -I	94	1.0
3g	C-S _A	85.5	13.7
	S _A -I	97.5	1.3

^a Observed on a Leitz polarizing microscope equipped with a variable temperature stage (Mettler FP80). ^b Measured on a Perkin-Elmer DSC-2 (1 kcal = 4.184 kJ). ^c Decomposition. ^d Unmeasurable (crystalline polymorphism, decomposition or shoulder). ^e Monotropic transition.

Series **2** only exhibits nematic properties, while in series **3** a smectic A phase can be observed besides a nematic phase (Table 1). This second series is devoid of smectic C properties, in spite of the presence in each complex **3** of two chains of equal length.⁷ However, the smectic A phase of optically active **3** can probably be used in electro-optic devices by application of the electroclinic effect.⁸ As usual, the nematic stability decreases and smectic A stability increases as the paraffinic chains lengthen (only a nematic phase with C₆ chains **3b**, nematic and smectic A phases with C₁₀ chains **3e** and only a smectic A phase with C₁₂ chains **3g**). Anyway, enantiomers **2** and **3** can act as dopants by inducing ferroelectricity when dissolved in a non-chiral smectic A or C phase.

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