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Synthesis and mesomorphic behaviour of a homologous series of 1,1'-bis[4(4'-alkyloxy)benzaldimine]ferrocene dicarboxylates

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A new series of ferrocene derivatives, 1,1'-bis[4(4'-alkyloxy)benzaldimine]ferrocene dicarboxylates, (FeESAD C_n , where the number of carbon atoms in the alkyloxy chain, n , varies from 4-12) have been synthesized. The thermal behaviour was investigated by means of polarizing microscopy and differential scanning calorimetry. All members of the series exhibit liquid-crystalline behaviour. While the shorter chain members exhibit a nematic mesophase, the longer chain members exhibit a smectic A mesophase. The electronic spectrum of the $n=7$ member is also presented.

1. Introduction

In recent years there has been considerable interest in liquid crystals that contain organometallic components, because of their potential for possessing interesting and novel properties. The organometallic functionality offers the appealing prospects of imparting unique anisotropic optical, electrical and magnetic properties. The first liquid crystals prepared containing a transition metal were ferrocene monoesters, reported by Malthete *et al.* [1]. These compounds were also characterized by the presence of a benzaldimine functionality in the organic chromophore attached to ferrocene. In this series the ferrocene moiety is at the end of the molecule rather than being incorporated into the core. Recently Bhatt *et al.* [2] have reported the synthesis of a series of diesters in which the ferrocene moiety is at the centre of the molecule. The crystal structure of a diester reveals that these molecules attain an S geometry, with the two alkyl chains extending in the opposite directions [3]. The ferrocene function has the effect of producing an offset of the two extended molecular halves. The corresponding ferrocene monoesters are not liquid-crystalline, in contrast to the behaviour exhibited by the monoesters reported by Malthete *et al.* [1]. Recently P. Singh *et al.* reported the synthesis of other mesomorphic ferrocene diester derivatives [4]. In all the homologous series of 1,1'-ferrocene derivatives reported so far, a sporadic distribution of the liquid-crystalline phases has been observed. Herein, we report the synthesis of a series of mesomorphic ferrocenes derived from Schiff's bases, in which the shorter chain members exhibit a nematic mesophase and the longer chain members exhibit a smectic A mesophase, as is typical of a homologous series.

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2. Experimental

2.1. General procedures

The syntheses of 1,1'-ferrocene dicarbonyl chloride and 1,1'-bis(4-benzaldehyde)ferrocene dicarboxylate were carried out in an inert atmosphere. The 4-alkyloxy anilines ($n = 4-12$) were prepared according to the procedure reported in the literature [5]. Methylene chloride, triethylamine and pyridine were distilled from P_2O_5 , NaOH and CaO, respectively, under nitrogen atmosphere. Transition temperatures and enthalpy changes were determined using a Perkin-Elmer DSC-2 instrument. The instrument was calibrated with a high purity indium sample. The DSC spectra were recorded with a scanning rate of 10 K min^{-1} . Microscopic observations of the textures were made using a Leitz-Laborlux 12 POL polarizing microscope equipped with a Linkam hot stage and thermal control unit. The ^1H NMR spectra of the compounds were recorded with a QE-300 NMR spectrometer. Electronic spectra of a dilute solution of the $n = 7$ analogue in CHCl_3 were recorded on a HP 8452A diode array spectrophotometer. Elemental analysis for C, H, N and Fe were performed by the microanalytical laboratories at the University of Illinois at Urbana-Champaign and are in good agreement with the calculated values (see table 1).

2.2. Preparation of 1,1'-ferrocene dicarbonyl chloride

1,1'-Ferrocene dicarbonyl chloride was prepared by slightly modifying the procedure available in the literature [6]. A 50 ml three necked round bottomed flask equipped with a nitrogen inlet adapter, condenser and a stopper was evacuated and purged thoroughly with nitrogen. The flask was then charged with 1.00 g (3.6 mmol) of ferrocene dicarboxylic acid, 25 ml of dry methylene chloride, 1.54 ml (17.6 mmol) of freshly distilled oxalyl chloride and one drop of dry pyridine. The reaction mixture was stirred in the dark for 12 h at room temperature and then refluxed for 6 h. The contents of the flask were then evaporated to dryness under reduced pressure and the residue extracted repeatedly with dry hexane. Recrystallization from petroleum ether (boiling range, $90-110^\circ\text{C}$) yielded 0.876 g (78 per cent) of 1,1'-ferrocene dicarbonyl chloride as dark red crystals. ^1H NMR (CDCl_3): δ (ppm) 4.76 (C_5H_4 , 4H, t, $J_{\text{H-H}} = 1.9\text{ Hz}$), 5.05 (C_5H_4 , 4H, t, $J_{\text{H-H}} = 1.9\text{ Hz}$). Found: C, 46.41 per cent; H, 2.62 per cent; Cl, 22.73 per cent; Fe, 17.96 per cent. $\text{C}_{12}\text{H}_{28}\text{Cl}_2\text{O}_2\text{Fe}$ Calculated: C, 46.35 per cent; H, 2.60 per cent; Cl, 22.80 per cent; Fe, 17.96 per cent.

Table 1. Per cent yield and elemental analysis for the FeESADC n series—found (calculated).

n	C/%	H/%	N/%	Fe/%	Yield/%
4	71.03 (71.12)	5.70 (5.72)	3.55 (3.61)	7.45 (7.19)	52
5	71.61 (71.63)	6.02 (6.02)	3.43 (3.48)	6.83 (6.94)	55
6	72.07 (72.10)	6.36 (6.31)	3.36 (3.36)	6.62 (6.70)	41
7	72.47 (72.54)	6.58 (6.57)	3.35 (3.25)	6.45 (6.49)	83
8	72.72 (72.95)	6.94 (6.82)	3.08 (3.15)	6.54 (6.28)	80
9	73.06 (73.34)	7.19 (7.05)	2.96 (3.05)	6.36 (6.09)	80
10	73.70 (73.70)	7.32 (7.27)	2.89 (2.96)	5.95 (5.91)	80
11	73.78 (74.04)	7.44 (7.47)	2.79 (2.88)	5.98 (5.74)	74
12	73.13 (74.37)	7.65 (7.67)	2.69 (2.80)	5.63 (5.58)	72

2.3. Preparation of 1,1'-bis(4-benzaldehyde)ferrocene dicarboxylate

A 250 ml three necked round bottomed flask equipped with a nitrogen inlet adapter, condenser and a stopper was evacuated while still hot and purged thoroughly with nitrogen. The flask was then charged with 3.86 g (12.4 mmol) of 1,1'-ferrocene dicarbonyl chloride, 3.03 g (24.8 mmol) of 4-hydroxybenzaldehyde, 200 ml of dry methylene chloride and 4 ml (28.6 mmol) of freshly distilled triethylamine. The reaction mixture was stirred at room temperature for 16 h and then refluxed for 5 h. The contents of the flask were cooled to room temperature and then washed successively with 4 per cent hydrochloric acid, NaHCO₃ solution and water. The organic layer was then dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. The orange powder was purified by passing through a column of silica gel (25 per cent ethyl ether in ethyl acetate) to yield 3.87 g (65 per cent) of crude 1,1'-bis(4-benzaldehyde)ferrocene dicarboxylate. ¹H NMR (CDCl₃): δ (ppm) 4.66 (C₅H₄, 4 H, t, J_{H-H} = 1.9 Hz), 5.09 (C₅H₄, 4 H, t, J_{H-H} = 1.9 Hz), 7.38 (C₆H₄, 4 H, d, J_{H-H} = 8.6 Hz), 7.90 (C₆H₄, 4 H, d, J_{H-H} = 8.6 Hz).

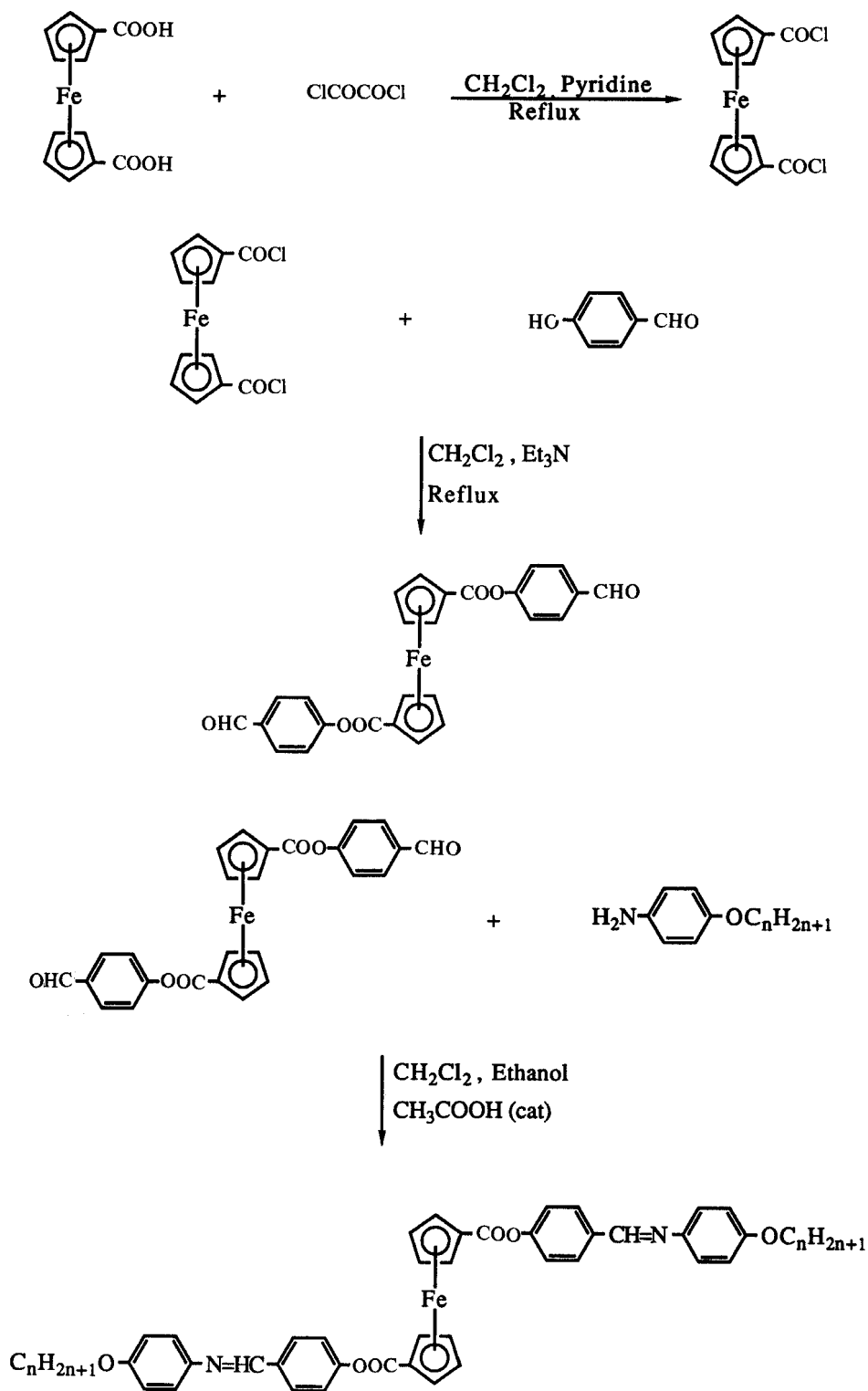
2.4. Preparation of 1,1'-bis[4(4'-alkyloxy)benzalimine]ferrocene dicarboxylate

0.200 g (0.41 mmol) of 1,1'-bis(4-benzaldehyde)ferrocene dicarboxylate was dissolved in 10 ml of methylene chloride. To this was added 20 ml of ethanol, the appropriate 4-alkyloxy aniline (0.83 mmol) and three drops of CH₃COOH and stirred at room temperature for approximately 15 h. The orange powder was collected by suction filtration, washed with cold ethanol and dried under vacuum. A representative ¹H NMR spectrum of the *n* = 6 analogue in CDCl₃ is as follows: δ (ppm) 0.92 (methyl, 6 H, t, J_{H-H} = 6.8 Hz), 1.3–1.8 (methylene, 16 H, m), 3.97 (CH₂-O, 4 H, t, J_{H-H} = 6.6 Hz), 4.64 (C₅H₄, 4 H, t, J_{H-H} = 1.8 Hz), 5.09 (C₅H₄, 4 H, t, J_{H-H} = 1.8 Hz), 6.91 (C₆H₄, 4 H, d, J_{H-H} = 8.8 Hz), 7.21 (C₆H₄, 4 H, d, J_{H-H} = 8.7 Hz), 7.29 (C₆H₄, 4 H, d, J_{H-H} = 8.5 Hz), 7.89 (C₆H₄, 4 H, d, J_{H-H} = 8.5 Hz), 8.45 (CHO, 2 H, s). IR (nujol, 1750–1100 cm⁻¹) of strong and medium intensity bands: 1727(vs); 1715(sh); 1623(m); 1605(m); 1579(m); 1509(s); 1467(s); 1380(m); 1305(m); 1284(s); 1248(s); 1211(s); 1196(sh); 1168(s); 1120(s).

3. Results and discussion

The members of the FeESADC_{*n*} series were prepared according to the procedure outlined in the scheme. Ferrocene dicarbonyl chloride (I) was prepared in 78 per cent yield by the reaction of ferrocene dicarboxylic acid with oxalyl chloride in the presence of pyridine as a catalyst and methylene chloride as a solvent. Subsequent reaction involved the esterification of ferrocene dicarbonyl chloride with 4-hydroxybenzaldehyde using triethylamine as a base and methylene chloride as a solvent. The crude product, 1,1'-bis(4-benzaldehyde)ferrocene dicarboxylate (II) was obtained in 65 per cent yield. Finally, the desired product, FeESADC_{*n*} (III) is obtained by the reaction of II with the appropriate 4-alkyloxy aniline in a mixture of methylene chloride and ethanol as a solvent and acetic acid as a catalyst. The yields and elemental analysis of the members of FeESADC_{*n*} series are provided in table 1.

The thermal behaviour of FeESADC_{*n*} was investigated by optical microscopy and differential scanning calorimetry. The assignments of the liquid crystal phases are based upon the observed textures under the polarizing microscope. The phase transition temperatures and enthalpies are given in table 2. Figure 1 shows a graph of the transition temperatures versus the number of carbon atoms in the terminal alkyloxy chain. An odd–even alternation in the transition temperatures in the series is evident (see figure 1) except for an anomalous behaviour on going from *n* = 9–10. This

Scheme. Synthesis of FeESAD_n.

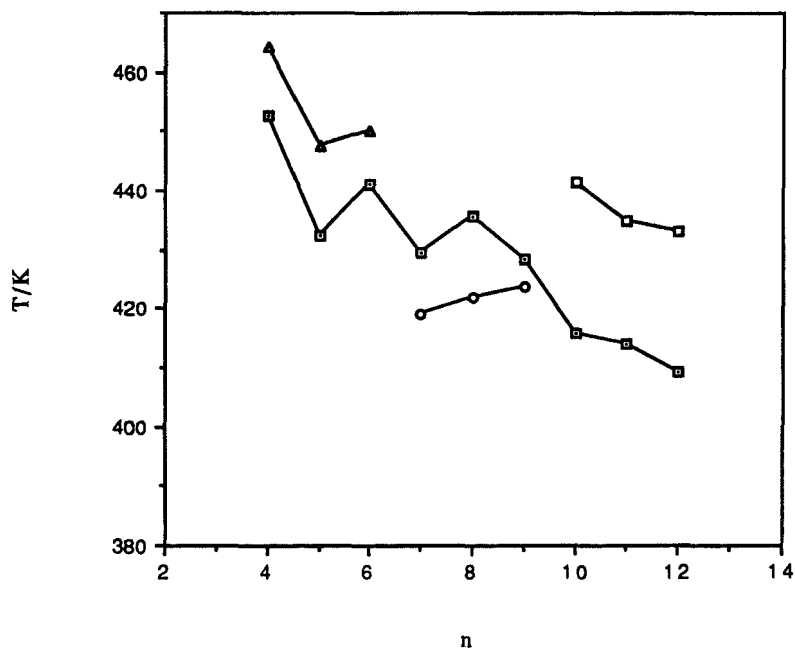


Figure 1. Transition temperatures versus number of carbon atoms in the alkyloxy chain. \square , C-S_A or N-I; \triangle , N-I; \circ , I-N or S_A; \square , S_A-I.

Table 2. Phase transition temperatures and enthalpy changes of the FeESADC_n series.

n	Transition	Temperature/K	$\Delta H/kJ mol^{-1}$
4	C-N	453	56.94
	N-I	464	4.31
5	C-N	433	72.51
	N-I	447	3.30
6	C-N	441	58.91
	N-I	450	4.18
7	C-I	430	36.69
	I-N	419	-1.63
8	C-I	436	72.30
	I-S _A	422	-2.26
9	C-I	428	61.80
	I-S _A	424	-1.71
10	C-S _A	416	51.96
	S _A -I	441	8.37
11	C-S _A	414	41.00
	S _A -I	435	5.98
12	C-S _A	409	38.32
	S _A -I	433	4.89



Figure 2. Optical micrograph showing the schlieren threaded texture of the nematic mesophase in FeESADCn ($n=6$) at 451 K (heating cycle).

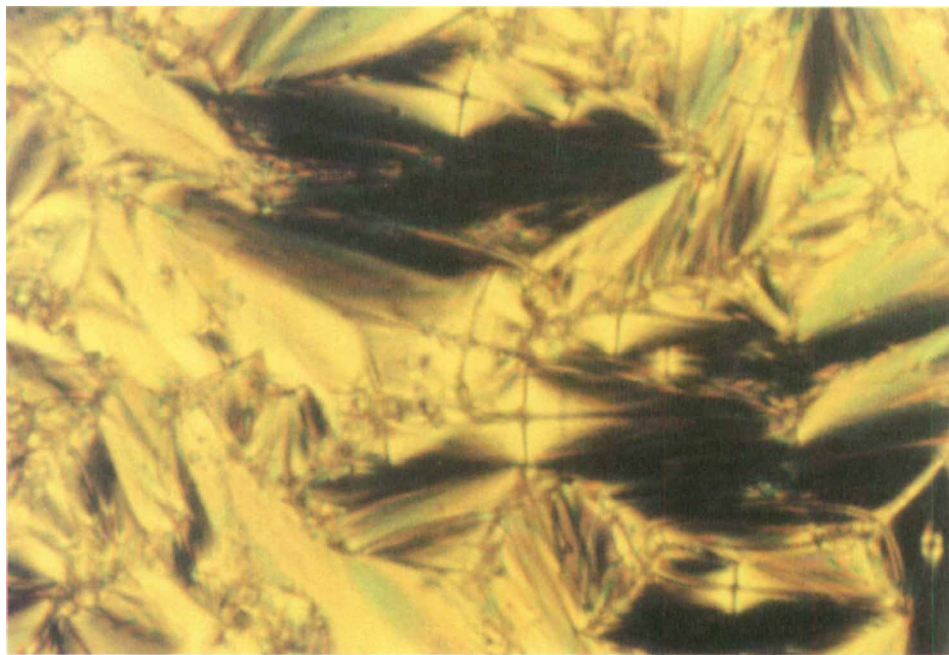


Figure 3. Optical micrograph showing the focal conic texture of the smectic A mesophase in FeESADCn ($n=9$) at 407 K (cooling cycle).

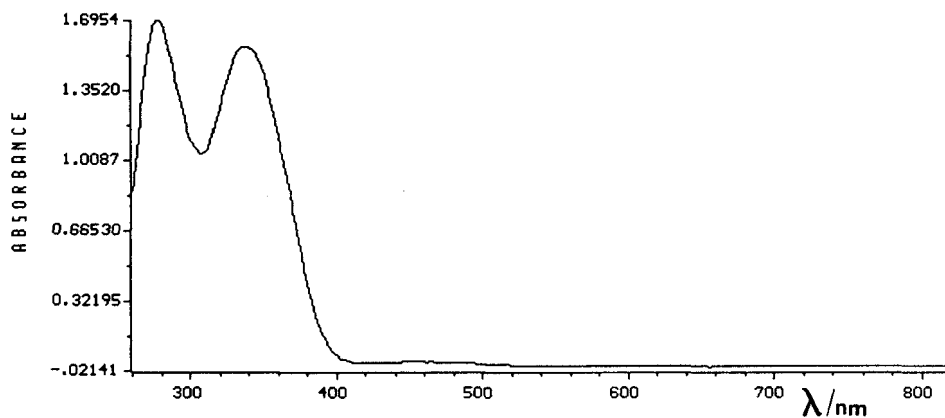


Figure 4. Electronic spectrum of FeESADC7 in CHCl_3 .

probably arises from a significant change in the packing arrangement in the longer chain molecules. The thermograms of FeESADC_n (where $n=4-6$ and $9-12$) show at least two well-separated endothermic peaks in the heating cycle, corresponding to the melting and clearing phenomena. When viewed between crossed polarizers, a schlieren threaded texture (see figure 2) typical of the nematic mesophase is observed upon approaching the melting temperature in the case of $n=4-6$ [7]. On the other hand when $n=10-12$ we observe a focal conic texture typical of the smectic A mesophase [8].

The DSC thermograms of $n=7-9$ show only one endothermic peak during the heating cycle. However, two exothermic peaks are observed during the cooling cycle, which is indicative of monotropic behaviour. Under examination in the polarizing microscope these three members of the series are seen to go directly to the isotropic phase. However we observe nematic droplets for $n=7$ and focal conic texture typical of a smectic A mesophase (see figure 3) for $n=8$ and 9 upon cooling. These observations are consistent with the DSC results.

The observation of mesomorphic behaviour in all members of the present series of ferrocene derivatives, suggests that ferrocene does not impede the formation of liquid-crystalline phases. Thus it seems feasible to employ the ferrocene function as a component of a main chain liquid crystal polymer. In fact P. Singh *et al.* [9] recently reported the synthesis of the first main chain liquid crystal polymers containing the ferrocene moiety.

In general it is possible to order the liquid-crystalline phases with respect to an electric or magnetic field or some anisotropic substrate property. We have investigated the electronic spectra of the ferrocene derivatives, since anisotropic optical properties can provide the basis for useful applications. The dilute solution spectra of the $n=7$ member (see figure 4) shows a long wavelength band at 452 nm ($\log \epsilon=2.7$) which is ascribed to the $3d-3d$ transition [10]. The bands at 276 nm ($\log \epsilon=4.5$) and 338 nm ($\log \epsilon=4.5$) are due to a combination of the electronic transitions involving the iron-carbon bond and the intra-ligand transitions of the organic chromophore attached to the cyclopentadienyl ring of ferrocene [11]. The slight bathochromic shift of these bands relative to that observed in ferrocene is presumably due to a delocalization of electron density from one organic chromophore to the other through the iron atom of the ferrocene moiety [12]. It has also been shown chemically that substitution in one

ligand has a definite effect on the second ligand of the sandwich type compounds and is presumably transmitted through the metal atom [13, 14]. In the future we propose to study poling of these ferrocene derivatives, and their ordering in polymer films.

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